THE SULFUR FERTILITY STATUS OF FLORIDA SOILS

BY

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TABLE-OF CONTENTS

	Page
ACKNOWLEDGEMENTS.	ii
LIST OF TABLES.	vii
LIST OF FIGURES	x
ABSTRACT.	xii
SECTION	
I. INTRODUCTION	1
II. REVIEW OF LITERATURE	4
1. SOURCES OF SULFUR.	4
1.1 SOIL SOURCES.	4
1.1.1 Sulfur-Containing Minerals.	4
1.1.2 Soil Organic Matter	5
1.1.2.1 C:N:S relationships	6
1.1.2.2 Organic sulfur fractionation.	8
1.1.3 Soil Sulfur Reactions	13
1.1.3.1 Oxidation-reduction	13
1.1.3.2 Precipitation reactions	16
1.1.3.3 Adsorption reactions.	20
1.1.3.3.1 Factors Affecting Adsorption.	20
1.1.3.3.2 Mechanisms of Sulfate Adsorption.	22
1.1.3.4 Leaching.	26
1.2 ATMOSPHERIC SOURCES	28
1.2.1 Sulfur as a Pollutant	28
1.2.1.1 Damage to plants.	28
1.2.1.2 Damage to animals	29
1.2.2 Sources of Atmospheric Sulfur	29
1.2.2.1 Anthropogenic sources	30
1.2.2.2 Biogenic sources.	32
1.2.3 Local and Regional Studies of Rainfall and Atmospheric S	32
1.3 FERTILIZER SOURCES.	36
2. PLANT SULFUR NUTRITION	39
2.1 THE ROLE OF SULFUR IN PLANT NUTRITION	39
2.2 SULFUR UPTAKE BY PLANTS	41
2.2.1 Root Uptake	41
2.2.2 Absorption from the Atmosphere.	42

	Page
2.3 EVALUATING THE SULFUR REQUIREMENT OF CROPS.	43
2.3.1 Critical Concentrations	43
2.3.2 N:S Ratios.	43
2.3.3 Sulfate Sulfur.	48
2.4 EVALUATING THE SULFUR FERTILITY STATUS OF SOILS . . .	50
2.4.1 Extraction Techniques	50
2.4.1 Biological Techniques	55
3. SULFUR FERTILITY STUDIES IN FLORIDA.	57
III. MATERIALS AND METHODS.	62
4. EXPERIMENTAL METHODS	62
4.1 SULFUR DISTRIBUTION IN SELECTED FLORDIA SOILS	62
4.2 A GREENHOUSE EVALUATION OF SUBSOIL SULFUR IN FOUR FLORIDA SOILS.	62
4.3 SULFUR IN BAHIAGRASS AND BERMUDAGRASS	70
5. LABORATORY ANALYSES.	72
5.1 NITROGEN.	72
5.1.1 Total Nitrogen in Plant Tissue.	72
5.1.2 Total Nitrogen in Soils	73
5.2 SULFUR.	73
5.2.1 Tissue Digestion for Total Sulfur	73
5.2.2 Soil Extraction for Sulfate Sulfur.	73
5.2.3 A Comparison of Two Extraction Procedures for Soil Sulfur	74
5.2.4 Estimation of Total Sulfur in Soils	76
6. ANALYTICAL TECHNIQUES FOR DETERMINING SULFUR	82
6.1 TURBIDIMETRY.	84
6.2 INDIRECT METHODS.	84
IV. RESULTS AND DISCUSSION	86
7. SULFUR DISTRIBUTION IN SELECTED FLORIDA SOILS.	86
7.1 SPODOSOLS	86
7.2 ENTISOLS.	91
7.3 ULTISOLS.	97
7.4 C:N:S RELATIONSHIPS	106
8. A GREENHOUSE EVALUATION OF SUBSOIL SULFUR.	109
8.1 CHEMICAL AND MINERALOGICAL PROPERTIES OF SOILS STUDIES	109
8.2 YIELDS.	112
8.2.1 Harvest 1	112
8.2.2 Harvests 2,3, and 4	117
8.2.2.1 Myakka.	117
8.2.2.2 Lakeland.	119
8.2.2.3 Orangeburg and Norfolk.	119
8.3 SULFUR CONCENTRATIONS AND N:S RATIOS.	122

	Page
9. SULFUR IN BAHIA GRASS AND BERMUDA GRASS IN THE FIELD.	124
9.1 SULFUR IN BAHIA GRASS ON A MYAKKA FINE SAND.	124
9.2 SULFUR IN BERMUDA GRASS ON A KENDRICK FINE SAND.	134
9.3 FORAGE SULFUR CONCENTRATIONS AND N:S RATIOS	143
10. SOURCES AND CYCLING OF SULFUR IN THE FIELD	146
V. SUMMARY AND CONCLUSIONS.	151
BIBLIOGRAPHY.	153
APPENDICES.	167
A. DIGESTION PROCEDURE FOR ESTIMATION OF TOTAL SULFUR IN PLANT TISSUE.	168
B. DIGESTION PROCEDURE FOR ESTIMATION OF TOTAL SULFUR IN SOILS	169
C. PROCEDURE FOR THE TURBIDIMETRIC DETERMINATION OF SULFATES IN SOIL EXTRACTS, DIGESTED SOIL EXTRACTS, AND DIGESTED PLANT TISSUE.	170
D. AN INDIRECT METHOD FOR THE DETERMINATION OF SULFATES IN SOIL EXTRACTS	172
E. MEAN AND TOTAL VALUES FOR FOUR HARVESTS OF A SORGHUM- SUDANGRASS CROP IN THE GREENHOUSE.	173
F. THE EFFECT OF HORIZON SEQUENCE AND SULFUR ON ROOT DRY MATTER YIELD AT HARVEST.	174
G. NUTRIENT LEVELS IN COMPOSITE SAMPLES FROM EXPERIMENTAL AREAS AT THE BEEF RESEARCH UNIT AND AT GREEN ACRES AGRONOMY FARM.	175
H. RAINFALL DISTRIBUTION AT THE BEEF RESEARCH UNIT, GAINESVILLE, FLORIDA, FOR 1978 AND 1979.	176
VITA.	177

LIST OF TABLES

Table	Page
1. Mean sulfur fractions and C:N:S ratios for different soils.	12
2. The oxidation states of sulfur in soils.	14
3. Sulfur oxidation reactions by certain species of thiobacilli.	17
4. Sources of biogenic S from wetlands in Florida	33
5. The use of selected sulfur-containing fertilizers in Florida.	38
6. Critical levels of total sulfur, sulfate sulfur, and N:S ratios for selected crops.	44
7. Selected methods used to determine sulfate and extractable sulfur in soils.	51
8. Nutrients applied to surface soils used in a greenhouse evaluation of subsoil sulfur.	67
9. Sulfate sulfur removed by four extraction methods and percent recovery of added sulfur	77
10. Sulfur content of finely ground soil and screened soil using the $MgNO_3/HNO_3$ digestion procedure	79
11. A comparison of three rapid methods of estimating total sulfur in soils.	81
12. Selected chemical and mineralogical properties of some Florida Spodosols	87
13. Correlation coefficients of some soil properties with extractable and total sulfur in Florida Spodosols.	92
14. Selected chemical and mineralogical properties of some Florida Entisols.	93

Table	Page
15. Correlation coefficients of some soil properties with extractable and total sulfur in Florida Entisols	98
16. Selected chemical and mineralogical properties of some Florida Ultisols	99
17. Correlation coefficients of some soil properties with extractable and total sulfur in Florida Ultisols	104
18. Carbon, nitrogen, and sulfur relationships in Florida soils.	107
19. Some chemical and mineralogical properties of soils used in a greenhouse evaluation of subsoil sulfur	110
20. Nutrient levels in soils used in a greenhouse evaluation of subsoil sulfur before treatment	111
21. Sulfur and nitrogen nutrition and yields of 28-day old sorghum-sudangrass in a Myakka fine sand in the greenhouse	113
22. Sulfur and nitrogen nutrition and yields of 28-day old sorghum-sudangrass in an Orangeburg fine sand in the greenhouse.	114
23. Sulfur and nitrogen nutrition and yields of 28-day old sorghum-sudangrass in a Norfolk fine sand in the greenhouse	115
24. Sulfur and nitrogen nutrition and yields of 28-day old sorghum-sudangrass in a Lakeland fine sand in the greenhouse	116
25. Extractable sulfate sulfur in treated soils used in a greenhouse evaluation of subsoil sulfur availability	118
26. The effect of nitrogen and sulfur fertilization on bahiagrass in a Myakka fine sand--1978	127
27. Sulfur removed in herbage.	130
28. The effect of nitrogen and sulfur fertilization on bahiagrass in a Myakka fine sand--1979	131
29. Extractable and total sulfur in bahiagrass plots from the Beef Research Unit.	133

Table	Page
30. Stolon-root mass from bahiagrass plots at the Beef Research Unit.	135
31. The effect of nitrogen and sulfur fertilization on bermudagrass in a Kendrick fine sand--1978	136
32. The effect of nitrogen and sulfur fertilization on bermudagrass in a Kendrick fine sand--1979	138
33. Extractable and total sulfur in bermudagrass plots from Green Acres Agronomy Farm	142

LIST OF FIGURES

Figure	Page
1. Rajan's (1978) proposed mechanism of sulfate adsorption.	25
2. Sources and sinks of sulfur compounds	31
3. Annual deposition of total sulfur, 1952 to 1955 and 1978 to 1979, and the mean pH of rainfall in Florida, 1978 to 1979.	35
4. Location of soil pedons where samples were collected for a survey of sulfur in Florida soils	63
5. Soil pH buffer curves for four Florida soils.	66
6. Schematic of one experimental unit in the greenhouse evaluation of subsoil S in Florida soils.	69
7. Mean distribution of total and extractable sulfate sulfur in nine Florida Spodosols.	90
8. Mean distribution of total and extractable sulfate sulfur in ten Florida Entisols.	96
9. Mean distribution of total and extractable sulfate sulfur in ten Florida Ultisols.	102
10. Total yields of four harvests of sorghum-sudangrass as affected by sulfur and subsurface soil horizons	120
11. The effect of herbage sulfur concentration on relative yield of 4-week old sorghum-sudangrass tops	123
12. The effect of herbage N:S ratio on relative yield of 4-week old sorghum-sudangrass tops.	125
13. The effect of sulfur and nitrogen rates on the annual yield of bahiagrass in a Myakka find sand	129
14. The effect of sulfur and nitrogen rates on the annual yield of bermudagrass on a Kendrick fine sand	141

Figure	Page
15. A contour plot of the depth the the argillic horizon (cm) in the experimental area on a Kendrick fine sand at Green Acres Agronomy Farm.	144
16. The effect of S concentration in bahiagrass and bermuda- grass on relative yields at high N rates	145
17. Annual sources and cycling of sulfur (kg/ha/yr) in the surface (0-15 cm) of a north Florida Spodosol.	147

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Extractable and total sulfur (S) in 29 soil profiles from central and north Florida were measured and compared to selected soil properties. The surface horizons of most Florida Ultisols and the entire profile to 200 cm of Spodosols and Entisols contained less than 6 ppm of 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ extractable sulfate S. Total S was highly correlated with organic C ($r = 0.89$) and total N ($r = 0.95$) in the surface horizons of all soils and with Na-pyrophosphate soluble Al ($r = 0.86$) in the spodic horizons of Spodosols. Both extractable and total S were significantly correlated with citrate-dithionite soluble Al and Fe in the surface horizons of Ultisols. The argillic horizons of Ultisols contained an average of 33 ppm extractable sulfate S which represented over 40% of the total S. Extractable sulfate S represented less than 7% of the total S in the entire profiles of Entisols and

Spodosols and the surface horizons of Ultisols. The mean C:N:S ratios for the surface soils of the three soil orders were 112:7.1:1 for Ultisols, 150:6.4:1 for Spodosols, and 166:5.9:1 for Entisols.

The relative contribution of subsurface soil S to plant nutrition was studied in a greenhouse experiment with a sorghum-sudangrass hybrid (Sorghum sudanese (Piper) stapf 'Dekalb SX16A') in four soils with and without the subsurface soil included in a simulated horizon sequence. The surface soils were treated with 0 or 20 ppm S as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Plants were harvested each 4 weeks over a 16-week period and analyzed for S and N. Sulfur increased yields at all harvests in Myakka fine sand (Aeric Haplaquod, sandy siliceous, hyperthermic). The presence of soil from the spodic horizon did not improve the S status of the plants; the presence of soil from the C horizon of Lakeland fine sand (Typic Quartzipsamment, thermic, coated) increased S uptake slightly over the check but not enough to prevent severe S deficiencies and decreased dry matter yield where S was omitted. Applied S did not increase yields in the surface soils of Orangeburg and Norfolk fine sands (Typic Paleudults, fine-loamy, siliceous, thermic) until the third harvest. The argillic horizon of the Norfolk provided adequate S to maintain optimum dry matter production throughout the 16-week experiment. The presence of the argillic horizon of the Orangeburg improved the S status of the plants and increased S uptake but not enough to prevent S deficiencies by the third harvest. In all soils, S increased yields before deficiency symptoms appeared in the plants. Critical S concentration in the 4-week old plants was 0.12%, and the critical N:S ratio was 16.

Sulfur application with two rates of N (200 and 400 kg/ha) did not increase yields of bahiagrass (Paspalum notatum Flugge 'Pensacola') and bermudagrass (Cynodon dactylon L. 'Coastcross I') in the field until the second year and only at the highest rate of N. All rates of applied S increased S uptake by the plants during the growing season. There seemed to be no advantage to applying S in split applications during the season over a single application in early spring.

Atmospheric and soil sources of S account for an estimated minimum of 21 kg/ha of plant-available S during a growing season. With an average of 15 to 39 kg of S per fertilized hectare applied in fertilizers in Florida, S deficiencies among field crops are unlikely except where high yields are maintained and little or no S is applied in fertilizers.

SECTION I INTRODUCTION

In 1971, Beaton et al. made the following statement concerning the S status of Florida soils:

Sulphur fertilizers are needed on most of the soils of Florida. Except for the Everglades and associated areas, most of the soils are coarse textured. Such soils account for about 28 million acres (11.3 million ha) or about 80% of the land area of the state. (Beaton et al., 1971, p. 6).

Research during the 1940's and early 1950's showed conclusively that many crops growing on Florida soils would respond to S fertilization. However, the conscious application of S as a fertilizer nutrient has never received wide acceptance. Sulfate is applied in many fertilizer materials as an associate anion or as a by-product of the fertilizer manufacturing process. Ammonium sulfate, ordinary superphosphate, sulfate of potash-magnesia, and gypsum may supply adequate quantities of S to growing crops. Micronutrients applied in the soluble sulfate form will also contribute to the S nutrition of plants. However, intensively grown, high-producing crops are often fertilized with large quantities of N as urea, anhydrous ammonia, or ammonium nitrate, P as concentrated superphosphate, diammonium phosphate, or ammonium polyphosphates, and K as muriate of potash. If no S is included in the fertilizer, this practice could lead to soil-S depletion and reduced yields.

Soils serve as a source and a sink for plant available S, but attempts to measure plant-available and labile S have been only

marginally successful. Organic matter is the largest source of soil S in most Florida soils, but the availability and dependability of this S are difficult to determine. Soils which contain an argillic horizon such as the Ultisols of northern Florida contain large quantities of adsorbed S associated with the clay and minerals in this subsurface horizon. This S may be an important source for crops, but the roots of young seedlings must germinate and grow through 20 to 60 cm of leached, sandy soil to reach it. Spodic horizons of flatwoods soils (Spodosols) and subsurface horizons of Florida's sandy Entisols supply an unknown amount of S to crops and are incapable of retaining much applied S.

The atmosphere may be an important contributor to the S nutrition of Florida crops. Sulfate-S in rainfall and the direct absorption of SO_2 through plant leaves may supply all of a plant's S needs in some locations, but this source has not been evaluated in Florida.

Because S is an essential component of certain amino acids, it is an important consideration in assessing forage quality. Forages such as bahiagrass (Paspalum notatum Flugge) and bermudagrass (Cynodon dactylon L.) require high rates of N for optimum yields, but their protein contents and quality remain quite low when compared to some other grasses and legumes. Sulfur fertilization has been shown to improve crop quality, and where large quantities of S have been removed in successive cropping of these forages, yields may be increased with S fertilization.

Little research has been conducted with S as a plant nutrient in Florida soils during the past 25 years. This dissertation will review pertinent S research as it relates to soil fertility and crop nutrition, and evaluate the current S fertility status of representative

Florida soils. The overall objectives of this study were (1) to identify the sources of soil S in the profiles of some Florida soils, (2) to evaluate the effects of subsoil S on plant nutrition, and (3) to evaluate the relative response to S by crops growing on different soils and under different S fertility levels.

SECTION II REVIEW OF LITERATURE

1. SOURCES OF SULFUR

1.1 SOIL SOURCES

All of a growing plant's S requirement can be supplied from the soil. Ensminger and Jordan (1958) reported that the amounts of S absorbed by crops at moderate yield levels ranged from about 9 to 39 kg/ha. Terman (1978) compiled values which averaged 26 kg/ha for grain crops, 35 kg/ha for hay crops, cotton, and tobacco, and 48 kg/ha for fruit, sugar and vegetable crops. This S is absorbed as sulfate from the soil solution primarily due to mass flow of ions (Barber and Olsen, 1968). The sources of this available soil sulfate may be primary and secondary S-containing minerals, soil organic matter, adsorbed sulfate, atmospheric S, and fertilizers containing S.

1.1.1 Sulfur-Containing Minerals

The original source of most soil S was probably the sulfides of metals contained in plutonic rocks. As life evolved and these minerals were decomposed, sulfate was taken up by living organisms and incorporated into organic matter. Under anaerobic conditions, S was reduced to inorganic sulfides or elemental S. Sulfate was also precipitated as soluble or insoluble salts of Ca, Mg, Ba, Sr, K, Fe, Cu, Zn, etc. in arid climates; in humid climates, much of this sulfate was washed into the sea (Tisdale and Nelson, 1975).

Although plants take up S in the inorganic, sulfate form, only 0 to 14% of the total soil S in the surface horizons of humid-region soils is present as the sulfate ion (Ensminger, 1954; Williams and Steinbergs, 1959; Neller, 1959; Freney, 1961; Tabatabai and Bremner, 1972a; Bonner, 1973). The inorganic sulfate and sulfide minerals are associated with alkaline or acid-sulfate soils. Sulfate minerals that have been identified in alkaline soils include gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), thenardite (Na_2SO_4), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), and bloedite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) (Doner and Lynn, 1977). These are all very soluble minerals and are quickly removed from soils where precipitation is high enough to cause deep leaching. These minerals may be used as soil amendments in humid regions but do not persist in the soil.

Acid-sulfate soils or "cat-clays" develop when tidal flats or interdistributary basins of river deltas are drained. Reduced forms of S such as amorphous mackinawite (FeS), pyrite (FeS_2), or greigite (Fe_3S_4) are oxidized by Thiobacillus sp. The soil becomes extremely acidic (pH 3.0 to 3.5), and crystalline jarosite [$\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$] can develop within 1 to 2 years after draining. If carbonates are present in the sediments, the acidity is neutralized and gypsum forms. Few of these soils are arable and where they are used for farming, S as a plant nutrient is certainly not limiting. The presence of 0.05% water soluble sulfates has been suggested as an indicator of an acid sulfate soil (Doner and Lynn, 1977).

1.1.2 Soil Organic Matter

Most of the total S in the surface horizons of humid regions is organic (Eaton, 1922; Evans and Rost, 1945; Williams and Steinbergs,

1959; Freney, 1961; Freney et al., 1962; Nelson, 1964a; Tabatabai and Bremner, 1972a). This fraction may account for 50 to 75% of the total soil S (Alexander, 1977). In a study with 22 soils from eastern Australia, Freney (1961) found an average of 93% of the total S was in organic form. Bonner (1973) found this value to be 63% for Louisiana soils, but he was unable to account for a large percentage of the total soil S.

The availability of this organic S to growing plants is dependent upon the rate of decomposition of the soil organic matter and the nature of the organic matter itself. Environmental factors which favor the proliferation of microorganisms such as moisture, temperature, energy sources, aeration, pH, etc. will affect the mineralization of soil S (Parker and Prisk, 1953; Nelson, 1964a; Burns, 1967).

Soil organic matter can serve as either a source or a sink for plant-available S (Burns, 1967). The decomposition of plant residues low in S can induce S deficiencies of crops growing on a soil. Available S can become assimilated by a growing population of microorganisms just as available N can become tied-up when low-N energy sources are added to a soil. Since S is a component of the amino acids, cystine and methionine, it is an essential nutrient of microorganisms as well as of plants and animals. Starkey (1966) stated that the cells of microorganisms may contain 0.1 to 1% S.

1.1.2.1 C:N:S relationships

During the 1960's, much research emphasis was devoted to studying the C:N:S relationships in soils. Williams et al. (1960) found that total soil S was very highly correlated with both C and N in Scottish soils. They found a mean C:N:S ratio of 100:7.1:1. These values were

similar to C:N:S relationships reported earlier for soils in Australia and New Zealand (Williams and Donald, 1957; Walker and Adams, 1958; Williams and Steinbergs, 1958). Nelson (1964a) found an average organic C:N:S ratio of 114:9.1:1 in the surface horizons of 12 Mississippi soils which had a wide range of organic matter contents. Organic S was highly correlated with total S ($r = 0.920$) and organic C ($r = 0.947$) but not with soluble sulfate-S. The C:N:S ratio of Louisiana soils was found to be 88:8.3:1 for surface horizons and 94:10:1 for subsurface horizons (Bonner, 1973). Tabatabai and Bremner (1972b) also found significant correlations between total S and organic C ($r = 0.86$) and between total S and total N ($r = 0.87$) in Iowa soils. Total S decreased with depth in the soil profile but remained significantly correlated to organic C ($r = 0.86$) and total N ($r = 0.92$).

The organic C:S ratio, like the N:S ratio, can be used to predict S mineralization or immobilization by soil microorganisms. Massoumi and Cornfield (1965) showed that the addition of cellulose to a soil resulted in a decline in available sulfate levels as the microorganism populations growing on the polysaccharide assimilate inorganic S. If the organic matter contains less S than required for microbial proliferation, immobilization will be dominant; if the element is in excess, mineralization of S will result. Barrow (1960a) found that mineralization of S from soil organic matter did not occur until catabolism had lowered the C:S ratio to about 50:1. He also found that immobilization of S occurred in soils during a 12-week decomposition period when the C:S ratio of the original organic material was greater than 200:1 (Barrow, 1960b). Tabatabai and Bremner (1972b) found that most Iowa soils immobilized S when incubated for 2 weeks,

and none released more than 6 ppm of sulfate-S when incubated for 10 weeks under aerobic conditions. They found no significant correlation between mineralized S and total S, sulfate S, organic C, total N, or mineralized N.

Bettany et al. (1980) found C:N:total S ratios of 79:7.9:1 in a Udic Haploboroll under pasture and ratios of 71:6.6:1 for the same soil that had been cultivated for 65 years in Saskatchewan. The relatively narrower C:S and N:S ratios of the cultivated soil, along with a relatively smaller decrease in S than both C and N in the cultivated soil, suggested that S is more resistant to mineralization than C and N. Earlier, they had found the largest amount of S mineralization occurred in soils with the lowest C:N:S ratios (Bettany et al., 1974).

Kowalenko and Lowe (1975) concluded from their research that while the interrelationships of C, N, and S would be important in a consideration of the S supplying power of a soil, more complex interrelationships than simple C:N:S ratios may exist.

1.1.2.2 Organic sulfur fractionation

At the same time investigators were studying C:N:S relationships in soils, many developed techniques to fractionate organic S to find the form or forms of organic S that might influence S mineralization. Williams and Steinbergs (1959) separated soil S into alkali-soluble S, soluble sulfate after ignition, heat-soluble S, reducible S, and sulfate released by hydrogen peroxide oxidation. Each method removed part of the organically-bound S, but only the heat-soluble fraction was highly correlated with the amount of S taken up by plants. Heating the soil on a water bath, followed by heating for 1 hour at 102°C in a hot-air oven, released a maximum amount of S from the soil. Most of

this S was assumed to be organic sulfates that could easily be split from the organic matter. Barrow (1961) deducted from his observations that sulfate released by heat treatment was inorganic because it could be removed with a 0.15% CaCl_2 solution. This extractant does not decompose organic sulfate, and plant uptake of S was closely related to sulfate extracted by this procedure. The fact that organically bound sulfates form a considerable fraction of the total soil S was based on these early reports where NaOH was used to extract most of the total soil S (Williams and Steinbergs, 1959; Freney, 1961).

Organic soil S is generally separated into the C-bonded fraction and the HI-reducible or ester-sulfate fraction. The C-bonded fraction is believed to consist largely of S in the form of S-containing amino acids such as methionine and cystine. The HI-reducible S is the fraction which is not bonded directly to C and is reducible to H_2S by HI. This fraction is believed to consist of S in the form of ester sulfates, e.g., organic sulfates which contain C-O-S linkages such as choline sulfate, phenolic sulfates, sulfated polysaccharides, etc.

Prior to the 1960's, only small amounts of cystine and methionine could be detected in soil organic matter (Bremner, 1950; Sowden, 1955, 1956; Stevenson, 1956). Due to uncertainties in extraction and analysis, the highest values reported for these organic S constituents were only around 10% of the total S content (Freney et al., 1970). DeLong and Lowe (1962) were able to separate this C-bonded fraction by reducing the S to inorganic sulfide with Raney nickel. Carbon-bonded S occupied 47 to 58% of the total S in organic soils and 12 to 35% in mineral soils from Quebec (Lowe and DeLong, 1963). Data suggested that much of the C-bonded S may have been associated with humic acid

materials and was more stable than the HI-reducible fractions. However, Lowe and DeLong were unable to account for all of the organic S in their soils, and made no conclusions as to the significance of this organic-S fraction on plant S nutrition under field conditions.

Freney, Melville, and Williams (1970) found that Fe and Mn could interfere with the determination of C-bonded S by the method of Lowe and DeLong. An average of 23% of the organic S in 15 Australian surface soils could not be accounted for by this method even when it was modified to reduce interferences. They calculated C-bonded S by the difference of total S and HI-reducible S. Each form accounted for about 50% of the total soil S in Australian soils. Similar values were obtained for organic S fractions in 37 Iowa soils (Tabatabai and Bremner, 1972a). Bonner (1973) reported that in 23 Louisiana soils, 44% of the total S was HI-reducible and 25% was C-bonded. This was slightly more than the 63% organic S present in the soil. He also found 14% was calcium phosphate-extractable sulfate S but did not account for all of the total S. No significant relationship was found among total S, organic S, and the various organic-S fractions with yield, S uptake, and S concentration in the plant tissue of a sorghum-sudangrass hybrid.

Analyses of S fractions in some surface soils from Brazil and surface soils from Iowa in the United States indicated that the Brazilian soils contain much more adsorbed inorganic S than Iowan soils (Neptune et al., 1975). The average percentage of total S as ester sulfate S and as C-bonded S was 50 and 7%, respectively, for the Brazilian soil and 50 and 11% for the Iowan soils. However, they were unable to identify 42% of the organic S in the Brazilian soils and 34% in the

Iowan soils. Values for C:N:S relationships in soils and soil-S fractions reported in the literature are compiled in Table 1.

Bettany et al. (1973, 1979) found a gradual increase in both the C:S and N:S ratios of soils along an environmental gradient in Saskatchewan, Canada. Brown chernozemic soils (Aridic Haploborolls) had a C:N:S ratio of 61:6.5:1 with 52% of the total S as HI-reducible while grey luvisolic soils (Typic Cryoboralfs) had ratios of 112:9.7:1 with 32% HI-reducible S. These values for the C:N:S ratios agree with earlier values for similar soils in the northern United States and Canada (Evans and Rost, 1945; Lowe, 1965). Intermediate soils were the dark brown and black chernozemic soils (Typic Haploborolls and Udic Haploborolls) with a mean C:N:S ratio of 80:7.8:1 and 50% HI-reducible S. However, differences in C:N:S ratios of humic acid (HAA) fractions of these soils were greater than those of the total soil organic matter. Differences in the comparable ratios of conventional fulvic acid (FAA), clay-associated humic acid (HAB), and less than 2- μ m humin were smaller than for HAA along the environmental gradient. In 1973, Bettany proposed that C-bonded S is more likely to be incorporated into the strongly aromatic humus whereas the HI-reducible S fraction would be associated with active side-chain components.

A more recent, refined proposal suggests FAA, HAB, and less than 2- μ m humin as the sources of potentially labile organic S (Bettany et al., 1979). However, a study of cultivated versus uncultivated soils showed that the HAA, HAB, and humin fraction accounted for 80% of the total S lost upon cultivation. The FAA fraction had narrower C:N:S ratios and contained more HI-reducible S but contributed only 14% of the total S loss (Bettany et al., 1980). The small loss by the FAA

Table 1. Mean sulfur fractions and C:N:S ratios for different soils.

Location and description	Num-ber	Total S	S fractions				C:N:S ratio		References
			C-bonded	Ester-sulfates	In-organic sulfates	Others	Total	Organic	
-----ppm-----%									
Australia (0-10cm)	15	426	53	47	--	--	--	--	Lowe & Delong, 1963
Brazil (surface)	6	166	7.3	39.8	11.2	41.7	121:6.2:1	--	Neptune et al., 1975
U.S.A.-Iowa (surface)	6	319	11.3	50.1	4.5	34.2	85:7.7:1	--	Neptune et al., 1975
U.S.A.-Iowa (surface)	37	292	10.7	50.2	2.6	36.5	72:6.7:1	--	Tabatabai and Bremner, 1972
U.S.A.-La. (surface)	23	153	25	44	14	--	88:8.3:1	--	Bonner, 1973
(subsoil)	23	187	13	34	22	--	94:10:1	--	
Canada-Quebec (organic)	2	5515	52.5	--	--	--	--	--	Lowe and Delong, 1963
(podzol)	1	440	27	--	--	--	--	--	
(gleisolic)	1	410	32	--	--	--	--	--	
Canada-Sask. (uncultivated)	--	497	--	50.2	1.0	--	79:7.9:1	--	Bettany et al., 1980
(cultivated)	--	308	--	55.4	1.0	--	71:6.6:1	--	
(brown soils)	19	329	49	51	1.9	--	--	61:6.5:1	Bettany et al., 1973, 1979
(gray soils)	26	188	64	35	1.7	--	--	112:9.7:1	Williams et al., 1960
Scotland (plow layer)	50	--	--	--	--	--	100:7.1:1	--	

fraction was explained as probably due to the accumulation of low molecular weight S compounds released by the decomposition of some resistant fraction. The FAA fraction might not lose a large proportion of its S because of the constant addition and faster turnover rate. Bettany et al. (1980) suggested that it might be fractions such as the FAB which show little net change in total S content that are important in supplying available S in the short term.

1.1.3 Soil Sulfur Reactions

1.1.3.1 Oxidation-reduction

No other element is known to occur in as many different forms as S. Its valence ranges from -2 to +6 with sulfides and sulfates representing the two extremes (Table 2). As previously mentioned, the reduced forms of S occur primarily in soil organic matter, amino acids, and the B vitamins including thiamine, biotin, and lipoic acid. Reduced forms of S may also be found in the soil as sulfides of primary minerals such as FeS or as intermediate reaction products such as H_2S , thiosulfates, thiocyanates, polythionates, or elemental S (Burns, 1967).

Sulfide is the principal, stable form of S under anaerobic conditions, but elemental S and organic compounds of S may persist in some natural anaerobic environments such as in sedimentary rocks associated with S domes and in peat, coal, and oil (Starkey, 1966).

Reduction occurs through microbial assimilation of sulfate under aerobic conditions and by obligate anaerobes that use sulfate as the H-ion acceptor and organic matter as an energy source under anaerobic conditions. All of the natural organic and inorganic compounds of S are susceptible to microbial attack. Even the S that occurs in

Table 2. The oxidation states of sulfur in soils.

Name	Oxidation state	Example
Sulfate (most oxidized)	+6	H_2SO_4 , SO_4^{2-} , SO_3
Sulfite	+4	H_2SO_3 , SO_3^{2-} , SO_2
Polythionates (tetra-, tri-, penta-)	+2 to +4	$\text{S}_4\text{O}_6^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_5\text{O}_6^{2-}$
Thiosulfate	+2	$\text{Na}_2\text{S}_2\text{O}_3$, $\text{S}_2\text{O}_3^{2-}$
Sulfomonoxyde	+2	SO
Disulfur monoxyde	+1	S_2O
Elemental sulfur	0	S^0
Disulfide	-1	Na_2S_2 , S_2^{2-}
Sulfide (most reduced)	-2	H_2S , S^{2-}

natural deposits as sulfate, elemental S, and sulfide can be oxidized or reduced by microorganisms in suitable environments. The types of transformations are affected by the state of the S and the environmental conditions, particularly the availability of O.

The predominant microorganisms concerned with the reduction of sulfates are bacteria of the genera Desulfovibrio and Desulfotomaculum. A number of carbohydrates, organic acids, and alcohols may serve as energy sources or electron donors while sulfates are the electron acceptors:

(Alexander, 1977)

Microorganisms that reduce S are extremely important to soil fertility because they reduce the availability of S in the soil, and the primary product of their metabolism, H_2S , can be toxic to plants such as rice, citrus, and other crops and trees of economic importance (Alexander, 1977).

In most well-drained, arable soils, S oxidation is of much more agricultural importance than S reduction. Several reviews have been made of the S-oxidation processes that occur in soils (Gleen and Quastel, 1953; Vishniac and Santer, 1957; Starkey, 1966; Burns, 1967; Kelley, 1968; Aleem, 1975; Alexander, 1977). Although not all soil S oxidation reactions are enzymatic, and chemical oxidation of sulfides, elemental S, and thiosulfates can occur, microbiological oxidation is much more rapid under favorable conditions.

Organisms capable of oxidizing reduced forms of S may be either autotrophs or heterotrophs. The most significant microorganisms are members of the genus, Thiobacillus. Most of these bacteria are

chemoautotrophic, obligate aerobes. The ideal, overall, oxidation reactions of the thiobacilli bacteria are:

sulfide sulfur thiosulfate tetrathionate sulfate

Some of the common species of thiobacilli found in soils and the oxidation reactions associated with each species are shown in Table 3 (Burns, 1967).

The acid produced in the oxidation process is of significant agricultural interest. As previously mentioned, the draining of wetlands may result in acid-sulfate soils or "cat clays." Elemental S, polysulfides, or sulfuric acid may be used to amend alkaline soils or to lower the soil pH for acidophilic plants:

The H_2SO_4 produced by microbial oxidation reacts with free lime in the soil to form gypsum. The Ca^{2+} from gypsum replaces adsorbed Na^+ to reclaim sodic soils (Reuss, 1975).

1.1.3.2 Precipitation reactions

Reducing conditions can result in the precipitation of FeS and other metal sulfides in soil systems. However, in well-drained soils, metallic sulfides are not a sink for soil S. As previously mentioned, inorganic sulfates are associated with alkaline soils in arid or semi-arid climates. Harward and Reisenauer (1966) noted that sulfate retention in arid soils is merely a consequence of gypsum solubility. Most sulfate salts are quite soluble in water and leach rapidly from soils in humid regions.

Table 3. Sulfur oxidation reactions by certain species of thiobacilli (from Burns, 1967).

<u>Thiobacillus thioparus</u>	
$S_2O_3^{2-} + H_2O + 4O_2 \rightarrow 5SO_4^{2-} + H_2SO_4 + 4S$	
$S_4O_6^{2-} + CO_3^{2-} + \frac{1}{2}O_2 \rightarrow 2SO_4 + CO_2 + 2S$	
$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$	
$2KSCN + 4O_2 - 4H_2O \rightarrow (NH_4)_2SO_4 + K_2SO_4 + 2CO_2$	
$S_2O_2^{2-} + 2O_2 + H_2O \rightarrow SO_4^{2-} + H_2SO_4$	
$S_4O_6^{2-} + 7O_2 + 6H_2O \rightarrow 2SO_4^{2-} + 6H_2SO_4$	
<u>T. thiooxidans</u>	
$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow SO_4^{2-} + H_2SO_4$	
$2S + 3O_2 + H_2O \rightarrow 2H_2SO_4$	
$2S_4O_6^{2-} + 7O_2 + 6H_2O \rightarrow 2SO_4^{2-} + 6H_2SO_4$	
<u>T. denitrificans</u>	
$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$	
$5S + 6NO_3^- + 2H_2O \rightarrow 3SO_4^{2-} + 2H_2SO_4 + 3N_2$ (anaerobically)	
$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow SO_4^{2-} + H_2SO_4$	
$2S_4O_6^{2-} + 7O_2 + 6H_2O \rightarrow 2SO_4^{2-} + 6H_2SO_4$	
$2SCN^- + 4O_2 + 4H_2O \rightarrow (NH_4)_2SO_4 + SO_4^{2-} + 2CO_2$	
$5S_2O_3^{2-} + 8NO_3^- + H_2O \rightarrow 9SO_4^{2-} + H_2SO_4 + 4N_2$ (anaerobically)	
<u>T. novellus</u>	
$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow SO_4^{2-} + H_2SO_4$	
$2S_4O_6^{2-} + 7O_2 + 6H_2O \rightarrow 2SO_4^{2-} + 6H_2SO_4$	

Table 3. (Continued)

No specific inorganic mineral has been identified as a sink for soluble sulfates in the well-drained, acid soils of the southeastern United States. Adams and Rawajfih (1977) proposed that sulfate retention by acid soils may be a consequence of the solubility of basaluminite, $\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 5\text{H}_2\text{O}$, and/or alunite, $(\text{Na/K})\text{Al}_3(\text{OH})_6(\text{SO}_4)_2$, as well as adsorption reactions. Based on earlier work by Singh and Brydon (1967, 1969), Adams and Rawajfih were able to show through precipitation experiments and calculated soil solution ionic activities that soil solution sulfate could be removed by precipitation as basaluminite and alunite. An increase in soil pH could be expected to be accompanied by an increase in solid-phase $\text{Al}(\text{OH})_3$ and solution SO_4^{2-} because of the following reactions:

These minerals have not been identified in soils, but Adams and Hajek (1978) further demonstrated that formation of these compounds in sulfate-containing acid soils was thermodynamically feasible. Precipitation occurred with as little as 10 mM sulfate in the reacting solution.

Using basaluminite and alunite as sources of sulfate for cotton seedlings (Gossypium hirsutum L.) grown in a greenhouse in a sandy loam soil from a Typic Hapludult at a pH of 6.5, Wolt and Adams (1979) demonstrated that S in basaluminite was more available while that in alunite was almost unavailable. Their data supported the previous thesis of Adams and Rawajfih that sulfate "adsorption" and "desorption" in acid soils could be partially due to solubility behavior of Al and Fe hydroxy-sulfates.

1.1.3.3 Adsorption reactions

1.1.3.3.1 Factors Affecting Adsorption

In well-drained soils of humid regions, almost all of the inorganic S occurs in the sulfate form. Because of its anionic nature and the solubility of its common salts, leaching losses of sulfate can be rather large. Yet plants depend on the availability of this form for the S they absorb from the soil.

Ensminger (1954) demonstrated the possibility of sulfate adsorption in soils from Alabama. Water or 0.1 N HCl extracted very little sulfate from these soils, whereas extractants containing a replaceable anion such as phosphate (H_2PO_4^-) or acetate (CH_3COO^-) extracted considerable sulfate. A 500 ppm P solution of KH_2PO_4 was the most efficient extractant used. He also showed that increasing amounts of superphosphate and lime applied to a Cecil sandy clay loam (Typic Hapludult) resulted in decreasing amounts of soluble sulfate. Hydrated Al_2O_3 was found to adsorb more sulfate than a number of other soil minerals and clays. Kaolinite also adsorbed significant amounts of sulfate. Kamprath et al. (1956) found that 1:1 type clay minerals adsorbed more sulfate than 2:1 types, and adsorption was related to pH and the amounts of sulfate and phosphate in solution.

Subsequent research by others has shown that sulfate retention in soils is closely related to 1:1 type clay minerals, the presence of Al and Fe hydroxides and oxyhydroxides, soil pH, and the presence of competing anions, particularly phosphates (Neller, 1959; Chao, Harward, and Fang, 1962a, 1962b, 1962c; Chang and Thomas, 1963; Elkins and Ensminger, 1971). Neller (1959) examined acetate-extractable sulfate S in 10 soil series at different profile depths from various locations

in Florida. The sulfate-S contents of the surface horizons of most of these soils ranged from 0 to 4.5 ppm. Ultisols contained considerable amounts of sulfate-S. There was a highly significant increase ($r = 0.82$) in sulfate content with an increase in the clay-size fraction of the soil.

In contrast to cation adsorption, data from Chao et al. (1962b) indicated that sulfate retentive soils did not possess adsorption maxima or definite anion exchange capacities. They suggested that perhaps some other mechanism of sulfate retention is functional. No other mechanism has been identified except the proposed possibility of the precipitation of sparingly soluble aluminum sulfate minerals (Adams and Rawajfih, 1977; Adams and Hajek, 1978). Chao et al. (1962c) also found that the removal of organic matter, free aluminum oxides, and free iron oxides, considerably reduced sulfate adsorption in soils from Oregon. They also showed that Al-saturated clays adsorbed much more sulfate than H-saturated clays. The amounts of sulfate retained by reference clays were in the order:

kaolinite > illite > bentonite.

These results are consistent with the observations of Berg and Thomas (1959).

Three possible mechanisms of sulfate adsorption were proposed:

1. Anion exchange due to positive charges developed on hydrous Fe and/or Al oxide or on the crystal edges of clays, especially kaolinite, at low pH values.
2. Sulfate retention by hydroxy-Al complexes through coordination.
3. "Salt Adsorption" resulting from attraction between the surface of soil colloids and the salt.
4. Amphoteric properties of soil organic matter which develop positive charges under certain specific conditions.

1.1.3.3.2 Mechanisms of Sulfate Adsorption

Sulfate, as are anions such as phosphate and silicate, may be adsorbed by nonspecific or specific adsorption mechanisms. Nonspecific adsorption involves the coulombic attraction of negatively charged species to positively charged sites on soil colloids or metal oxide surfaces where they are held in the Stern layer or as counterions in the diffuse part of the electrical double layer (Gast, 1977; Bohn et al., 1979). This type of adsorption involves a hydrolysis mechanism for the development of surface sites for anion adsorption. The number of sites formed depends on the pH and the type of surface but not on the type of anion (Hingston et al., 1967).

Some anions may be specifically adsorbed on mineral surfaces. The mechanism involved is frequently referred to as ligand exchange (Gast, 1977). Specific adsorption coordinates the adsorbing anion with the metallic cation such that the anion is not easily replaced. This involves the displacement of a coordinated OH^- or H_2O on the surface of metal oxides or hydroxides and forms partly covalent bonds with the structural cations (Hingston et al., 1967). Mineral surfaces containing partially coordinated oxygen atoms and broken edges of layer silicates are the sites for specific adsorption in soils.

The exact mechanism of sulfate adsorption is not fully understood. Chang and Thomas (1963) proposed the following mechanism to explain their observation that the quantity of anions held by a Cecil subsoil increased with time.

Divalent sulfate ions replace OH^- from $\text{Al}(\text{OH})$ or $\text{Fe}(\text{OH})$ coatings on the clay surface and substitute for them. The replaced hydroxyl

ions react with H^+ in solution which may have resulted from cation exchange involving a similar mechanism. They explain that sulfate adsorption is increased as the pH is lowered because the replaced hydroxyl ions are more effectively neutralized. As the pH increases, cation affinity increases also, and this results in the replacement of more Al and more hydrolysis. They used this model to explain the pH and time-dependent processes which had been observed in sulfate adsorption.

Hingston et al. (1972) studied specific anion adsorption by goethite and gibbsite and found that where the acid (in this case, H_2SO_4) was fully dissociated, specific adsorption occurred only to the extent of the positive charge of the surface. Little specific adsorption was found at pH values greater than the zero point of charge (ZPC) of the mineral. Maximum adsorption would occur when the $pH = pK_a$. At this pH both the amounts of anion (dissociated acid) available for ligand exchange and the amounts of proton donor (undissociated acid) capable of neutralizing liberated OH^- are greatest. Only the monovalent species, HSO_4^- , could be specifically adsorbed without creating additional negative charge at the surface. Their mechanism involves SO_4^{2-} accepting a proton from the surface at pH values near the pK of the acid:

One mole of SO_4^{2-} adsorbed as HSO_4^- neutralizes one equivalent of surface charge. Gebhardt and Coleman (1974) agreed with the mechanism of Hingston et al. by concluding that sulfate was adsorbed as HSO_4^- .

Rajan (1978) studied sulfate adsorption on hydrous alumina and offered a refined mechanism for specific adsorption. He discounted sulfate adsorption as HSO_4^- because, under experimental conditions (and conditions in most soils), sulfate exists as SO_4^{2-} . He proposed that sulfate is adsorbed as SO_4^{2-} across two Al atoms, forming a six-membered ring. At low sulfate concentrations, water is displaced from the positive sites; as the concentration increases, increasing proportions of OH groups are displaced from neutral sites (Fig. 1). His proposed mechanism is in agreement with experimental findings that the final surface, after adsorption, carries close to a zero charge, that the relationship between sulfate adsorbed and charge neutralized is curvilinear, and that the process is time dependent.

Allophanic and highly weathered tropical soils possess extremely high sulfate adsorbing capacities when compared to mineral soils of temperate regions (Chao et al., 1962b; Bornemisza and Llanos, 1967; Hanson et al., 1970). Andepts from Mexico, Colombia, and Hawaii were found to adsorb 10 to 20 meq of sulfate per 100 g in surface soils and 15 to 60 meq sulfate per 100 g in subsoils (Gebhardt and Coleman, 1974). Minerals associated with these soils are primarily amorphous silicates and hydroxides and oxyhydroxides of Fe and Al. Experimental ZPC's for some pure minerals that may be associated with high sulfate adsorbing soils are listed below (Yoon et al., 1979):

Fig. 1. Rajan's (1978) proposed mechanism of sulfate adsorption.

<u>Mineral</u>	<u>Experimental ZPC</u>
Al(OH) ₃ (gibbsite)	5.1
α-AlO(OH)	7.7
γ-AlO(OH)	7.5
α-Fe ₂ O ₃	9.04
γ-FeO(OH)	7.4
α-FeO(OH)	6.7

Soils containing large quantities of these oxides and hydroxides and a pH below the ZPC of the dominant minerals would be expected to retain large amounts of sulfate by nonspecific adsorption. Gillman (1974) found that phosphate-extractable sulfate increased with profile depth in an Australian rain-forest soil (Rodic Hapludult). He showed that the ZPC also increased with depth from a ZPC of 4.5 at the 10 to 20-cm depth to 5.8 at the 210 to 240-cm depth.

1.1.3.4 Leaching

Many humid-region soils have argillic horizons which contain large amounts of hydrated oxides of Al and Fe and 1:1 type clay minerals. These materials may accumulate sulfate because of adsorption as explained in the previous section. In coarse-textured, sandy soils such as the Entisols, Spodosols, and the surface horizons of Ultisols in Florida, very little sulfate adsorption takes place (Ensminger, 1954; Neller, 1959; Jordan, 1964). Mineralized sulfate or sulfate applied in fertilizer may be readily lost by leaching under the high rainfall conditions which exist during most of the growing season in Florida.

Chao et al. (1962a) studied the movement of ^{35}S as gypsum through columns of 15 Oregon soils. The depth of ^{35}S movement was dependent on the amount of water moving through the columns and the sulfate adsorbing properties of the soils. When 20 cm of water was applied to a sandy loam soil, 15.2% of the S appeared in the leachate at 51 cm. Less than 5% remained in the upper 10 cm. On the other hand, those soils with a high clay content (greater than 30%) containing 1:1 type minerals and greater than 1 meq/100g exchangeable Al retained all of the applied sulfate above 15 cm when 20 cm of water was applied. Lime and phosphate applications increased sulfate leaching as would be expected from knowledge of the adsorption process. Similar leaching losses of sulfates were observed in undisturbed cores of some Australian soils (Peverill et al., 1977) and in two Caribbean soils (Haque and Walmsley, 1974).

Rhue and Kamprath (1973) studied the effects of different sources of S on leaching of sulfate in two North Carolina soils during the winter. They found that all of the applied S had leached out of the surface 45 cm of a Wagram loamy sand (Arenic Paleudult) 180 days after treatment. Elemental S, 325-mesh and prilled, was oxidized during the winter months, and after 180 days, extractable sulfate-S was at the original level in the upper 45 cm of surface soil. Oxidation and leaching rates were much slower in a Georgeville silty clay loam (Typic Hapludult).

The Wagram loamy sand from the coastal plain of North Carolina would be similar in properties to many of the Ultisols of northern Florida. Winter rainfall in north Florida would be comparable to that in North Carolina. However, the milder temperatures of Florida would

encourage more rapid oxidation of elemental S, and leaching losses of mineralized or fertilizer-applied S would be high.

1.2 ATMOSPHERIC SOURCES

1.2.1 Sulfur as a Pollutant

Most studies of atmospheric S were done by those concerned with S as an environmental pollutant. Atmospheric S is the cause of acid-rainfall and direct SO₂ damage to plants in areas of high atmospheric concentrations. Areas of heavy industrial development have been concerned with this problem for decades, but rural areas of the southeastern United States have not been as concerned with atmospheric S as a pollution source. A few researchers have discussed the beneficial aspects of atmospheric S as a nutrient source for crops (Fried, 1948; Hoeft et al., 1972; Jones et al., 1979). This subject will be discussed in a later section.

1.2.1.1 Damage to plants

The Copper Basin of southeastern Tennessee is an extreme example of an area where 9,300 ha were denuded of vegetation by a combination of SO₂ from Cu smelting, forest removal, and over-grazing. Acute damage can occur on certain forest trees at concentrations less than 0.25 ppm SO₂ for 8 hours. Chronic injury or long-term effects were noted in a Canadian forest when the trees were exposed to an average SO₂ concentration of 0.017 ppm for 5 months (Linzon, 1975). Acute and chronic damage to agronomic plants by atmospheric SO₂ has been reported, but critical atmospheric levels of SO₂ have been difficult to define (Heagle, 1972; Taniyama and Sawanaka, 1973; Tingey et al., 1973).

Once S is in the atmosphere, it can travel many kilometers from the source and affect forests and cropland. A study of soil and vegetation around a high-S, Fe-sintering plant in Ontario showed that birch trees were totally killed on 108 km^2 , heavily killed on 191 km^2 , and damaged on 589 km^2 downwind from the plant. Damage occurred up to 48 km from the plant in the direction of the prevailing air currents (Rao and Leblanc, 1967; McGovern and Balsillie, 1974).

1.2.1.2 Damage to animals

The levels of SO_2 in the atmosphere which may be harmful to higher animals and humans are greater than that which may be harmful to plants. Levels greater than 1 ppm were necessary before significant airway resistance occurred in healthy male adults exposed for 10 to 30 minutes (Frank et al., 1962). Other cases of the effects of SO_2 and H_2SO_4 in the atmosphere on human health are reviewed by Schlenker and Jaeger (1980).

1.2.2 Sources of Atmospheric Sulfur

Sulfur can exist in the atmosphere as SO_2 , H_2SO_4 , particulate sulfates, H_2S , and methylmercaptan (CH_3SH) (Terman, 1978; Urone and Kenny, 1980). Sulfur dioxide constitutes about 95% of the S compounds produced by the combustion of S-containing fossil fuels (Kellogg et al., 1972). Hydrogen sulfide, the primary S-containing product of anaerobic decomposition of organic matter, is rapidly oxidized to SO_2 and SO_3 in the atmosphere.

When SO_2 dissolves in a cloud or fog droplets or is adsorbed on particle surfaces, it reacts with water to form H_2SO_3 which is rapidly oxidized by dissolved oxygen or ozone to H_2SO_4 . The detailed mechanism

of these reactions is not well known, and even the nature of the species undergoing oxidation has not been clearly established (Cadle, 1975; Gaspar, 1975).

On a global scale, natural sources of S emissions are estimated to be greater than anthropogenic sources (Junge and Werby, 1958; Robinson and Robbins, 1972; Terman, 1978). Kellogg et al. (1972) estimated that man is contributing about half as much atmospheric S now as is nature. However, recent studies in Florida indicate that man-made sources of atmospheric S account for more than 85% of the total S in the air over Florida (E. S. Edgerton, personal communication). The burning of fossil fuels accounts for most of this S. World-wide, about 70% of this S is from the burning of coal, 16% from petroleum combustion, 4% from petroleum refining, and 10% from the smelting of ores (Gaspar, 1975; Terman, 1978). A quantification of the sources and sinks of S compounds present in the biosphere is shown in Fig. 2 (Cadle, 1975).

1.2.2.1 Anthropogenic Sources

In Florida, most of the anthropogenic S comes from 36 electric power plants (most of which are oil burning), eight pulp and paper mills in the northern portion of the state, the phosphate industry in west-central Florida, sugar refineries around Lake Okeechobee, various oil companies, cement plants, and chemical companies, and automobile emissions (Urone, 1975). Many of the power plants which are presently burning low-S oil may have to convert to high-S coal because of the cost of imported oil and the availability of coal. This conversion would increase the output of SO_2 into the environment. Burning of wood

ATMOSPHERE

* Total terrestrial, aquatic, and marine biological emission = 262×10^6 metric tons/year.

Fig. 2. Sources and sinks of sulfur compounds. Units are 10^6 metric tons per year calculated as sulfate (from Cadle, 1975).

for domestic heat and the controlled burning of forests and rangeland also contribute a small amount of S to the atmosphere.

1.2.2.2 Biogenic sources

Natural sources of atmospheric S, unrelated to human activity, include the decomposition and combustion of organic matter, spray from the oceans, and volcanic and other geothermal activity. Seawater is one of our greatest natural sinks for S and also one of our greatest sources. The average concentration of sulfate in the oceans is 2.65 ppm. The concentration of H_2S cannot be detected in seawater; the oceans are supersaturated with dimethyl sulfide (Cadle, 1975), but it is doubtful if any of this S escapes into the atmosphere in the sulfide form. The sulfate released annually from the surface of oceans has been estimated to be around 40 to 130 million metric tons, but only 10% of this passes over land (Eriksson, 1959, 1960; Friend, 1973).

Vegetative decay under anaerobic conditions releases large quantities of H_2S to the atmosphere where it is rapidly oxidized. Freshwater swamps and salt water marshes are abundant sources of biologically-produced atmospheric S. These sources are difficult to quantitate, and most estimates seem to be based on the theoretical need to balance the S cycle. Gaspar (1975) reviewed literature which indicated 30 to 202 million metric tons of H_2S released by biological decay on land. Edgerton et al. (1980) compiled estimates of biogenic S emitted from wetlands in Florida (Table 4).

1.2.3 Local and Regional Studies of Rainfall and Atmospheric S

Recent studies by Edgerton et al. (1980) and Brezonik et al. (1980) have helped to delineate the areas of acid precipitation in

Table 4. Sources of biogenic S from wetlands in Florida.

Source	Area -ha-	Potential S emission rate -kg/ha/yr-	Total S emission -mton/yr-
Poorly drained organic soils and freshwater swamps	2,800,000	0.1-1	280-2,800
Tidal marshes and mangrove swamps	490,000	1-100	490-49,000
Total	3,290,000	--	770-52,000

Florida, to estimate the amounts of S added to Florida soils through precipitation, and to evaluate the importance of oceanic aerosols and biogenically-produced S to Florida rainfall chemistry. While the deposition of H^+ and excess sulfate (i.e., total sulfate minus sea-salt sulfate) in Florida rainfall is 30 to 90% of the deposition rates in the northeastern United States, the acidity of rainfall in Florida has increased markedly in the past 25 years; the average sulfate concentrations have increased 450%. The relative annual deposition of S on Florida soils in bulk precipitation at five sites from 1952 to 1955 and from 1978 to 1979 and the relative acidity of rainfall are shown in Fig. 3 (Brezonik et al., 1980).

Northern Florida receives more than 1.5 times as much S as sulfate annually from bulk precipitation as southern Florida (8.4 and 5.5 kg/ha, respectively). Northern Florida is the most industrialized area of the state, and accounts for 85% of the total anthropogenic S emissions in the state. Coastal areas receive only around 4 kg/ha in rainfall. These data were based on samples collected from 24 sites throughout the state. The bulk of this S in north Florida (69%) fell during the summer months when it could be of most benefit as a nutrient to growing plants. This period also corresponds to the season of maximum rainfall in Florida. Sea sulfate was estimated to constitute only a small portion of the total sulfate in Florida precipitation. The percentage of sea sulfate in precipitation decreased rapidly from coastal to inland sites.

The occurrence of acid rainfall, which is directly related to atmospheric S, is more frequent in northern counties than in southern and coastal regions of the state. The most acidic rainfall in 1978

Fig. 3. Annual depositon of total sulfur, 1952 to 1955 and 1978 to 1979, and the mean pH of rainfall, 1978 to 1979 (from Brezonik et al., 1980).

occurred at Jay (pH 3.76) and at Gainesville (pH 3.93) in northern Florida. Sites north of Lake Okeechobee have annual (volume-weighted) pH values in the range of 4.6 to 4.8 while those south of the lake have pH values approaching geochemical neutrality (pH 5.6).

These data for Florida are similar to those reported by Jones (1976) and Jones et al. (1979) for South Carolina. For the period 1973 to 1975, the mean annual amount of S deposited in South Carolina soil through precipitation was 11.3 kg/ha. This compared to 6.3 kg/ha for 1953 to 1955. In addition, Jones et al. (1979) used a factor reported by Alway et al. (1937) to estimate gaseous S adsorbed by the soil from S adsorbed by PbO candles at 15 locations. This value increased from 2.8 kg/ha in 1973 to 13 kg/ha in 1977. Total S added annually to South Carolina soils from atmospheric sources ranged from 11.2 kg/ha in 1973 to 20.3 kg/ha in 1976.

1.3 FERTILIZER SOURCES

The sources of plant-available S that have been previously discussed are largely beyond the control of the crop producer. The amount of fertilizer S applied to a crop or soil is completely dependent upon management and may be the most significant source of S for modern crops growing on sandy, low-S soils.

Sulfur has traditionally been applied in fertilizers containing ordinary superphosphate (12% S), ammonium sulfate (24% S), gypsum (18% S), and other S-containing materials. When sufficient amounts of the macronutrients were applied, available S was abundant. With the introduction of high-analysis N and P materials, the S content of fertilizer materials and mixes has decreased. Beaton et al. reported that "... while the consumption of N, P_2O_5 , and K_2O

increased from about 4 million tons in 1950 to just under 18 million tons in 1976, the total amount of sulfur in fertilizers decreased from 1.8 to 1.1 million tons for the same period " (Beaton et al., 1974, p.4).

This trend does not appear to be as dramatic for Florida. Table 5 indicates that while ordinary superphosphate consumption is down 40% from 1950, the use of other S-containing materials has risen in Florida. Most references do not list S-containing fertilizers separately nor do they summarize S applied as is the custom for N, P, and K. Therefore, the total amount of S applied to Florida soils over the years is difficult to estimate. Mixed fertilizer consumption has also increased considerably since 1945.

Using data from Beaton et al. and data for fertilizer consumption in Florida in 1978 (Crop Reporting Board, 1978), one can estimate that mixed fertilizers and fertilizer materials used in Florida contain an average of 2.2% S. If this S was distributed evenly on the major cropland in Florida (1,089,300 ha of field crops, hay, citrus, and vegetables), then approximately 39 kg of S/ha was applied. If major cropland and fertilized grasslands are included (2,725,300 ha), then this value is only 15 kg/ha.

Table 5 shows that the total S as a percent of the $N + P_2O_5 + K_2O + S$ has decreased from 32.5% in 1950 to 7.2% in 1973 for the south Atlantic states (Beaton et al., 1974). However, concentrated superphosphate (0-1% S), ammonium phosphates (0-2% S), ammonium polyphosphates (0% S), etc. are used more as fertilizer materials or in mixes, and these contain very little incidental S.

The total harvested area of field crops in Florida has increased from 518,000 ha in 1965 to 623,000 ha in 1979 (21% increase) while the

Table 5. The use of selected sulfur-containing fertilizers in Florida (from Fertilizer Statistic Division, 1945-1979 and Beaton et al., 1974).

Fertilizer material	Year				
	1945	1950	1960	1970	1979
	-----metric tons-----				
Ammonium sulfate & ammonium nitrate sulfate	1,263	1,149	9,137	4,265	6,506
Ordinary superphosphate	12,600	15,676	9,137	4,265	6,506
Sulfate of potash	217	260	596	289	381
Sulfate of potash magnesia	227	141	1,026	12,090	9,745
Elemental sulfur	---	---	437	366	6,404
Calcium sulfate (gypsum)	904	675	3,345	1,692	23,573
Mixed fertilizers	643,682	712,843	1,255,669	1,292,691	1,730,406
Total fertilizers used on farms	---	---	---	---	1,914,400
Total S as a percent of $N+P_2O_5+K_2O+S^+$	---	32.5%	19.0%	9.2%	7.2% (1973)
N:S ratio in fertilizer ⁺	---	0.5	1.3	3.8	4.9 (1973)
P_2O_5 :S ratio in fertilizer ⁺	---	0.9	1.4	2.5	3.5 (1973)

⁺Data for south Atlantic states (Florida, Georgia, North Carolina, South Carolina, and Virginia).

total amounts of plant nutrients (N , P_2O_5 , and K_2O) applied per ha have only increased from 720 to 775 kg/ha (7.6% increase) (Statistical Reporting Service, 1965-1979; Hargett, 1976). These data are surprising when considering the increased yields and intensive management of modern crop production, but point out the trend toward less fertilizer S applied to Florida farmlands.

Most fertilizer-applied S is in the soluble, sulfate form in ordinary superphosphate, gypsum, potassium sulfate, sulfate of potash-magnesia, etc. All of these soluble sulfates as well as thiosulfates and polysulfides are about equally effective and immediately available to growing plants (Beaton et al., 1974). Finely-ground, elemental S is rapidly oxidized in most arable soils (Burns, 1967). Rhue and Kamprath (1973) showed that finely-ground elemental S was completely oxidized during the winter months in a North Carolina soil. Prilled S (325-mesh) offered some resistance to oxidation and remained in the surface soil longer. Beaton et al. (1974) recommended that 25% of the total S should be in a soluble sulfate form if the soil is extremely low in S and if the elemental form cannot be applied 4 to 6 weeks prior to planting a crop.

2. PLANT SULFUR NUTRITION

2.1 THE ROLE OF SULFUR IN PLANT NUTRITION

Sulfur is considered a secondary nutrient along with Ca and Mg, but it is needed by many plants in about the same quantity as P (Tisdale, 1977). The Technical Affairs Committee of the Canadian Fertilizer Institute recommended in 1978 that S should be ". . . classified in governmental regulations and by the fertilizer industry

as a 'macronutrient,' and not as a 'lesser nutrient' as it is currently described " (The Sulphur Institute, 1978, p. 21).

Sulfur is found in three general forms in the plant: (1) protein, (2) sulfate-S, and (3) organic S compounds of low molecular weight such as free S-containing amino acids or volatile organic S compounds such as glycosides, mercaptans, and sulfides. The primary role of S in plant nutrition is as a constituent of the S-containing amino acids, cystine, cysteine, and methionine, and for protein synthesis. Cysteine and methionine may be responsible for more than 90% of the organic S in plants (Thompson et al., 1970). Plants adequately supplied with S will contain more true protein than plants without adequate S, and the quality of this protein may be higher (Sheldon et al., 1951). Within limits, the amount of methionine present in a protein is a measure of the quality of that protein. Beaton et al. (1971) reviewed literature showing where increasing amounts of added S improved the quality of plant protein as indicated by the increase in methionine content.

If true protein is not synthesized in plants due to inadequate S, non-protein N such as amides and amino acids or even inorganic nitrates may accumulate and reduce crop quality (Tisdale et al., 1950; Rendig and McComb, 1956; Coleman, 1957; Dijkshoorn and Van Wijk, 1967; Stewart and Porter, 1969; Cowling and Jones, 1971). When available S is abundant and N is limited in non-legumes, sulfate-S may accumulate while dry-matter and protein yields are restricted. Metson (1973) pointed out that in practice, the first situation (excess N in relation to S) is more frequently encountered, particularly in crops regularly fertilized with N. All of the available S is utilized in the

formation of protein and little remains to accumulate in non-protein, organic compounds or as inorganic sulfate.

Many of the volatile organic S compounds found in plants are characteristic of particular plant families such as the Cruciferae, which include the Brassica (cabbage), the Amaryllidaceae, which include the Alliae (onion) tribe, and the Tropaeolaceae, which include the nasturtium (Metson, 1973). These plants have a high S requirement, and the volatile S compounds impart a characteristic odor to many of them. A relatively high proportion of the organic S is present as glycosides which yield organic iso-thiocyanates on hydrolysis (Dijkshoorn and Van Wijk, 1976).

Sulfur has also been found to be important to plants in other ways. Disulfide linkages (-S-S-) have been associated with the structure of protoplasm. Sulfur is required for N fixation by legumes since it is part of the nitrogenase enzyme associated with this reaction (Anderson and Spencer, 1950). Sulfhydryl groups (-SH) in plants have been related to increased cold resistance in some plants (Levitt et al., 1961). Other quality factors improved by S fertilization are chlorophyll and vitamin A content of forages. Alfalfa fertilized with P and S contained almost twice as much carotene and vitamin A as alfalfa fertilized with P alone (Tisdale, 1977).

2.2 SULFUR UPTAKE BY PLANTS

2.2.1 Root Uptake

Sulfur may be absorbed by plant roots exclusively as the sulfate (SO_4^{2-}) ion or absorbed as SO_2 directly through plant leaves. Sulfur uptake has been shown to be a function of the sulfate concentration of the soil solution (Spencer, 1959; Barrow, 1967) or of nutrient

solutions (Olsen, 1957). Barrow (1967) was able to relate 0.01 M monocalcium phosphate extractable sulfate to the decrease in S uptake by plants grown for 183 days in a greenhouse. The uptake of S was also greatly influenced by the nature of the soil; these differences were also indicated in the total extractable sulfate-S. Both plant uptake and extractable S were significantly modified by the nature of the soil, time of sampling, and previous fertilization.

2.2.2 Absorption from the Atmosphere

Crops growing on soils low in extractable sulfates may not always respond to direct applications of S in the field (Bremer, 1976; Jones et al., 1979). A possible explanation for these observations is direct absorption of SO₂ from the atmosphere. Fried (1948) first demonstrated that alfalfa plants could take in SO₂ through the leaves and convert it into organic S compounds. Olsen (1957) found that the amount of SO₂ absorbed by healthy cotton plants was a function of the effective leaf surface. Healthy plants obtained about 30% of their S from the atmosphere whereas S-deficient plants absorbed over 50% of their S from the atmosphere. He concluded that while the SO₂ concentration of the atmosphere is inadequate as the sole source of S for plants, the atmosphere could provide an important supplementary source of S to growing plants.

Sulfur-deficient alfalfa plants exposed to a greenhouse atmosphere during the winter months in Wisconsin were capable of absorbing as much as 73% of their total S from the air (Hoeft et al., 1972). Total S collected by PbO candles during the period the plants were grown was 1.05 mg S/100 cm² for a candle located in the greenhouse and 10.57 mg S/100 cm² for a candle located outside the greenhouse. Air movement

around plants would be expected to increase SO_2 absorption. Hill (1971) found that absorption of SO_2 by vegetation increased with wind velocity above the plants, height of the canopy, and temperature.

2.3 EVALUATING THE SULFUR REQUIREMENT OF CROPS

2.3.1 Critical Concentrations

The S requirement of a plant has been defined as the ". . . minimum uptake of this nutrient associated with maximum yield of dry matter" (Stanford and Jordan, 1966, p. 258). The concentration of the nutrient present in a plant when this condition is met is usually referred to as the critical concentration or the critical percentage (Ulrich, 1952; Thompson et al., 1970). As with any nutrient, the critical concentration of S in plant tissue can vary with species, the type of tissue (leaves, stems, roots, grain, etc.), and the age of the tissue. Some values for critical S concentrations in different crops are reported in Table 6.

Since the protein contents of plants vary widely with species, age, environment, and nutrition, the wide variability in S content of plants is not surprising; the S requirement will depend on the amount of S associated with plant protein. The protein content of the vegetative part of a plant decreases with age as a result of growth dilution of the protein by carbohydrates, hemicellulose, lignin, etc.

2.3.2 N:S Ratios

The relationship of S to plant protein and the corresponding relationship of N to protein has led to the realization that the ratio of N to S in the plant may be a more reliable measure of the S requirement than is the absolute level of S. Genetics determine the sequence and number of amino acids in the polypeptide chains of a specific protein, but nutritional and environmental factors may influence the

Table 6. Critical levels of total sulfur, sulfate sulfur, and N:S ratios for selected crops.

Crop	Type of tissue	Critical Concentration		Total N:total S ratio	Reference
		Total S	Sulfate S		
		-----%			
<u>Legumes</u>					
White clover (<i>Trifolium repens</i> L.)	above ground	0.26	---	17-18.5	McNaught & Crisstoffels, 1961; Jordan & Bardsley, 1958
Subterranean clover (<i>T. subterraneum</i> L.)	leaflets & petioles	0.20	---	15-21	Drlica & Jackson, 1979
Clover (<i>T. sp.</i>)	above ground	0.10-0.16	---	---	Jordan, 1964
Sweetclover (<i>Melilotus alba</i>)	"	0.30	---	---	Bartlett, E. D. 1955. Ph.D. Dissertation. Univ. of Fla.
Alfalfa (<i>Medicago sativa</i> L.)	"	0.22	---	---	Harward et al., 1962; Pumphrey & Moore, 1965b
Hairy indigo (<i>Indigofera hirsuta</i> L.)	"	0.20	---	---	Bartlett, 1955 (same as above)
Soybeans (<i>Glycine max</i> L.)	"	0.20	---	---	Bartlett, 1955 (same as above)
<u>Grasses</u>					
Bermudagrass (<i>Cynodon dactylon</i> L.)	above ground	0.10-0.15	---	---	Bremer, 1976
"	"	0.14	---	---	Jordan & Bardsley, 1958; Jordan, 1964
"	"	---	---	17	Woodhouse, 1969

Table 6. (Continued)

Crop	Type of tissue	Critical Concentration		Total N:total S ratio	Reference
		Total S	Sulfate S		
		---	----		
Perennial ryegrass (<i>Lolium perenne</i> L.)	above ground	---	---	20	Cowling & Jones, 1971
Italian ryegrass (<i>L. multiflorum</i> Lam.)	leaf blade	0.14	0.01	---	Ulrich & Hylton, 1968
Pangolagrass (<i>Digitaria decumbens</i> Stent.)	above ground	0.13	---	---	Bartlett, 1955 (same as above)
Millet (<i>Avena sativa</i> L.)	"	0.15	---	---	Bartlett, 1955 (same as above)
		Grain Crops			
Corn (<i>Zea mays</i> L.)	tops	0.06-0.15	---	11	Stewart & Porter, 1969
"	ear-leaf	0.14	---	---	Kang & Osiname, 1976
"	above ground (6-8 wks)	---	0.045	16	Terman et al., 1973
Sweetcorn	ear-leaf	0.24	---	---	Daigger & Fox, 1971
Wheat (<i>Triticum aestivum</i> L.)	tops (joint stage)	---	---	---	---
"	tops	0.07-0.17	---	15	Stewart & Whitfield, 1965; Stewart & Porter, 1969
"	immature leaves (97 days)	0.12	0.01	20	Freney et al., 1978
"	mature leaves	0.09	---	13-20	"
"	stems	0.03	0.004	20-37	"

Table 6. (Continued)

Crop	Type of tissue	Critical Concentration		Total N:total S ratio	Reference
		Total S	Sulfate S		
		-----%			
<i>Triticum aestivum</i> L.)	above ground (61 days)	0.30	14% of total S	15	Spencer & Freney, 1980
"	above ground (134 days)	0.15	11% of total S	19	"
		<u>Other Crops</u>			
Cotton (<i>Gossypium hirsutum</i> L.)	leaves & petioles	0.20	---	---	Jordan & Bardsley, 1958; Jordan, 1964
"	top growth (early bud)	0.15	----	----	Nearpass et al., 1961
Tobacco (<i>Nicotiana tabacum</i> L.)	leaf (early bud)	~0.15	----	----	"

amounts and relative proportions of proteins formed (Thompson et al., 1970)

The N:S ratio is relatively constant in plant protein. Dijkshoorn et al. (1960) found an atomic ratio of S to N in the protein [(N:S)_p] of perennial ryegrass foliage (Lolium perenne L.) of 0.027. This is equivalent to a (N:S)_p of 16.2:1 on a percentage basis. Dijkshoorn and Van Wijk (1967) reviewed the literature on the N and S relationships in plants and found that the organic N:organic S ratio [(N:S)_o] in plants ranged from 13.7 for grasses to 17.5 for legumes. These values were similar to those for the (N:S)_p ratio, since proteins constitute about 80% of the organic N and S present. Jones et al. (1971) found that the (N:S)_p in the dried tops of the legume, Stylosanthes humilis L., decreased as the S supply increased, but most researchers found this ratio in legumes to be fairly constant and within the ranges defined by Dijkshoorn and Van Wijk (Stewart and Whitfield, 1965; Stewart, 1969; Stewart and Porter, 1969). The (N:S)_o in plants of the Brassica tribe is lower because of the presence of other forms of organic S.

With adequate S fertilization, grasses tend to accumulate sulfate in luxury amounts resulting in a very narrow total N:total S ratio [(N:S)_t]. If S is limiting, non-protein forms of N tend to accumulate, and the (N:S)_t ratio exceeds the (N:S)_p ratio of about 14 normally found in gramineous plants. Consequently, the (N:S)_t ratio would appear to be an effective index of the S status of many grasses (Metson, 1973). Roberts and Koehler (1965) found a (N:S)_t ratio of 25 in wheat that had not been fertilized with S and ratios of 11 to 15 where S was applied. Woodhouse (1969) regarded high (N:S)_t ratios in bermudagrass (Cynodon dactylon L.) as one of the factors resulting in

poor animal performance when this forage was fed. He considered values of 12 to 17 to be normal. Bremer (1976) also found that the (N:S)_t ratios widened greatly in bermudagrass as S became deficient. Cowling and Jones (1971) considered 20 the critical ratio for perennial ryegrass.

Terman et al. (1973) used the (N:S)_t ratio at the minimum concentrations of N and S necessary for continued growth of corn to compute a critical ratio of 16 for this crop. However, they concluded that ". . . the ratios appear to be meaningful only to indicate the relative amounts of labile N and S present for assimilation by the crop" (Terman et al., 1973, p. 636). The ratios were not closely related to the corresponding dry matter yields. Daigger and Fox (1971) and Kang and Osiname (1976) also failed to relate (N:S)_t ratios to yields and S responses in corn. Their poor correlations were associated with late sampling of the ear leaf, low (N:S)_t ratios, and variations in the (N:S)_t ratio with location.

2.3.3 Sulfate Sulfur

Sulfur in excess of that required for protein synthesis will accumulate in the plant as inorganic sulfate (Rendig, 1956; Walker and Bentley, 1961; Jones, 1962, 1963; O'Connor and Vartha, 1969). Using data from Walker and Bentley (1961), Dijkshoorn and Van Wijk (1967) calculated that a yield response by legumes to applied sulfate could be expected when the sulfate-S content of the dry matter was below 0.006 g-atoms per kg (0.0192% S as sulfate). A slow rate of redistribution and the localization of metabolic consumption require that this small amount of sulfate must be present within the plant and available for metabolism. This sulfate concentration was proposed as a guide for diagnosing S deficiency since the sulfate concentration in a plant

depends on the supply of mineral ions and varies to a much greater extent than that of organic S.

The ability of the species to accumulate sulfate in excess of metabolic requirements must also be considered. Grasses are vigorous sulfate accumulators, whereas the legumes rarely accumulate high concentrations of sulfate (Metson, 1973). Dijkshoorn et al. (1960) reported a critical level of sulfate in ryegrass herbage of 0.01 g-atoms S per kg dry weight (0.032%). Some critical sulfate-S levels in selected crops from the literature are given in Table 6.

Metson (1973) compiled an excellent review of the literature relating to total S, sulfate-S, and N:S ratios and the S fertility of grasses and legumes. He found that sulfate-S varied in a similar fashion to total S and concluded that the preferred diagnostic technique might be whichever property is the more conveniently determined.

Freney et al. (1978) studied total S, sulfate-S, (N:S)_t, amide N, and sulfate as a percentage of total S as indices for diagnosing the S status of wheat in Australia. They found that each of the indices was strongly related to dry matter yield. Critical, total S values varied considerably with type of the tissue and age (Table 6). Sulfate-S changed only slightly with age and N supply but failed to provide any discrimination between plants suffering from different degrees of S deficiency; only "deficient" and "adequate" categories could be identified. The (N:S)_t was most appropriate for young wheat plants only. Amide N provided the greatest relative change in values between S-deficient and S-adequate plants, but could be influenced by the Zn and Fe supply to the plant. They concluded that sulfate-S expressed as a percentage of the total S provided the best correlation with

yield; this index was unaffected by plant age, N level, or plant part. Their data indicated that wheat plants with more than 10% of their S in sulfate form were adequately supplied with S.

Recently, Spencer and Freney (1980) reported a critical value for sulfate S (as a percent of total S) of 13% for field-grown wheat. This value was least affected by the age of the plant or N supply and was recommended as a convenient index of the S fertility status of wheat.

2.4 EVALUATING THE SULFUR FERTILITY STATUS OF SOILS

2.4.1 Extraction Techniques

Soil testing for S to evaluate S available to growing crops is not as developed nor as precise as it is for P, K, Ca, Mg, and even some of the micronutrients. The complicated and relatively unknown nature of soil S and the multiplicity of sources of S to plants makes the rapid assessment of plant-available S even more difficult. We know that soil-solution sulfate and adsorbed sulfate are readily available sources of S. Other sources include soil organic matter, precipitation and irrigation water, atmospheric S, and fertilizers and pesticides. Therefore, crop response to S is frequently as dependent upon management practices and location as it is upon available soil S.

Excellent reviews of available techniques to assess the S fertility status of soils have been written by Reisenauer et al. (1973) and Beaton et al. (1968). Few new developments have been made in recent years to improve analytical techniques for S determination or the soil test calibration necessary to apply these techniques to crop response in the field. Some soil S extractants that have been used are listed in Table 7. Reisenauer et al. (1973) pointed out that no one

Table 7. Selected methods used to determine sulfate and extractable sulfur in soils (from Reisenauer et al., 1973).

Extractant	Correlations of measured S with plant response	Estimated critical level for most crops
<u>Soluble Sulfates</u>		
water (cold)	0.98** with S uptake (Barrow, 1961)	
	0.94** with S uptake (Fox et al., 1964)	
	0.73** with yield (Spencer & Freney, 1960)	
CaCl ₂	0.99** with S uptake (Barrow, 1961)	
	0.78** with S uptake (Williams & Steinbergs, 1959)	
	0.36* with S uptake & 0.28* with yield (Hoeft et al., 1973)	
	0.86 with S uptake (Roberts & Koehler, 1968)	3.3-5.8 ppm S (Bettany et al., 1974)
LiCl	0.89 with S uptake (Roberts & Koehler, 1968)	
<u>Soluble + Adsorbed Sulfates</u>		
KH ₂ PO ₄	0.93** with S uptake (Fox et al., 1964)	
	0.83** with S uptake and 0.76** with yield (Spencer & Freney, 1960)	
Ca(H ₂ PO ₄) ₂ ·H ₂ O	0.95** with S uptake (Fox et al., 1964)	
	0.37* with S uptake & 0.32* with yield (Hoeft et al., 1973)	6-10 ppm S
	0.92 with S uptake (Barrow, 1967)	
NH ₄ OAc	0.69** with S uptake & 0.60** with yield (Spencer & Freney, 1960)	6-7 ppm S
	0.55** with yield (Bardsley & Kilmer, 1963)	
NaOAc (pH 4.8)	(Ensminger & Freney, 1966)	

Table 7. (Continued)

Extractant	Correlations of measured S with plant response	Estimated critical level for most crops
<u>Soluble + Adsorbed Sulfates + Portions of Organic S</u>		
Ca(H ₂ PO ₄) ₂ ·H ₂ O in 2N HOAc	0.39** with yield & 0.58** with S uptake (Hoeft et al., 1973)	6-10 ppm S
NaHCO ₃	0.59** with yield (Bardsley & Kilmer, 1963) Suggested by Kilmer & Nearpass (1960) & recommended by Ensminger & Freney (1966) & Bardsley & Lancaster (1965)	10 ppm S
NaH ₂ PO ₄ in 2N HOAc	0.22 with yield and 0.42** with S uptake (Hoeft et al., 1973)	
<u>Soluble + Labile Organic S</u>		
water (hot)	0.91 with S uptake & 0.93 with yield (Spencer & Freney, 1960) 0.84** with S uptake (Fox et al., 1964) 0.90** with S uptake (Williams & Steinbergs, 1959)	
<u>Biological Methods</u>		
"A" values	0.91 with S concentration & 0.96 with S uptake (Nearpass et al., 1961)	15 ppm S
"L" values	Availability index increased with successive harvests due to net S mineralization (Bettany et al., 1974)	

*Significant at the 95% probability level.

**Significant at the 99% probability level.

procedure has been consistently superior in predicting response to applied S.

Most surface soils contain so little water-soluble S that frequently poor correlations with S uptake are obtained with water extracts, dilute, neutral-salt extracts, and weak-acid extracts which contain no replacing anion. Water, especially hot water, may extract a portion of the soil organic matter. This imparts a color to the solution and interferes with the precipitation of sulfate. The organic matter must be digested before sulfates can be determined turbidimetrically, and digestion could increase the measured sulfate concentration of the extract. If only reducible S is determined (Johnson and Nishita, 1952), then color and organic matter are no problem in the extract. Neutral salts such as CaCl_2 , MgCl_2 , and LiCl extract less organic matter than water but are not effective in removing adsorbed sulfate (Ensminger and Freney, 1966; Harward and Reisenauer, 1966; Roberts and Koehler, 1968).

Extractants which have gained confidence among researchers as the most satisfactory indices of plant S uptake and yield have been those extractants which remove readily-soluble sulfates, portions of the adsorbed sulfates, and possibly some organic S. Beaton et al. (1968) pointed out that adsorbed sulfate is in kinetic equilibrium with the sulfate in solution, and it may be replaced by other anions of greater coordinating ability according to the lyotropic series:

hydroxyl > phosphate > sulfate = acetate > nitrate = chloride .

Ensminger (1954) showed that adsorbed sulfate could be extracted with a KH_2PO_4 solution containing 500 ppm P. Fox et al. (1964) used $\text{Ca}(\text{H}_2\text{PO}_4)_2$ because it gave similar values to KH_2PO_4 and also eliminated

the problem of turbid extracts. The Ca ions suppress organic matter extraction by promoting flocculation, and the phosphate anions displace adsorbed sulfate. Hoefft et al. (1973) also obtained significant correlations with $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extracts and S uptake and yield of alfalfa. A $\text{Ca}(\text{H}_2\text{PO}_4)_2$ solution of 500 ppm P in 2 N acetic acid solution extracted an average of 4 ppm more S per sample and gave slightly higher correlations than $\text{Ca}(\text{H}_2\text{PO}_4)_2$ solutions alone; this was probably due to the extraction of some plant-available, organic sulfates. Other researchers have used $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extractions as effective indices of available S (Barrow, 1967; Rehm and Caldwell, 1968). Sodium acetate and ammonium acetate solutions have been effectively used as sulfate extractants (Ensminger, 1954; Bardsley and Lancaster, 1960; Bartlett and Neller, 1960; Bardsley and Kilmer, 1963; Jordan, 1964; Nelson, 1964a, 1964b; Rehm and Caldwell, 1968). However, acetate is not a strong replacer of sulfate in neutral solutions (Beaton et al., 1968).

Acidic solutions would not be expected to increase sulfate extraction because the adsorption of sulfate by soils increases with decreasing pH (Ensminger and Freney, 1966). Spencer and Freney (1960) compared a number of extraction methods and found that the amount of sulfate extracted from soils increased in the following order:

acetate < cold-water < phosphate < hot-water .

Bardsley and Lancaster (1965) reported that the alkaline extraction of soils with NaHCO_3 removed more S than is obtained with acetate extractants. Sulfur extracted from 30 soils with NaHCO_3 at pH 8.5 correlated well ($r = 0.89$) with S "A" values. Plants with less than 10 ppm extractable S responded to applications of S. This extractant was effective in solubilizing and replacing anions as well as some

organic fractions. The Johnson and Nishita (1952) reduction technique and S determination as methylene blue must be used with alkaline extracts. Color due to organic matter and cations does not interfere with this method as it may with BaSO_4 precipitation in the turbidimetric determination of sulfate (Beaton et al., 1968).

2.4.2 Biological Techniques

Several biological methods have been used for measuring available S in soils. These include "A" and "L" values where radioactive ^{35}S is used to determine availability of soil sulfate (Nearpass et al., 1961; Bettany et al., 1974). "A" values were developed for measuring available macronutrients, particularly P (Fried and Dean, 1952), but have been adapted for S measurements. A known amount of ^{35}S is applied to a soil and the subsequent proportion of ^{35}S in the plant allows calculation of an "A" (availability) value. Nearpass et al. (1961) found "A" values from 9.8 to 42 ppm in 30 soils from the southeastern United States by growing cotton plants at six levels of applied S. These values were significantly correlated with S concentration in the plants ($r = 0.91$) and S uptake ($r = 0.96$).

Bettany et al. (1974) used a modification of the "A" value which they called the "L" (labile) value (Fried, 1964; Larsen, 1967). The following equation was used to calculate the availability index:

$$L = \frac{{}^{35}\text{S added to soil} ({}^{35}\text{S}_{\text{plant}} - {}^{32}\text{S}_{\text{seed}}) - {}^{32}\text{S added to soil}}{{}^{35}\text{S}_{\text{plant}}}$$

They found that "L" values increased with subsequent harvests of alfalfa and concluded that this increase in the availability index was a direct result of isotopic dilution of the added S due to mineralization of native soil S. Labile S apparently changes with time as a

result of mineralization of organic matter; this change could explain some of the variable correlations obtained with chemical extractants.

Robertson and Yuan (1973) studied S availability on two Florida soils using the "relative specific activity" (RSA) ratios of ^{35}S in plant tissue at two rates of S fertilization. Their calculations were similar to S "A" values. Increased S availability would be indicated by a narrower ratio of RSA at two rates of S. They found a ratio of 2.6 in soybean tissue for an Orangeburg fine sandy loam (Typic Paleudult) and a ratio of 2.9 for a Lakeland fine sand (Typic Quartzipsamment). A significant yield increase with soybeans was observed in the greenhouse on the Lakeland soil when 45 ppm S was applied. No response was observed at the low S rate (15 ppm S). Plants did not respond to applied S on the Orangeburg soil.

Beaton et al. (1968) list several other "biological" methods which have been used to evaluate available soil S. Since all of these involve either a bioassay or incubation procedure, they are time-consuming and are not conveniently adapted to most soil chemistry laboratories. These techniques are listed below:

"a" value	obtained by extrapolation of yield of nutrient curves, and is closely related to "A" values.
algae	growth of algae indicates soil S status.
Aspergillus	growth of <u>Aspergillus niger</u> indicates soil S status.
incubation	soil incubated to measure biological conversion of organic S to inorganic sulfate.
Neubauer	seedlings of spring barley used to extract soil S.

respirometer	degree of S deficiency assessed by comparing respiration curves with and without applied S.
short-term uptake	intense, short-term extraction by root pods of turnips or wheat.

3. SULFUR FERTILITY STUDIES IN FLORIDA

Most of the research with S as a plant nutrient occurred during the 1950's and 1960's as is evident by the citations in this paper. An important contribution to this research was by scientists studying crops and soils in the southeastern United States (Ensminger, 1954; Neller, 1959; Kilmer and Nearpass, 1960; Chang and Thomas, 1963; Jordan, 1964; Nelson, 1964a). By 1971, S deficiencies had been identified or suspected in every state in the Southeast (Beaton et al., 1971). Most of the S-deficient crops were on the sandy soils of the Coastal Plain. The Coastal Plain includes all of Florida, but only the coarse-textured soils of north and central Florida are expected to be low in S.

Some of the earliest reports of S deficiency in crops in Florida were in the 1940's and early 1950's by Harris, Bledsoe, and coworkers (Harris et al., 1945, 1954; Bledsoe and Blaser, 1947). Harris et al. (1945) achieved a highly significant response to S by cotton on an Arredondo lcamy fine sand (Grossarenic Paleudult). Two-week-old cotton seedlings were severely stunted and yellow where no S was applied and produced 70% of the dry matter of S-fertilized plants. At 6-weeks, the deficient plants produced less than 20% of the dry matter of S-fertilized plants. They also observed a response to S on a Norfolk fine sand (Typic Paleudult) and suggested that S deficiency could occur in wide areas of Florida.

Bledsoe and Blazer (1947) found that red and black medic clovers (Medicago sp.) were highly responsive to S fertilization on a virgin Leon fine sand. Pensacola bahiagrass showed little or no response to S. Ordinary superphosphate was shown to be an effective source of plant-available S.

In 1954, Harris et al. found that corn plants in a greenhouse study produced four times more dry matter when S was applied to an Arredondo loamy fine sand as compared to treatments without S.

Volk and Bell (1945) conducted a study in lysimeters containing a Norfolk loamy fine sand and found that sulfate leaching from gypsum in bands was only 20 to 30% of that from gypsum applied broadcast.

In 1951, Neller et al. (1951a, 1951b) reported significant responses to added S by clover and clover-grass mixtures on a Rutledge fine sand (Typic Humaquept) in northern Florida, on an Immokalee fine sand (Arenic Haplaquod) in south-central Florida, and on Carnegie and Tifton fine sandy loams (Plinthic Paleudults) in west Florida. Clover failed to grow at all on the Immokalee fine sand where the fertilizer did not contain a source of S. Water-soluble sulfate in the surface soil was less than 1 ppm S where no S was applied and 7 to 9 ppm S where superphosphate or gypsum had been applied. The Ultisols of west Florida failed to produce a response to added S as dramatically as the soils of the Peninsula. Improved growth of the legume during the cooler months due to S fertilization resulted in higher yields and higher protein content of bahiagrass (Paspalum notatum Flugge) during the summer months.

Neller (1956) also studied S as it affected the availability of other nutrients. Plants on most of the soils of Florida which

responded to S also responded to P; he found that elemental S increased the availability of rock phosphate and supplied an essential nutrient to oats and clover on a Leon fine sand (Aeric Haplaquod).

Ozaki conducted an extensive greenhouse experiment with seven soils from fields in north and west Florida to evaluate the value and source of S as a nutrient (Ozaki, C. T. 1950. Sulfur fertilization of Florida soils. Master's thesis. University of Florida. Gainesville, Florida). He made the following conclusions from his study:

1. Oats and clover responded to S on all soils studied. The Ultisols (Ruston and Greenville fine sandy loams) did not produce a definite response to S until the second cutting.
2. Gypsum applications above 16 kg/ha of S as gypsum did not produce further increases in yield.
3. All S applications increased S uptake by oats and clover.
4. S-deficient oats had a higher concentration of N than those plants with adequate S while S-deficient clover had a much lower concentration of N.
5. All sources of applied S were equally effective in improving the yield of oats and clover (gypsum, elemental S, normal superphosphate, ammonium sulfate, and potassium sulfate).
6. Peanuts responded to S applications at pegging time but did not respond to Ca.

In 1955, Bartlett, working with Neller, concluded a more extensive study of soil S and plant nutrition in Florida (Bartlett, F. D. 1955. Nature and distribution of sulfur in five soil profiles correlated with plant responses. Ph.D. Dissertation. University of Florida. Gainesville, Florida). He found about 10% of the total S in Florida soils was extractable with a buffered acetic acid solution; this S correlated well with S uptake by six forage and field crops in a greenhouse experiment. Leon (Aeric Haplaquod), Blanton (Grossarenic Paleudult), and Gainesville (Typic Quartzipsamment) series were the most S-deficient

soils studied and produced increased yields of grasses and legumes an average of 1100 kg/ha when S was added. A Red Bay fine sandy loam (Rhodic Paleudult) from west Florida did not produce a S response by the crops studied, but the addition of S did cause higher S concentrations in the plant tissue. The addition of S to all soils at the rate of 34 kg/ha increased the S concentration of the plants by 0.10 of a percent. Critical levels of S were established for several crops. These are listed in Table 6.

Neller's paper on the increase in extractable sulfate with an increase in the clay content in the profile of a number of Florida soils (Neller, 1959), led to the realization that some deep-rooted crops may not respond to S on low-S soils because adequate S is available from deeper soil horizons. Researchers working with Ultisols in other areas of the southeastern United States have made similar conclusions (Ensminger, 1958; Jordan, 1964; Anderson and Futral, 1966; Murdock and Lund, 1979).

Recently, Mitchell and Gallaher (1980) observed S-deficient, seedling, field corn on an Arredondo fine sand in north Florida. They were unable to increase yields by foliar and soil S applications although S concentrations were increased in the plant tissues by the S treatments. All plants had grown out of the S-deficient conditions by 55 days; they assumed that plant roots were able to reach adsorbed S associated with the argillic horizon at 60 to 80 cm. Soil in the Bt horizon contained 5 to 8 times more S than soil in the 0 to 60-cm depth.

Most of the research with S on Florida soils was done during the 1940's and 1950's. Since that time there have been few positive

reports of S deficiencies on crops within the state. Although these workers clearly demonstrated the need for S on crops on most of Florida's sandy soils, little attention has been devoted to this nutrient. Less S is applied through fertilizers, but more is reaching the soils through precipitation and direct SO_2 adsorption. Yields of most field crops have doubled, and in some cases, tripled since the 1950's. New, higher-yielding varieties and even some new crops have been introduced to Florida farms. Management practices have changed dramatically, and fertilization is more intense. A re-evaluation is needed of the S fertility status of Florida soils to determine if crop yields can be improved by S fertilization during the 1980's, and to identify the sources and availability of soil S in Florida.

SECTION III MATERIALS AND METHODS

4. EXPERIMENTAL METHODS

4.1 SULFUR DISTRIBUTION IN SELECTED FLORIDA SOILS

Soil series which represented some of the major soils of Florida and which are important in crop production were selected. These were grouped into the orders Ultisols, Entisols, and Spodosols. The county where profile samples were taken and the soil order are shown in Fig. 4.

Pedon samples were collected by personnel of the Soil Characterization Laboratory of the University of Florida. Samples were taken from each horizon or subhorizon and prepared for physical, chemical, and mineralogical analyses for characterization purposes (Calhoun et al., 1974; Carlisle et al., 1978). After all characterization data were collected, the air-dried, screened samples were used for extractable sulfate, total S, total C, and total N determinations by the author. Ten Ultisols, ten Entisols, and nine Spodosols were selected and a total of 174 profile samples were studied. The parameters were compared and correlated with chemical and mineralogical data collected by the Soil Characterization Laboratory on these same samples. Chemical methods used for analyses will be discussed in sections 5 and 6.

4.2 A GREENHOUSE EVALUATION OF SUBSOIL SULFUR IN FOUR FLORIDA SOILS

A greenhouse experiment was designed to evaluate the contribution of subsurface horizons to the S nutrition of plants. The experiment

Fig. 4. Location of soil pedons where samples were collected for a survey of sulfur in Florida soils.

involved four soil series, two horizon sequences nested within each series, and two S rates within each horizon sequence. Each treatment was replicated four times. Four soils which represented a Spodosol, an Entisol, and two Ultisols were collected from unfertilized sites near cultivated fields or improved pastures. The four soils and their locations are listed below:

<u>Series</u>	<u>Pedon location</u>
Myakka fine sand (Aeric Haplaquod, sandy siliceous, hyperthermic)	Beef Research Unit, Alachua Co.
Lakeland fine sand (Typic Quartzipsamment, thermic, coated)	16 km SW of Williston, Levy Co.
Orangeburg fine sand (Typic Paleudult, fine-loamy, siliceous, thermic)	A.R.E.C., Quincy, Gadsden Co.
Norfolk fine sand (Typic Paleudult, fine-loamy, siliceous, thermic)	A.R.E.C., Quincy, Gadsden Co.

Bulk samples of soil were collected from the surface 0 to 20 cm and from the upper 0 to 20 cm of the argillic and spodic horizon of the Orangeburg, Norfolk, and Myakka soils. Soil was collected from the surface 0 to 20 cm and from the upper 0 to 20 cm of the C horizon in the Lakeland soil. Soil from each location and profile depth was air dried and screened twice through a 4-mm stainless steel screen and once through a 2-mm screen. Samples were collected for mechanical, chemical, and mineralogical analysis.

Mechanical analysis was by the Bouyoucos (1962) hydrometer method. The less than 2 μ m clay-size fraction from each horizon was separated and prepared for X-ray diffraction for mineral identification by the method outlined by Jackson (1969). Citrate-dithionite soluble Fe and

Al was determined on samples from every soil and horizon. Sodium pyrophosphate extractable Fe and Al were determined only on the Myakka soil (Jackson, 1969).

A pH-buffer curve was determined on soil from the surface horizon by adding increasing increments of CaO to given weights of soil. The limed samples were moistened with demineralized water, mixed well, and allowed to air dry. This was repeated three times during a two-week period. At the end of 2 weeks, the soil pH was determined in a 1:1 soil:water ratio. The soil pH-buffer curves of the four soils are shown in Fig. 5.

A mixture of CaO and MgO (1.4:1 ratio) was added to raise the soil pH of the surface horizons to near 7.0. Lime was mixed with the bulk soil in a mechanical, cement mixer. The soil was moistened with distilled water, allowed to equilibrate in plastic bags for 1 week, air dried, and screened again. A basic N, P, K, and micronutrient mix was added to all surface soils (Table 8). Two rates of S, 0 and 20 ppm S, were applied as reagent-grade $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and the soil was mixed again. The S treatment was inadvertently omitted from the Lakeland soil. The error was noticed after the first harvest of plants in the greenhouse, and the appropriate rate of S as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was added in solution.

Polyvinyl chloride (PVC) pipe with a diameter of 15.2 cm (6 in.) was cut into 50-cm sections for use as containers for the bioassay. The pipe was thoroughly cleaned and rinsed with distilled water. A plastic bag, perforated at the bottom for drainage, was fitted over the lower end of each pipe section. Each section was placed in a 20.3-cm (8 in.) plastic saucer for support and drainage.

Fig. 5. Soil pH buffer curves for four Florida soils.

Table 8. Nutrients applied to surface soils used in a greenhouse evaluation of subsoil sulfur.

Nutrient applied	Source	Basic rate of nutrient	
		Myakka & Lakeland soils	Orangeburg & Norfolk soils
-----ppm-----			
N	NH ₄ NO ₃	50.0	50.0
P	Ca(H ₂ PO ₄) ₂ ·H ₂ O	50.0	250.0
K	KCl	50.0	50.0
Cu	Cu(NO ₃) ₂ ·3H ₂ O	2.0	2.0
Fe	FeCl ₂ ·4H ₂ O	5.0	5.0
Mn	MnCl ₂ ·4H ₂ O	2.0	2.0
Zn	ZnO	5.0	5.0
B	H ₃ BO ₄	0.25	0.25

The two horizon sequences were established by placing either washed, quartz sand or the dried, screened, subsurface soil in the bottom of the pipe. Distilled water was added to settle the soil and moisten it to near field capacity (1/3 bar suction). The amount of soil or sand added was predetermined so that a final depth of approximately 24 cm was achieved. The moistened soil was allowed to equilibrate for 3 days to ensure uniform moisture distribution.

The treated, surface soil was weighed and placed above the subsurface layer so that the final depth, after wetting, would also be approximately 24 cm. Distilled water was added to moisten the surface soil slightly beyond field capacity. The soil-filled tubes were arranged on a center, greenhouse bench and randomized within soil series. A schematic of one experimental unit is shown in Fig. 6.

After 1 week of equilibration, all tubes were planted on 5 February 1980 to a sorghum x sudangrass hybrid (Sorghum sudanese (Piper) stapf 'Dekalb SX16A'). After emergence, seedlings were thinned to allow eight per pot (tube) to grow. Two weeks after emergence, all pots were fertilized with 25 ppm N and 25 ppm K as NH_4NO_3 and KCl based on the weight of the surface soil. Plants were watered as needed with distilled water in an attempt to maintain a reasonably uniform moisture level throughout the tube. Greenhouse temperatures were adjusted for a maximum of 30°C and a minimum of 16°C.

Plants were harvested every 4 weeks for a total of 4 harvests. Plants were clipped 7.5 cm above the soil line, placed in paper bags, and dried in a forced-air oven at 70°C. Samples were then weighed, ground to pass a 1-mm screen, ashed, and analyzed for N and S. Details of tissue analyses will be given in a later section. Relative dry

Fig. 6. Schematic of one experimental unit in the greenhouse evaluation of subsoil S in Florida soils.

matter yields were calculated within each harvest and soil series. The highest yielding treatment was assigned a relative yield of 100%.

All pots were fertilized with 50 ppm N and 50 ppm K after the first, second, and third harvests. After the third harvest, 50 ppm P as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and 1/2 of the original micronutrient rate were applied to all pots.

An infestation of red spider mites warranted spraying with Kelthane(TM) after the second harvest. The chemical spray caused severe "burning" of the foliage of most plants. The plants recovered rapidly from the damage, and yields from the third harvest were not affected.

After the fourth harvest, soil was washed from the roots with tap water; the roots were rinsed in distilled water, dried, and weighed.

4.3 SULFUR IN BAHIAGRASS AND BERMUDAGRASS

In the spring of 1978, two experiments were begun to study the response of bahiagrass (Paspalum notatum Flugge 'Pensacola') and bermudagrass (Cynodon dactylon L. 'Coastcross-1') to S fertilization in the field. The bahiagrass experiment was located at the Beef Research Unit, approximately 16 km northeast of Gainesville, on a Myakka fine sand; the bermudagrass experiment was located at the Green Acres Agronomy Farm, approximately 16 km west of Gainesville, on a Kendrick fine sand (loamy, siliceous, hyperthermic, Arenic Paleudult). The experiments were located in established fields of bahiagrass and bermudagrass which had not been fertilized for several years.

Dolomitic limestone was applied at the rate of 4,500 kg/ha 1 month before initial fertilizer treatments were begun. Phosphorus and K were applied uniformly to all plots in four applications during

the season at an annual rate of 49 kg/ha P (112 kg/ha P_2O_5) and 186 kg/ha K (224 kg/ha K_2O). The source of P and K was an 0-10-20 grade fertilizer mixture composed of concentrated superphosphate and muriate of potash. Micronutrients were applied each spring at 34 kg/ha of Fritted Trace Elements (F.T.E.) no. 503.¹

The experimental design at both sites was a randomized block with nine treatments and four replications. Plot size was 2.44 x 4.87 m (.00119 ha). Two annual rates of N--200 and 400 kg/ha--and four annual rates of S--0, 10, 20, and 40 kg/ha--were applied. Nitrogen and S were applied as agricultural grade NH_4NO_3 and $CaSO_4 \cdot 2H_2O$, respectively. The N was applied after each harvest in four split applications during the season. All of the S was applied in the spring before growth began except for the ninth treatment. This treatment included four split applications of S at an annual rate of 20 kg/ha and 400 kg/ha of N.

Plots were harvested four times during the growing season: (1) the second week in May, (2) the last week in June, (3) the first week in August, and (4) the last week in September. A 1-m strip the length of the plot (4.87 m) was harvested with a Gravelly tractor with a sicklebar mower. The forage was weighed, and a 300 to 500-g subsample was removed for moisture determination and chemical analysis. This sample was weighed, dried in a forced-air oven at 70°C for several days, weighed again, and double-ground to pass a 1-mm sieve. Total N and S were determined on the tissue by methods described in the next section.

¹Frit Industries, Inc., Ozark, Alabama.

Soil samples were taken at the end of each growing season from each plot. Samples were taken at depths of 0 to 15 cm and 15 to 30 cm. Samples were also taken at greater profile depths from those plots receiving 0 and 40 kg/ha S. These samples were air dried and screened through a 2-mm sieve. Sulfate S was extracted with a 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ solution and determined either turbidimetrically (Massoumi and Cornfield, 1963; Chaudry and Cornfield, 1966) or by indirect barium (Ba) absorption spectroscopy (Hue and Adams, 1979). An estimate of total S was made on samples from 1978.

Stolon-root samples of bahiagrass were collected in the fall of 1979 from the 0 and 40 kg/ha S plots at the Beef Research Unit. These were carefully washed, rinsed three times with distilled water, dried, weighed, and ground. Total N and S were determined on the tissue.

5. LABORATORY ANALYSES

5.1 NITROGEN

5.1.1 Total Nitrogen in Plant Tissue

Plant tissue for N determination was dried and ground twice to pass a 1-mm screen. Digestion was in an aluminum digestion block similar to the one described by Gallaher et al. (1975). The reagents and procedure were from Nelson and Sommers (1973). A 0.2 g sample of tissue was weighed into pyrex tubes. A 1.1-g scoop of a K_2SO_4 - CuSO_4 -Se salt-catalyst mixture and 4 ml of concentrated H_2SO_4 were added to each sample. A small glass funnel was placed in the top of tubes to ensure efficient refluxing of the sample. Samples were placed on a preheated digestion block at 375°C and digested for 1.5 hours after the solution cleared. The digested sample was cooled and quantitatively transferred to micro-Kjeldahl flasks with demineralized water. Ammonium in the

digested sample was then determined by a conventional, semi-micro Kjeldahl distillation procedure.

5.1.2 Total Nitrogen in Soils

Total N in soils was determined by the same method as total N in plant tissue. Soil samples were finely ground for 5 minutes using a mechanical mortar and pestle. A 0.2-g sample was weighed and digested on an aluminum digestion block for 3 hours after the solution cleared. Ammonium was determined by a semi-micro Kjeldahl procedure.

5.2 SULFUR

5.2.1 Tissue Digestion for Total Sulfur

Plant tissue was digested using a $\text{Mg}(\text{NO}_3)_2/\text{HNO}_3$ solution on a hot plate followed by heating in a muffle furnace at 500°C for 2 hours. The procedure is a slight modification of the methods of Butters and Chenery (1959) and Chaudry and Cornfield (1966) and is similar to the digestion procedure for the gravimetric determination of S as given by the Association of Official Analytical Chemists (1970). A preliminary study indicated that this method resulted in more complete digestion of the tissue and gave comparable recovery of added S when compared to the $\text{HNO}_3/\text{HClO}_4$ wet digestion technique described by Beaton et al. (1968). Sulfate S was determined on the digested tissue by the turbidimetric procedure of Massoumi and Cornfield (1963) and Chaudry and Cornfield (1966) and will be given in a later section. The digestion procedure is given in Appendix A.

5.2.2 Soil Extraction for Sulfate Sulfur

Extractable sulfate S was determined on air-dried, screened soils by extracting 10 g of soil with 25 ml of a $0.01 \text{ M Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ solution. Soil and extractant were placed in 100-ml bottles and

shaken for 30 minutes on a reciprocating, mechanical shaker. All extracts were filtered through Whatman no. 42 filter paper. A 5 or 10-ml aliquot was used for the turbidimetric determination of sulfate S. Values reported for the study of S distribution in selected Florida soils were obtained by the indirect method of Hue and Adams (1979) and a 10-ml aliquot was used. All other extractable sulfate-S values were determined turbidimetrically (Massoumi and Cornfield, 1963; Chaudry and Cornfield, 1966).

Some difficulties were encountered with the turbidimetric determination of sulfate S in soil extracts. These difficulties, along with the justification for using the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ extractant, and a preliminary study of extractants are discussed in section 5.2.3.

5.2.3 A Comparison of Two Extraction Procedures for Soil Sulfur

A suitable technique for extracting and determining sulfate S in soils should be convenient to use with the laboratory facilities available; the procedure should be rapid and reproducible. The extractant should remove a minimum of soil organic matter which could interfere with sulfate determination. Extractable S must also be correlated with plant uptake and/or yield. A study of the available extractants indicated that a $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ solution (Fox et al., 1964; Beaton et al., 1968) or an $\text{NH}_4\text{OAc} + \text{HOAc}$ solution (Bardsley and Lancaster, 1960, 1965) would be most suitable for this investigation. However, preliminary studies showed that both of these solutions alone would extract some color from a few Florida soils. This color was difficult to remove with the $\text{HNO}_3/\text{HClO}_4$ digestion described by Beaton et al. (1968).

Bardsley and Lancaster (1960, 1965) used activated charcoal to remove color from their extracts before determining S turbidimetrically.

A 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ extractant (approximately 500 ppm P) and the $\text{NH}_4\text{OAc} + \text{HOAc}$ extractant of Bardsley and Lancaster (39 g NH_4OAc in 1 liter of 0.25 N HOAc) were compared. Both extractants were studied with and without activated charcoal. Since most of Florida soils are low in extractable S, a narrow soil:solution ratio was used (Bardsley and Lancaster, 1960). Ten grams of air-dried, screened soil were shaken for 30 minutes with 25 ml of the extractant in 100-ml extraction bottles on a reciprocating, mechanical shaker. Where charcoal was used, approximately 0.25 g of "Darco G-60" activated charcoal was added after the 30-minute shaking period using a calibrated scoop. The samples were reshaken for 3 minutes. All extracts were filtered through Whatman no. 42 filter paper; sulfate-S was determined turbidimetrically. Ten milliliters of the extract were used for sulfate determination. An equal volume of the extracting solution was added to all standards and blanks. Charcoal "blanks" were run to determine any sulfate-S extracted from the charcoal.

Where no charcoal was used and color appeared in the extract, duplicate samples were read on the spectrophotometer when determining S by turbidimetry. No BaCl_2 or BaSO_4 seed suspension was added to one of the samples. Absorbance was read on both samples, and the absorbance due to color in the extract was subtracted from the absorbance of the sample with BaCl_2 added. From this value, S in the extract was calculated.

Air-dried, screened soil from a Myakka fine sand and from a Kendrick fine sand at 0 to 15 cm and 15 to 30 cm depths was used for

extraction. Three rates of S--0, 4, and 8 ppm--were added to each soil. The soil was moistened and allowed to dry and screened before extraction. The results are given in Table 9. All values are the mean of two determinations.

None of the methods were comparable in the amounts of S extracted from the soils. The 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ without the charcoal (Method A) produced the most consistent results. Considerable amounts of S were extracted from the charcoal (Methods B and D). The amount of S in the charcoal blank was subtracted from that in the sample. The amount of S was quite variable in the charcoal blanks, and this variability probably accounted for the differences in the samples extracted using charcoal. The $\text{NH}_4\text{OAc} + \text{HOAc}$ extractant (Method C) removed slightly less sulfate-S than the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ extractant since acetate is not as effective in replacing sulfate as the phosphate anion. ^{p. 53} The decision was made to use the 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ extractant. In those samples where color remained in the extract, a blank was run when S was determined turbidimetrically.

The 1979 paper by Hue and Adams on the indirect method of sulfate determination on soil extracts offered another alternative for sulfate determination on colored extracts. Sulfate sulfur in the 174 soil extracts in the study of S distribution in Florida soils was determined by this method and is discussed in section 6.2.

5.2.4 Estimation of Total Sulfur in Soils

The $\text{Mg}(\text{NO}_3)_2/\text{HNO}_3$ procedure used for plant tissue digestion was used for estimating total S in soils. Some modifications were needed and these are described in Appendix B. Some preliminary studies and justification for using this technique are described below.

Table 9. Sulfate sulfur removed by four extraction methods and percent recovery of added sulfur.

Soil series	Depth	Added S	Extraction method ^{†‡}			
			A	B	C	D
	--cm--	-ppm-	-----ppm-----			
Myakka	0-15	0	3	5	2	2
"	"	4	7(100)	8(75)	2(0)	10(200)
"	"	8	10(88)	11(75)	8(75)	12(125)
"	15-30	0	4	6	2	2
"	"	4	7(75)	8(50)	2(0)	8(150)
"	"	8	11(88)	13(88)	8(75)	15(162)
Kendrick	0-15	0	3	8	2	2
"	"	4	6(75)	9(25)	5(75)	8(150)
"	"	8	10(88)	12(50)	8(75)	12(125)
"	15-30	0	4	7	2	7
"	"	4	9(125)	10(75)	10(200)	15(200)
"	"	8	16(150)	16(112)	16(175)	19(150)

[†]A = $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$; B = $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ + charcoal; C = $\text{NH}_4\text{OAc} + \text{HOAc}$; D = $\text{NH}_4\text{OAc} + \text{HOAc}$ + charcoal.

[‡]Figures in parentheses are percent recovery of added S.

In 1968, Beaton et al. listed more than 36 different methods for determining total S in soils. Most of these methods involved acid digestion or alkaline fusion of the soil to oxidize all reduced forms of organic and inorganic S to sulfate, extraction of the residue, and sulfate determination by BaSO_4 precipitation (gravimetric, turbidimetric, or titrimetric methods). Of the various acid treatments, HClO_4 and a mixture of $\text{HNO}_3 + \text{HClO}_4$ have been the most popular and convenient to use. These digestion procedures are not as tedious as sodium carbonate-sodium peroxide fusion techniques, but they may not decompose all the soil minerals in some soils. Since most of the soil S in the surface horizons of Florida soils is considered to be associated with soil organic matter, any technique that effectively digests organic matter and removes sulfate-S should be suitable for the estimation of total S in soils. The use of HClO_4 can be dangerous without proper ventilation. The required ventilation was not available in the Analytical Research Laboratory where most of these analyses were conducted; therefore, the $\text{Mg}(\text{NO}_3)_2/\text{HNO}_3$ digestion/oxidation procedure was adopted.

Soils which were only air dried and screened before digesting may not completely react with the digesting solution. Incomplete recovery of total S may result. Nine soil samples were finely ground with an agate mortar and pestle and digested according to the above procedure. Sulfate-S was determined turbidimetrically and compared to the results of soil samples that had been screened through a 2-mm sieve. These data are presented in Table 10. Grinding these samples did not seem to affect the amount of S extracted after digestion. Therefore, subsequent soil samples were only air dried and screened.

Table 10. Sulfur content of finely ground soil and screened soil using the $\text{MgNO}_3/\text{HNO}_3$ digestion procedure.

Soil identification	Sulfur content [†]	
	Finely-ground soil	Screened soil
	-----ppm-----	
1	60 ± 1	64 ± 1
2	25 ± 1	25 ± 0
3	17 ± 1	17 ± 1
4	46 ± 3	44 ± 3
5	73 ± 7	91 ± 9
6	29 ± 1	30 ± 2
7	26 ± 0	26 ± 2
8	92 ± 8	83 ± 2
9	81 ± 7	80 ± 6

[†]Values are the mean of 3 analyses.

The $\text{Mg}(\text{NO}_3)_2/\text{HNO}_3$ digestion procedure was compared to the digestion procedure of Bardsley and Lancaster (1960) and to total S estimation using a Leco Sulfur Analyzer.²

Bardsley and Lancaster mixed finely ground soil with NaHCO_3 in a porcelain crucible and ignited the mixture at 500°C for 3 hours in a muffle furnace. The oxidized mixture was then extracted with $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 2 N HOAc. Sulfate-S was determined turbidimetrically.

The Leco Sulfur Analyzer used in this study ignites a soil (or plant) sample in a high frequency induction furnace. A 0.5-g sample of finely-ground soil was treated in a ceramic crucible with Fe, Sn, and Cu accelerators. The crucible was covered with a porous cap and heated to a very high temperature (ca. $1,600^\circ\text{C}$) in a stream of oxygen. Sulfur is converted to gaseous SO_2 which is trapped in dilute HCl containing KI, starch, and a trace amount of KIO_3 solution. The reactions involved are indicated below (Bremner and Tabatabai, 1971):

The results of these comparisons are presented in Table 11. The soils studied and treatments were the same as those used in the comparison of different extraction methods (Table 9).

The Leco method was unsatisfactory for the determination of total S at the levels present in these soils. Tabatabai and Bremner (1970b) and Bremner and Tabatabai (1971) also experienced poor recovery of soil S and low precision using this technique for mineral soils. They

²Laboratory Equipment Corp., St. Joseph, Michigan.

Table 11. A comparison of three rapid methods of estimating total sulfur in soils.

Soil	S added	Total S		
		Mg(NO ₃) ₂ /HNO ₃ digestion	NaHCO ₃ digestion (Bardsley & Lancaster, 1960)	Leco
			-----ppm-----	
Myakka A	0	65	68	90
	4	70	68	110
	8	70	68	100
Myakka B	0	58	52	90
	4	60	53	60
	8	66	56	100
Kendrick A	0	68	57	100
	4	69	61	110
	8	74	61	110
Kendrick B	0	24	<20	30
	4	26	<20	<15
	8	30	<20	15

reviewed some of the problems with the Leco method and suggested that the problems may be related to (1) the size of sample and the mesh-size, (2) the amount and type of combustion accelerator, (3) the method of instrument calibration, and (4) the incomplete sample combustion or the release of SO_3 as well as SO_2 . They concluded that the Leco method was ". . . unsatisfactory for research requiring accurate and precise determination of total sulfur in soils" (Tabatabai and Bremner, 1970b, p. 419). However, the Leco method has proven to be of value in plant tissue analysis (Jones and Issac, 1972; F. Adams, personal communication).

The $\text{Mg}(\text{NO}_3)_2/\text{HNO}_3$ digestion resulted in slightly higher levels of S than the Bardsley and Lancaster method. This was probably due to more effective digestion of the soil minerals because of the predigestion step on the hotplate. The better contact of the soil particles with the $\text{Mg}(\text{NO}_3)_2/\text{HNO}_3$ may have resulted in less loss of S through volatilization. Therefore, the $\text{Mg}(\text{NO}_3)_2/\text{HNO}_3$ digestion procedure was adopted as a suitable alternative to either $\text{HClO}_4/\text{HNO}_3$ digestion or NaHCO_3 digestion with acid extraction.

6. ANALYTICAL TECHNIQUES FOR DETERMINING SULFUR

Sulfate S in soil extracts, in digested-soil extracts, and in digested plant tissue was determined by a turbidimetric procedure (Massoumi and Cornfield, 1963; Chaudry and Cornfield, 1966) or by the indirect method of Hue and Adams (1979). Because of difficulties associated with S analyses, these techniques and others are discussed below.

Most analytical techniques for determining S first involve the conversion of various forms of S to the sulfate ion and quantitatively

estimating S as sulfate. As previously mentioned, gravimetry, turbidimetry, titrimetry, and colorimetry are the most common methods for measuring sulfate in digested plant tissue, soil extracts, digested soil samples, and other aqueous solutions containing sulfate-S. In almost all of these techniques, the sulfate anion reacts with the Ba cation in solution to form insoluble BaSO_4 . An extensive review of some of these techniques has been made by Beaton et al. (1968).

Reduction of S to H_2S and determination of S as methylene blue has generally been accepted as the most satisfactory method for the colorimetric estimation of traces of S in soils, soil extracts, plant tissue, and tissue extracts (Johnson and Nishita, 1952; Steinbergs et al., 1962; Tabatabai and Bremner, 1970a, 1970b). This procedure was developed by Johnson and Nashita (1952) for soil and plant tissue analysis and has been reviewed by Beaton et al. (1968). This method is very sensitive but quite tedious. Often very small samples are necessary which may lead to sampling difficulties and erroneous results. Aliquots larger than 2 ml cannot be used. A heat source and S-free N are needed for the digestion-distillation apparatus. Each sample must be boiled and refluxed for an hour to reduce all S to H_2S . The large number of samples handled in this study could not be accommodated using the Johnson and Nashita method because of the time involved and the lack of necessary equipment. The author recognizes that some accuracy may have been sacrificed in estimating S by the standard turbidimetric method rather than using the more accurate but tedious methylene blue method.

6.1 TURBIDIMETRY

Most of the S analyses reported in this dissertation were done by turbidimetry. The procedure used in this study is given in Appendix C. The turbidimetric method is rapid and sensitive, but there are a number of problems and limitations with this technique which should be mentioned. Turbidimetry is subject to many interferences, and the formation of reproducible BaSO_4 suspensions under uniform precipitating conditions is extremely difficult. High concentrations of Na, K, Ca, Mg, NO_3 , PO_4 , and SiO_2 can all interfere with the turbidimetric sulfate determination, but only large amounts of Ca are likely to cause significant interference in practice (Butters and Chenery, 1959). Colloidal organic matter can interfere with the precipitation of BaSO_4 by acting as a protective colloid in solutions low in S and by coprecipitating with BaSO_4 at high concentrations of S.

Uniform precipitating conditions are essential in order to obtain reproducible results. The use of concentrated acetic and phosphoric acids buffers the pH and reduces variability due to acid concentration. A seed suspension of small and uniformly sized BaSO_4 crystals acts as nuclei or seed crystals and insures more rapid precipitation and uniform results at low concentrations. Uniform tubes, stoppered and carefully inverted a given number of times, also help to insure uniform precipitating conditions. Gum acacia added to the solution acts as a stabilizer and provides for greater reproducibility of the suspensions.

6.2 INDIRECT METHODS

Sulfate S in soils analyzed in the study of S distribution in selected Florida soils was determined by the indirect method of Hue

and Adams (1979). Several indirect methods of sulfate determination by measuring the removal of Ba, Pb, or Sr from solution by sulfate have been proposed (Roe et al., 1966; Gersonde, 1968; Dunk et al., 1969; Borden and McCormick, 1970; Loeppert and Breland, 1972; Hue and Adams, 1979). These methods are comparable to turbidimetry where accuracy and reproducibility are of concern. They also involve difficulties in analysis of the associated cation. The most successful techniques involve the indirect measurement of sulfate by Ba precipitation and determination of Ba by atomic absorption spectroscopy. Major difficulties associated with this technique are achieving complete precipitation of small quantities of sulfate, Ba ionization interferences by atomic absorption, Si and Al interferences with Ba absorption, and organic matter, K, and Ca interferences with BaSO_4 precipitation (R. H. Loeppert, Jr. 1972. Analysis of sulfate in soil extracts by atomic absorption spectroscopy. Master's thesis. University of Florida, Gainesville). Hue and Adams (1979) improved the technique by seeding samples with BaSO_4 , by precipitating in 50% ethanol solution to lower BaSO_4 solubility, by using ClCH_2COOH and KOH to control ionization interferences, and by determining Ba in a N_2O /acetylene flame.

Their technique was adopted for use in this study on soil extracts with very low concentrations of sulfate or where the presence of color due to Fe or organic matter might present problems with turbidimetric techniques. Their method is briefly outlined in Appendix D.

SECTION IV RESULTS AND DISCUSSION

7. SULFUR DISTRIBUTION IN SELECTED FLORIDA SOILS

7.1 SPODOSOLS

Extractable sulfate S was very low throughout the profile in all of the Spodosols studied (Table 12). Extractable S in the surface soils ranged from 1 ppm in a Myakka fine sand from Alachua County to 8 ppm in a Leon fine sand from Duval County. Most of these profiles were from rural locations. However, the City of Jacksonville encompasses Duval County, and the higher SO_2 emission rates from industry in that area could account for the higher sulfate-S level. Duval County had one of the highest SO_2 emission rates in Florida in 1978. Between 100 and 200 kg/ha of S were emitted on a county-wide basis. The average for the entire state is 32 kg/ha. Rainfall in the Jacksonville area was found to contain 43.5 $\mu\text{eq/liter}$ of SO_4^{2-} in 1979--also among the highest in the State (Brezonik et al., 1980; Edgerton et al., 1980). Spodic horizons contained slightly more sulfate S than the eluviated A2 horizons but less than the surface horizons.

Extractable sulfate S did not appear to be related to total S in the soil. Extractable S varied little with horizon depth, whereas considerable differences were observed in the total S levels. The distributions of the mean total and extractable S level in the nine Spodosol profiles are given in Fig. 7.

Table 12. (Continued)

Series	Hori- zon	Water pH	Total				Ex- tract. S	Sodium- pyro- phosphate soluble		<2µm clay frac- tion	Dominant clay mineralogy [†]				
			C	Total	N	S		Al	Fe		%				
											Mont.	Int.	Kaol.	Gib.	Qtz.
Mauchula (Hernando Co.)	Ap	4.0	1.93	0.060		70	4	0.021	0.010	2	0	0	29	0	71
	A12	4.4	0.36	0.010		26	2	0.015	0.010	2	--	--	--	--	--
	A2	4.7	0.11	--		20	2	0.009	0.009	1	--	--	--	--	--
	B21h	4.3	1.14	0.035		76	2	0.158	0.009	7	0	8	43	0	44
	B22h	4.6	0.66	--		54	1	0.143	0.008	5	--	--	--	--	--
	B1t	4.7	0.36	--		60	15	0.106	0.014	10	--	--	--	--	--
Mauchula (Marion Co.)	A21	--	--	--		20	2	--	--	0	--	--	--	--	--
	A22	--	--	--		14	1	--	--	0	--	--	--	--	--
	B21h	--	--	--		132	7	--	--	8	--	--	--	--	--
	B22h	--	--	--		132	4	--	--	8	--	--	--	--	--
Smyrna	A1	4.1	4.23	0.150		156	4	--	--	4	0	0	3	0	97
	A21	4.1	1.46	0.045		76	2	--	--	2	--	--	--	--	--
	A22	4.3	0.25	--		22	0	0.009	0.020	1	--	--	--	--	--
	B21h	4.2	0.82	--		32	1	0.028	0.021	3	0	41	27	0	32
	B22h	4.4	3.65	0.098		164	2	0.669	0.038	5	--	--	--	--	--
	B23h	4.5	1.72	--		96	1	0.419	0.028	5	--	--	--	--	--
	B3	4.9	0.56	--		72	8	0.294	0.034	3	--	--	--	--	--
Eau Gallie	Ap	4.8	2.15	0.131		134	6	--	--	1	0	0	1	0	99
	A21	4.5	0.28	0.011		18	3	--	--	0	--	--	--	--	--
	A22	5.5	0.17	--		16	3	--	--	1	--	--	--	--	--
	Bh	4.4	2.61	0.100		138	5	0.260	0.030	5	0	16	15	13	53
	B3	4.8	0.40	--		38	2	--	--	2	--	--	--	--	--
	A'2	5.6	0.40	--		20	2	--	--	1	--	--	--	--	--

Table 12. (Continued)

Series	Horizon	Water pH	Total C	Total N	Total S	Ex-tract.	Sodium-phosphate			<2μm clay fraction	Dominant clay mineralogy [†]				
							soluble		Fe		Mont.	Int.	Kaol.	Gib.	Qtz.
							Al	S							
Electra	A1	4.5	1.51	0.006	56	2	0.070	0.030	1	51	19	0	30		
	A21	5.5	0.06	0.004	10	1	0.100	0.050	0	--	--	--	--		
	A22	5.2	0.07	--	11	1	--	--	0	--	--	--	--		
	A23	5.3	0.15	--	12	1	--	--	0	--	--	--	--		
	B21h	4.6	1.16	0.032	44	1	--	--	4	25	26	9	40		
	B22h	4.7	0.88	--	60	2	--	--	3	--	--	--	--		
	B3	4.9	0.67	--	68	0	--	--	3	--	--	--	--		
	B1t	5.0	0.41	--	54	0	--	--	14	0	48	28	24		
B2t	5.1	0.22	--	32	0	--	--	14	12	42	38	8			

[†] Mont. = montmorillonite; Int. = 2:1 intergrade minerals; Kaol. = kaolinite; Gib. = gibbsite; Qtz. = quartz.

Fig. 7. Mean distribution of total and extractable sulfate sulfur in nine Florida Spodosols.

The area of each bar represents the total supply of S in that horizon. The surface horizon (0-16 cm) of these soils contained a mean total of 9 kg/ha of extractable S and 200 kg/ha of total S. The entire profile to 100 cm contained only 36 kg/ha of extractable S. This would probably be an adequate amount of S for a growing crop if roots were able to penetrate and absorb S from the entire soil volume. However, roots may not extend beyond the spodic horizon because of excess moisture, poor aeration, physical compaction, and an unfavorable chemical environment in this region.

Both extractable and total S were significantly correlated with organic C and total N in the surface horizons of these soils (Table 13). Most of these soils contained less than 5% of clay-size particles (Table 12), but where there was an increase in clay content, there was a significant increase in soil S. Soil mineralogy was not studied on a sufficient number of horizons to establish any reliable correlations between dominant clay minerals and soil S. Clay-size quartz and 2:1 intergrade minerals dominated the mineralogy of the soil colloids.

Organic C was also highly correlated ($r = 0.91$) with total S in the subsurface horizons. Sodium pyrophosphate soluble Al was higher in the spodic horizons and was highly correlated with total S ($r = 0.86$). The fact that Al was correlated with total S and not correlated with extractable S may indicate that sulfate is selectively held by Al in a non-exchangeable form in the spodic horizon.

7.2 ENTISOLS

Florida Entisols had more extractable S within their profiles than the Spodosols. Total S and extractable S were nearly uniform in all horizons below the surface (Table 14, Fig. 8). These soils had an

Table 13. Correlation coefficients of some soil properties with extractable and total sulfur in Florida Spodosols.

Soil property	Extractable S [§]			Total S [§]		
	n	r	α	n	r	α
<u>Surface Horizons</u>						
Total N	18	0.70	0.0012	18	0.97	0.0001
Organic C	26	0.69	0.0001	26	0.91	0.0001
Clay fraction	28	0.67	0.0001	28	0.78	0.0001
Soil pH	26	-0.48	0.0131	no significant correlation		
<u>Subsurface Horizons</u>						
Gibbsite [†]	10	0.78	0.0081	10	0.73	0.0165
Organic C	no significant correlation			25	0.91	0.0001
Total N	9	0.47	0.2026	9	0.88	0.0015
Soluble Al [‡]	no significant correlation			16	0.86	0.0001
Horizon depth	no significant correlation			27	-0.51	0.0068
Soil pH	no significant correlation			25	-0.45	0.0243

[†]Percent in clay fraction.

[‡]Na-pyrophosphate soluble.

[§]n = number of samples; r = correlation coefficient; α = significance level.

Table 14. Selected chemical and mineralogical properties of some Florida Entisols.

Series	Horizon	Water pH	Total C	Total N	Total S	Extract. S	<2µm clay fraction	Dominant clay mineralogy†				
								%				
								Mont.	Int.	Kaol.	Gib. Qtz.	
Astatula (Hernando Co.)	A1	5.7	0.71	0.025	--	2	1	0	52	28	3	17
	C1	6.0	0.16	0.008	50	6	1	0	49	15	30	6
	C2	5.4	0.06	--	33	7	1	--	--	--	--	--
	C3	5.7	0.04	--	27	7	1	0	57	25	0	8
Astatula (Osceola Co.)	Ap	5.7	0.60	0.038	57	1	2	--	--	--	--	--
	C1	5.5	0.20	0.018	40	8	3	--	--	--	--	--
	C2	5.3	0.01	--	42	9	3	--	--	--	--	--
	C3	5.3	0.10	--	38	6	3	--	--	--	--	--
Kershaw	C4	5.2	0.10	--	36	7	3	--	--	--	--	--
	A1	5.3	1.02	0.039	52	3	2	0	58	8	0	34
	C11	5.5	0.22	0.006	46	13	2	--	--	--	--	--
	C12	5.6	0.12	--	30	6	2	0	54	13	10	23
Lakeland (Jackson Co.)	C2	5.9	0.08	--	40	5	2	0	61	11	6	22
	A1	5.6	0.55	0.023	50	1	3	--	--	--	--	--
	AC	5.8	0.28	0.005	38	1	3	--	--	--	--	--
	C11	5.1	0.08	0.005	36	6	3	0	53	11	23	13
Lakeland (Walton Co.)	C12	5.0	0.04	--	26	6	4	0	53	13	13	21
	C2	5.6	0.03	--	15	3	2	--	--	--	--	--
	A	5.0	0.63	--	70	4	2	0	59	20	0	21
	C2	5.0	0.09	--	32	4	2	0	66	14	0	12
	C3	5.0	0.22	--	20	2	2	--	--	--	--	--
	C4	4.8	0.13	--	22	1	2	--	--	--	--	--
	C5	5.0	0.07	--	17	2	1	0	70	15	0	15

Table 14. (Continued)

Series	Horizon	Water pH	Total			Total			Extract. S	<2 μ m clay fraction	Dominant clay mineralogy [†]				
			C	N	S	S	S	%							
								Mont.			Int.	Kaol.	Gib.	Qtz.	
Pompano	A1	5.6	5.61	0.495	>200	>40	6	0	28	12	0	60			
	C1	6.6	0.04	0.004	70	4	0	--	--	--	--	--			
	C2	6.6	0.06	--	86	5	0	53	0	3	0	44			
	C3	6.9	0.04	--	140	16	1	25	0	0	0	75			
Ortega	A11	5.1	0.97	0.024	42	4	2	0	40	15	20	25			
	A12	5.2	0.39	0.006	26	6	0	--	--	--	--	--			
	C1	5.2	0.36	0.003	36	2	2	0	42	12	15	31			
	C2	5.1	0.08	--	28	6	2	--	--	--	--	--			
	C31	5.3	0.04	--	22	3	2	--	--	--	--	--			
	C32	5.6	0.04	--	18	0	1	--	--	--	--	--			
	C4	6.2	0.02	--	12	0	1	0	50	16	11	23			
Chipley	Ap	5.3	1.42	0.044	52	4	3	0	39	17	0	44			
	A2	5.7	0.66	0.026	38	5	3	--	--	--	--	--			
	AC	5.6	0.32	0.033	44	8	3	--	--	--	--	--			
	C11	5.6	0.24	--	26	7	4	0	43	19	0	38			
	C12	5.4	0.11	--	26	11	4	--	--	--	--	--			
	C21	5.7	0.09	--	48	11	2	--	--	--	--	--			
	C22	6.1	0.06	--	20	4	0	--	--	--	--	--			
	C3	6.5	0.04	--	22	1	0	--	--	--	--	--			
Gainesville	Ap	6.1	1.17	0.067	112	3	1	0	70	0	0	30			
	C1	6.5	0.39	0.024	48	3	5	--	--	--	--	--			
	C2	6.2	0.24	--	36	5	6	--	--	--	--	--			
	C3	5.8	0.07	--	30	4	10	0	47	30	0	23			
	C4	5.6	0.05	--	26	4	8	0	0	50	0	50			

Table 14. (Continued)

Series	Horizon	Water pH	Total			Total		Extract. S	<2 μ m clay fraction	Dominant clay mineralogy [†]			
			C	N	S	ppm	%			Mont.	Int.	Kaol.	Gib. Qtz.
Ft. Meade	Ap1	5.9	2.97	0.115	195	10			6	0	0	40	0 60
	Ap2	6.4	1.45	0.046	90	8			2	--	--	--	--
	C1	6.0	0.96	--	72	8			2	--	--	--	--
	C2	6.0	0.57	--	52	8			3	0	63	0	0 37
	C3	6.0	0.30	--	38	9			4	--	--	--	--
	C4	6.0	0.54	--	46	6			3	0	55	0	0 45

[†]Mont. = montmorillonite; Int. = 2:1 intergrade minerals; Kaol. = kaolinite; Gib. = gibbsite;
Qtz. = quartz.

Fig. 8. Mean distribution of total and extractable sulfate sulfur in ten Florida Entisols.

average of 5.6 ppm of sulfate S and 40 ppm of total S in the subsurface horizons. Soil texture and mineralogy changed very little with increasing depth in the profile which is characteristic of Entisols.

The large difference in total S from the surface horizons to the lower horizons was due to organic S. As in the Spodosols, total S was significantly correlated with organic C ($r = 0.91$) and total N ($r = 0.97$) in surface horizons (Table 15).

Extractable sulfate S was not highly correlated with any of the parameters studied in either the surface or subsurface horizons. Low correlations were also found with total S and the soil properties observed in subsurface horizons.

The surface 15 cm contained an average of 13 kg/ha of total extractable sulfate S. The Pompano and Ft. Meade soils were unusually high in both total and extractable S. If these are excluded from calculations, then an average of only 5 to 6 kg/ha of extractable S was available in the surface 15 cm of the other eight Entisols. Because of the lack of extensive profile development and the sandy texture of these soils, plant roots can penetrate several meters. Plants such as legumes which lack a fibrous root system and have a high S requirement may have difficulty obtaining adequate S from these soils even though an average of over 140 kg/ha of sulfate S is available within the upper 2 m.

7.3 ULTISOLS

The ten Ultisols showed the largest differences in S distribution with profile depth of the three soil orders studied (Table 16, Fig. 9). Extractable S was also very low in the surface horizons of these soils.

Table 15. Correlation coefficients of some soil properties with extractable and total sulfur in Florida Entisols.

Soil property	Extractable S [±]			Total S [±]		
	n	r	α	n	r	α
<u>Surface Horizons</u>						
Quartz [†]	6	0.88	0.0213	no significant correlation		
2:1 intergrade minerals [†]	6	-0.74	0.0888	no significant correlation		
Organic C	11	0.73	0.0114	10	0.91	0.0003
Total N	11	0.54	0.0837	10	0.97	0.0001
Clay fraction	no significant correlation			10	0.62	0.0562
<u>Subsurface Horizons</u>						
Quartz [†]	18	0.56	0.0152	18	0.65	0.0033
2:1 intergrade minerals [†]	no significant correlation			18	-0.57	0.0136
Kaolinite [†]	no significant correlation			18	-0.48	0.0461
Montmorillonite [†]	no significant correlation			18	0.68	0.0021
Soil pH	no significant correlation			41	0.52	0.0005

[†]Percent in clay fraction.

[±]n = number of samples; r = correlation coefficient; α = significance level.

Table 16. Selected chemical and mineralogical properties of some Florida Ultisols.

Series	Horizon	Water pH	Total			Total			Extract,			Citrate-dithionite soluble		<2µm clay fraction	Dominant clay mineralogy [†]		
			C	N	S	C	N	S	Al	Fe	Int. %	Kaol.	Gib.		Qtz.		
-----%-----ppm-----																	
Arredondo	Ap	6.0	0.64	0.033	40		4	0.080	0.168	3	32	17	0	51			
	A21	5.8	0.18	0.011	20		4	0.080	0.170	4	--	--	--	--			
	A22	5.6	0.05	--	12		5	0.070	0.150	3	38	15	0	47			
	B1	5.4	0.07	--	35		14	0.120	0.396	9	--	--	--	--			
	B21t	5.2	0.09	--	80		38	0.250	0.888	22	34	20	0	46			
	B22t	5.3	0.06	--	47		9	0.330	1.260	28	--	--	--	--			
Dothan	B23t	5.3	0.06	--	62		6	0.280	1.056	26	35	47	0	18			
	A1	4.3	1.34	0.055	41		6	0.175	0.375	10	--	--	--	--			
	B1	4.6	0.36	0.090	62		29	0.200	0.683	15	--	--	--	--			
	B21t	4.8	0.19	--	110		56	0.262	0.019	20	39	25	29	7			
	B22t	4.9	0.13	--	200		93	0.406	1.781	33	--	--	--	--			
	B23t	4.9	0.11	--	--		88	0.418	2.156	39	24	42	29	5			
Kendrick (Hernando County)	A1	4.8	1.17	0.048	62		3	--	--	5	29	45	0	26			
	A21	5.4	0.57	0.024	36		3	--	--	5	--	--	--	--			
	A22	5.5	0.21	0.011	23		0	--	--	6	--	--	--	--			
	A23	5.1	0.13	--	23		0	--	--	7	--	--	--	--			
	B21t	5.0	0.16	--	49		8	--	--	18	--	--	--	--			
	B22t	4.8	0.24	--	150		51	--	--	39	14	83	0	3			
Kendrick (Alachua County)	B23t	4.8	0.09	--	135		32	--	--	38	--	--	--	--			
	Ap	5.6	0.71	0.047	72		3	0.100	0.190	5	--	--	--	--			
	A3	5.6	0.20	0.010	22		3	0.100	0.230	7	--	--	--	--			
	B1	5.6	0.17	0.017	32		6	0.180	0.547	16	--	--	--	--			
	B21t	5.5	--	--	39		11	0.370	0.860	26	--	--	--	--			
	B22t	5.4	--	--	32		14	0.280	0.630	20	--	--	--	--			
	B23t	5.5	--	--	24		10	0.300	0.870	18	--	--	--	--			

Table 16. (Continued)

Series	Hori- zon	Water pH	Total			Total		Extract.		Citrate- dithionite soluble		<2µm clay frac- tion	Dominant clay mineralogy†		
			C	N	S	S	S	Al	Fe	Int.	Kaol.		Gib.	Qtz.	
			-----%			-----ppm		-----%		-----%					
Lucy	Ap	5.8	0.74	0.042	50	2		0.080	0.170	4	53	28	0	19	
	A21	6.0	0.34	0.020	24	0		0.100	0.180	6	--	--	--	--	
	A22	5.5	0.18	--	16	0		0.090	0.190	6	54	31	0	15	
	A23	5.4	0.09	--	16	5		0.100	0.260	7	--	--	--	--	
	B1	5.1	0.15	--	40	26		0.170	0.650	16	--	--	--	--	
	B21t	5.1	0.12	--	91	42		0.250	1.160	28	--	--	--	--	
	B21t	5.2	0.05	--	32	10		0.220	1.170	29	--	--	--	--	
	B22t	5.1	0.03	--	28	8		0.150	0.640	20	25	66	0	9	
Red Bay (Jackson County)	Ap	5.5	0.60	0.045	60	7		0.160	0.810	14	32	60	0	8	
	B21t	5.7	0.22	0.024	80	45		0.220	1.760	32	--	--	--	--	
	B22t	5.9	0.12	--	88	50		0.230	2.070	36	26	58	0	8	
	B22t	5.5	0.06	--	35	8		0.240	2.020	34	--	--	--	--	
	B23t	5.4	0.02	--	48	10		0.230	1.970	32	--	--	--	--	
	B23t	5.3	0.02	--	50	14		0.280	2.360	30	23	64	0	7	
	Ap	4.7	1.45	0.078	130	16		0.360	1.198	19	34	14	34	18	
	B21t	5.1	0.41	0.063	170	96		0.322	1.472	24	37	17	32	11	
Rosa Co.) Norfolk	B22t	5.2	0.23	--	175	99		0.288	1.698	25	36	15	34	12	
	A11	5.5	1.26	0.078	92	3		0.100	0.190	6	34	37	0	29	
	A12	5.5	0.47	0.028	42	4		0.100	0.230	8	--	--	--	--	
	A2	5.5	0.29	0.031	38	6		0.140	0.340	12	44	48	0	8	
	B21t	5.1	0.25	--	106	60		0.320	1.000	34	31	65	0	4	
	B22t	5.1	0.12	--	42	14		0.280	0.940	34	--	--	--	--	
	B23t	5.0	0.06	--	38	12		0.320	1.200	31	--	--	--	--	
	B3t	5.0	0.05	--	38	12		0.280	1.340	38	--	--	--	--	
C	4.9	0.06	--	22	9		0.240	1.420	42	8	92	0	0		

Table 16. (Continued)

Series	Hori- zon	Water pH	Total			Extract.			Citrate- dithionite soluble		<2µm clay frac- tion	Dominant clay mineralogy [†]		
			C	Total N	Total S	S	Al	Fe	Int. %	Kaol.		Gib.	Qtz.	
														ppm
Blanton	Ap	5.2	0.66	0.035	--	2	--	--	--	--	2	--	--	--
	A21	5.3	0.10	--	25	4	--	--	--	52	1	29	0	19
	A22	5.3	0.14	--	22	2	--	--	--	--	1	--	--	--
	B21t	4.8	0.13	--	60	--	0.900	0.310	--	29	17	36	10	35
	B22t	4.8	0.19	--	80	27	0.800	0.390	--	--	19	--	--	--
	B23t	4.8	0.10	--	60	20	0.700	0.170	--	20	19	52	11	17
Albany	Ap1	--	0.58	0.028	47	1	--	--	--	--	2	--	--	--
	Ap2	--	0.36	0.014	33	1	--	--	--	--	2	--	--	--
	A21	--	0.12	--	24	0	--	--	--	--	2	--	--	--
	A22	--	--	--	20	0	--	--	--	--	4	--	--	--
	B1	--	--	--	42	1	--	--	--	--	19	--	--	--
	B2t	--	--	--	54	4	--	--	--	--	38	--	--	--
	B3	--	--	--	47	3	--	--	--	--	26	--	--	--

[†] Mont. = montmorillonite; Int. = 2:1 intergrade minerals; Kaol. = kaolinite; Gib. = gibbsite;
Qtz. = quartz.

Fig. 9. Mean distribution of total and extractable sulfate sulfur in ten Florida Ultisols.

Only one soil, a Red Bay from Santa Rosa County, had more than 7 ppm extractable sulfate S in the surface horizon. This soil contained more than twice as much extractable S as any other Ultisol studied. In general, the mean values for the A1 and A2 horizons were similar to S levels in the Spodosol A1 and A2 horizons (Figs. 7 and 9). A remarkable increase in both total and extractable S occurred in all argillic (B2) horizons. Sulfate S accounted for only 8% of the total S in the surface horizon of the Ultisols and less than 7% of the total S in the entire profile of the Spodosols. However, more than 40% of the total S in the argillic horizons of the Ultisols was extracted as sulfate S.

Total S was also significantly correlated with organic C and total N in the surface horizon ($r = 0.85$ and 0.90 , respectively) (Table 17). Extractable S was significantly correlated with citrate-dithionite soluble Al ($r = 0.89$) and Fe ($r = 0.88$), gibbsite in the clay fraction ($r = 0.89$), the percent clay in the horizon ($r = 0.75$), as well as organic C ($r = 0.50$).

No single soil property was highly correlated with either total or extractable S in the subsurface horizons of Ultisols (Table 17). The highest correlation with total and extractable S was with crystalline gibbsite $[Al(OH)_3]$ ($r = 0.67$ and 0.79 , respectively). Only three series, Dothan, Blanton, and Red Bay from Santa Rosa County had gibbsite in the argillic horizons. With a higher clay content in these horizons and crystalline gibbsite in equilibrium with amorphous Al hydroxides and oxyhydroxides, larger sulfate adsorption was not surprising.

Extensive mineralogical studies would have to be made of individual soils in order to relate sulfate adsorption to the crystalline and

Table 17. Correlation coefficients of some soil properties with extractable and total sulfur in Florida Ultisols.

Soil property	Extractable S [§]			Total S [§]		
	n	r	α	n	r	α
<u>Surface Horizons</u>						
Soluble Al [†]	15	0.89	0.0001	15	0.73	0.0019
Soluble Fe [†]	15	0.88	0.0001	15	0.69	0.0045
Gibbsite [‡]	10	0.89	0.0006	10	0.75	0.0122
Clay fraction	26	0.75	0.0001	25	0.59	0.0018
Organic C	25	0.50	0.0102	24	0.85	0.0001
Total N	18	0.61	0.0073	17	0.90	0.0001
<u>Subsurface Horizons</u>						
Gibbsite [‡]	13	0.79	0.0014	13	0.67	0.0128
Horizon depth	36	-0.60	0.0001	36	-0.51	0.0014
Kaolinite [‡]	13	-0.59	0.0328	13	-0.50	0.0849
Organic C	30	0.59	0.0006	30	0.51	0.0041

[†] Citrate dithionite soluble.

[‡] Percent in clay fraction.

[§] n = number of samples; r = correlation coefficient; α = significance level.

non-crystalline Al and Fe compounds present. Citrate-dithionite soluble Al and Fe were not significantly correlated with soil S in the sub-surface horizons. This is surprising after finding such highly significant correlations with these soil properties in the surface horizon. The high levels of both total and extractable S probably resulted in less than complete extraction of S either by the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ solution or by the acid after digestion. The heat digestion and acid extraction of total S no doubt altered the anion exchange properties of the soils and could have resulted in incomplete acid extraction of total S.

Organic matter in these lower soil horizons could not possibly account for the high total S levels. The thesis of Adams and Rawajfeh (1977) concerning the formation of sparingly soluble aluminum sulfate minerals such as alunite or basaluminite in Ultisols would be a convenient proposition to explain these results. Although potential soil solution concentrations of SO_4^{2-} , Al^{3+} , and K^+ are unknown in these soils, data from Adams and Hajek (1978) suggested that basaluminite could form where SO_4/Al in the soil solution was greater than 0.25 and OH/Al was less than 3.0. Alunite became the dominant precipitate formed when a K/Al ratio of 0.1 existed in dilute solutions of K, Al, and SO_4 . If these minerals do exist in the argillic horizons of Ultisols, the solubilities in extractants such as the 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ used in this study are unknown. More data under controlled conditions would be needed in order to establish a precise relationship between measurable soil properties and total and extractable S in argillic horizons.

These argillic horizons are obviously an important source of plant-available sulfate. If extractable and total S are a reasonable measurement of the available and reserve S levels in a soil, then young seedlings would find little difference in the native fertility levels of the upper 50 to 60 cm of Florida Ultisols and Spodosols. Plants growing on Ultisols, on the other hand, have a tremendous supply of available sulfate in argillic horizons if the roots are able to penetrate and absorb this sulfate. If the two Red Bay soils are excluded from calculations, there were means of 8 and 25 kg/ha of available S in the A2 and A2 horizons, respectively. In the upper 200 cm, over 460 kg/ha of sulfate S was available. This value was estimated from the ten soils studied. Values ranged from a low of 34 kg/ha in an Albany soil from Washington County to a high of 1,350 kg/ha in a Dothan soil from Santa Rosa County.

7.4 C:N:S RELATIONSHIPS

The mean C:S and N:S ratios for the three soil orders are presented in Table 18. The values are probably meaningless for the B horizons of the Ultisols and the C horizons of the Entisols because there were no significant correlations between soil S and organic C in these horizons. The correlations of total S with organic C and total N in the surface horizons of the Florida soils studied are as high or higher than Nelson (1964) obtained for 12 Mississippi soils and Tabatabai and Nelson (1972b) found in soils from Iowa. Biederbeck pointed out in a recent review of organic S in soils that ". . . since the bulk of the S in non-calcareous soil is in organic forms, total S usually decreases sharply with soil depth" (Biederbeck, 1973, p. 279). This statement is apparently not true for many Florida soils. Sulfate S

Table 18. Carbon, nitrogen, and sulfur relationships in Florida soils.

Soil order	Horizon	C:S ratio			N:S ratio		
		No.	Mean	Standard deviation	No.	Mean	Standard deviation
Ultisol	A	24	112	61	17	7.1	2.1
	B	30	21	14	4	6.6	5.3
Spodosol	A	26	150	80	18	6.4	2.7
	B	25	156	67	9	5.8	1.2
Entisol	A	10	166	55	10	5.9	1.7
	C	41	46	35	10	2.8	2.3

and total S definitely increased with depth in Ultisols, and this increase is not related to organic matter. As previously noted, organic S is important in spodic horizons, but this study did not attempt to quantify the relative contribution of organic matter and soil minerals to total S present.

The surface horizons of all three orders of Florida soils had much wider C:S ratios and narrower N:S ratios than was found in soils from other areas (Table 1). The C:N:S relationship for the surface horizons of Florida Ultisols (112:7.1:1) more closely resembles the findings of Neptune et al. (1975) for six Brazilian surface soils (121:6.2:1) and is similar to the findings of Nelson (1964) for 12 Mississippi soils (114:9.1:1).

The significance of differences in the C:N:S ratios of soils may be related to the S supply to crops (Biederbeck, 1978). Mineralization of organic S has been found to increase as the C:N:S ratio decreases (Bettany et al., 1973, 1974; Kowalenko and Lowe, 1975). Bettany et al. (1979, 1980) found higher C:S and N:S ratios in humic acid and humin fractions of soil organic matter than in the more labile fulvic acid fractions. The humic acid A, humic acid B, and fulvic acid B fractions had C:N:S ratios of 101:7.9:1, 95:8.8:1, and 37:5.6:1, respectively, in undisturbed pasture soils and ratios of 127:8.7:1, 96:8.2:1, and 36:5.5:1, respectively, in cultivated soils. The humic acid fraction also had a higher percentage of C-bonded S associated with the more stable humin fractions. The present study did not involve organic S fractionation so only speculation can be made. This aspect of soil S and organic matter warrants closer study in future research.

8. A GREENHOUSE EVALUATION OF SUBSOIL SULFUR

8.1 CHEMICAL AND MINERALOGICAL PROPERTIES OF SOILS STUDIED

The surface horizons of the four soils used in this study contained more than 50% fine or very fine sand (0.05-0.25 mm) and were classified as fine sands (Table 19). The texture, citrate-soluble Al and Fe, and the mineralogy of the clay fractions of the surface (A) and argillic (B) horizons were similar in the Orangeburg and Norfolk soils. The argillic horizons of these soils contained almost three times as much citrate-soluble Al and almost seven times more Fe than the C horizon of the Lakeland soil. Citrate-soluble Fe was very low in the spodic horizon of the Myakka while Al was near that found in the argillic horizons of the Ultisols. The previous study showed that soluble Al and Fe were significantly correlated with extractable S and total soil S in the surface horizons of Ultisols.

The clay fraction and kaolinite and gibbsite in the clay fraction increased with depth in the two Ultisols. The two horizons of the Lakeland soil were relatively uniform. The most obvious change in the mineralogy of the Myakka soil from the A to B horizon was the presence of a 2:1 intergrade mineral in the spodic horizon.

The surface horizons of all these soils contained near immeasurable quantities of extractable sulfate S (Table 20). These levels would be considered below the critical levels for most crops growing on these soils (Table 7). Only the Orangeburg and Norfolk series contained significant quantities of extractable S in the subsurface horizons. Total S was highest in the A horizon of the Myakka because of

Table 19. Some chemical and mineralogical properties of soils used in a greenhouse evaluation of subsoil sulfur.

	Soil texture and horizon							
	Myakka		Lakeland		Orangeburg		Norfolk	
	A	B	A	C	A	B	A	B
	-----%							
Class and particle size distribution								
Sand (2-0.05mm)	92.0	91.8	96.0	96.5	86.0	67.0	87.5	75.0
Very coarse (2-1mm)	0	0.1	0.1	0.1	0.3	0.3	0.1	0.1
Coarse (1-0.5mm)	5.0	4.9	0.4	0.4	3.5	2.5	3.1	2.0
Medium (0.5-0.25mm)	30.5	30.3	13.7	14.7	16.6	12.1	18.9	13.4
Fine (0.25-0.1mm)	48.5	48.3	77.0	77.4	46.8	35.9	51.5	45.0
Very fine (0.1-0.05mm)	8.0	8.2	4.8	3.9	18.8	16.2	13.8	14.5
Silt (0.05-0.002mm)	5.5	4.8	1.0	0.5	8.0	7.0	6.5	5.0
Clay (0.002mm)	2.5	4.0	3.0	3.0	6.0	26.0	6.0	20.0
Dominant clay mineralogy								
2:1 intergrade minerals								
Kaolinite	0	11	46	49	54	36	52	38
Gibbsite	8	7	20	18	31	44	24	42
Quartz	0	0	14	17	6	11	8	14
	92	82	20	16	9	9	16	6
Citrate-dithionite soluble								
Al	0.05	0.20	0.10	0.10	0.10	0.25	0.10	0.30
Fe	0.07	0.01	0.12	0.14	0.22	0.94	0.21	1.00
Sodium-pyrophosphate soluble								
Al	0.05	0.25	--	--	--	--	--	--
Fe	0.02	0.01	--	--	--	--	--	--
Organic C	1.58	1.92	0.48	0.19	0.92	0.31	0.50	0.30

Table 20. Nutrient levels in soils used in a greenhouse evaluation of subsoil sulfur before treatment.

Soil series	Horizon	Water	KCl	Double-acid extractable nutrients							Sulfate		Total S
				P	K	Mg	Ca	Zn	Cu	Mn	S		
				ppm							S		
pH													
Myakka	A	5.7	4.1	1.7	12	12	480	1.00	0.08	0.16	2	83	
	B	4.8	4.1	1.6	4	8	104	--	--	--	1	67	
Lakeland	A	6.1	4.3	6.3	8	8	96	0.08	0.16	1.00	<1	50	
	C	6.0	4.6	2.6	4	4	76	--	--	--	<1	28	
Orangeburg	A	5.4	4.1	0.7	8	22	86	0.12	0	8.36	2	61	
	B	5.2	4.1	0.4	2	56	136	--	--	--	11	76	
Norfolk	A	5.6	4.4	0.5	16	15	58	0.08	0.04	3.80	<1	35	
	B	5.2	4.2	0.8	8	56	172	--	--	--	15	78	

organic matter and in the argillic horizons of the Ultisols because of mineralogy. The Lakeland soil had the least S within its profile. Other nutrient levels in these soils before treatment are presented in Table 20.

8.2 YIELDS

8.2.1 Harvest 1

The sorghum-sudangrass responded to S applications on the first harvest in the Myakka soil although symptoms of S deficiency were not observed (Table 21). The Orangeburg and Norfolk soils provided adequate S for the young plants during the 4 weeks of initial growth (Tables 22 and 23). Since no S was applied initially to the Lakeland soil, no statement can be made concerning initial response to S on this soil (Table 24). However, S concentration appeared to be adequate in the plant tissue during the first 4 weeks of growth. Sulfur applied after the first harvest significantly increased yields in the second harvest.

Part of the organic S in soils is considered to be unstable and is abiologically converted to sulfate by air or oven drying. Biederbeck (1978) reviewed the literature on this subject and found reports of 20 to 80% increases in extractable sulfate after air drying. Drying causes an immediate release of S but has little effect on subsequent S mineralization. Barrow (1961) warned of the effect this mineralized S may have on the interpretation of pot experiments. Extractable sulfate S was low in the soils of this study even after air drying for several weeks. After incubation at ambient temperature and subsequent drying, treated soils were extracted to determine any changes in the relative amounts of sulfate removed by the extractant. Extractable S was

Table 21. Sulfur and nitrogen nutrition and yields of 28-day old sorghum-sudangrass in a Myakka fine sand in the greenhouse.

Horizon sequence	Fertilizer S	Plant height [†]	Dry matter yield [†]	Herbage [†]			
				S	N	N:S ratio	S uptake
				---ppm---	--cm---	-g/pot-	-----%-----
<u>Harvest 1</u>							
A/sand	0	85	7.75	0.130	3.10	24	10.1
A/sand	20	92	9.20**	0.270**	3.32	12**	24.7**
A/B	0	90	7.98	0.132	2.95	22	10.6
A/B	20	88	8.44*	0.233**	3.33	12	19.7
<u>Harvest 2</u>							
A/sand	0	60	3.59	0.082	2.62	30	3.0
A/sand	20	68**	8.15**	0.187**	2.82**	15**	15.3**
A/B	0	56	3.27	0.077	2.66	34	2.6
A/B	20	75**	6.99**	0.197**	3.32**	17**	13.8**
<u>Harvest 3</u>							
A/sand	0	40	2.07	0.075	3.32	44	1.6
A/sand	20	78**	10.62**	0.120**	1.87**	16**	12.7**
A/B	0	35	1.38	0.075	4.32	58	1.0
A/B	20	65**	8.61**	0.115**	2.11**	18**	9.9**
<u>Harvest 4</u>							
A/sand	0	43	1.85	--	--	--	--
A/sand	20	73**	7.70**	--	--	--	--
A/B	0	35	0.58	--	--	--	--
A/B	20	59**	4.27**	--	--	--	--

[†]All values are the means of four replications.

*,** Significantly different between S treatments at the 0.05 and 0.01 levels, respectively.

Table 22. Sulfur and nitrogen nutrition and yields of 28-day old sorghum-sudangrass in an Orangeburg fine sand in the greenhouse.

Horizon sequence	Fertilizer S	Plant height ⁺	Dry matter yield ⁺	Herbage ⁺			
				S		N:S	S
				-----%		ratio	uptake
	---ppm---	--cm---	-g/pot-				-mg/pot-
<u>Harvest 1</u>							
A/sand	0	90	9.33	0.247	3.86	15	24.1
A/sand	20	86	9.48	0.355**	3.89	11**	33.7**
A/B	0	88	9.42	0.217	3.80	18	20.3
A/B	20	88	10.62	0.305**	3.47	11**	32.4**
<u>Harvest 2</u>							
A/sand	0	78	9.04	0.152	2.90	20	13.8
A/sand	20	94**	10.21	0.182	2.87	16**	18.5**
A/B	0	86	7.98	0.152	3.18	21	12.1
A/B	20	80	8.92	0.180	3.18	17**	15.0**
<u>Harvest 3</u>							
A/sand	0	56	5.85	0.072	2.20	30	4.2
A/sand	20	80**	11.68**	0.132	2.10	16**	15.4**
A/B	0	56	7.65	0.087	1.98	22	6.7
A/B	20	69**	11.92**	0.120**	2.31	19**	14.3
<u>Harvest 4</u>							
A/sand	0	51	3.40	0.055	2.26	41	1.8
A/sand	20	71**	8.14**	0.117**	2.44	21**	9.6**
A/B	0	68	6.38	0.065	2.16	33	4.1
A/B	20	68	8.70**	0.107**	2.44	23*	9.4**

⁺ All values are the means of four replications.

*,** Significantly different between S treatments at the 0.05 and 0.01 levels, respectively.

Table 23. Sulfur and nitrogen nutrition and yields of 28-day old sorghum-sudangrass in a Norfolk fine sand in the greenhouse.

Horizon sequence	Fertilizer S	Plant height [†]	Dry matter yield [†]	Herbage [†]			
				S	N	N:S ratio	S uptake
	---ppm---	--cm---	-g/pot-				
Harvest 1							
A/sand	0	91	9.39	0.155	2.92	19	14.5
A/sand	20	87	9.32	0.207**	2.88	14**	19.3**
A/B	0	98	10.98	0.140	2.73	20	15.4
A/B	20	91	9.80	0.202**	2.99	15**	19.4**
Harvest 2							
A/sand	0	86	6.24	0.097	2.48	26	6.1
A/sand	20	88	7.09	0.185**	2.85	15**	12.9
A/B	0	74	5.14	0.175	3.18	18	9.0
A/B	20	81	6.32	0.182	3.31	18	11.3
Harvest 3							
A/sand	0	40	2.18	0.067	2.09	31	1.5
A/sand	20	66**	7.87**	0.132**	2.21	17**	10.0**
A/B	0	68	8.32	0.130	2.23	17	10.7
A/B	20	60**	8.38	0.135	2.16	16	11.2
Harvest 4							
A/sand	0	37	1.12	0.037	2.75	74	0.4
A/sand	20	62**	6.39**	0.120**	2.01**	17**	7.6**
A/B	0	61	4.71	0.112	2.03	18	5.3
A/B	20	48	4.07	0.125	2.09	17	5.1

[†] All values are the means of four replications.

*,** Significantly different between S treatments at the 0.05 and 0.01 levels, respectively.

Table 24. Sulfur and nitrogen nutrition and yields of 28-day old sorghum-sudangrass in a Lakeland fine sand in the greenhouse.

Horizon sequence	Fertilizer S	Plant height [†]	Dry matter yield [†]	Herbage [†]			
				S	N	N:S ratio	S uptake
				-----	-----	-----	-----
-----ppm----- --cm----- -g/pot- -----%----- -mg/pot-----							
<u>Harvest 1</u>							
A/sand	0	94	7.78	0.135	2.98	22	10.5
A/sand	20	91	7.98	0.147	3.07	21	11.6
A/C	0	92	7.52	0.145	3.01	21	10.9
A/C	20	88	7.04	0.140	3.21	23	9.9
<u>Harvest 2</u>							
A/sand	0	60	3.46	0.102	2.76	27	3.5
A/sand	20	79**	6.31**	0.307**	3.34**	11**	19.4**
A/C	0	67	4.87	0.095	2.48	26	4.6
A/C	20	76**	6.95**	0.287**	3.19**	11**	19.9**
<u>Harvest 3</u>							
A/sand	0	49	2.78	0.080	2.97	37	2.2
A/sand	20	81**	13.77**	0.137**	1.92**	14**	18.9**
A/C	0	46	4.09	0.080	3.24	41	3.2
A/C	20	80**	11.68**	0.150**	2.14**	14**	17.4**
<u>Harvest 4</u>							
A/sand	0	49	1.85	--	--	--	--
A/sand	20	82**	9.04**	--	--	--	--
A/C	0	40	1.86	--	--	--	--
A/C	20	75**	8.98**	--	--	--	--

[†] All values are the means of four replications.

*,** Significantly different between S treatments at the 0.05 and 0.01 levels, respectively.

slightly higher in all soils than values obtained in earlier analyses (Tables 20 and 25). These differences could have been caused by drying of the soils or mineralization during incubation. In either case, adequate S was present in all soils except the Myakka for optimum growth during the first 4 weeks. No differences were observed due to subsoil S in the first harvest.

8.2.2 Harvests 2, 3, and 4

8.2.2.1 Myakka

The yield response to S in the Myakka soil was intensified in subsequent harvests (Table 21). Ratoon crops in soil without added S showed immediate symptoms of S deficiency in growth following the initial harvest. Leaves showed marked interveinal yellowing with some reddening of stems and leaf edges. These symptoms were obvious throughout the next 12 weeks of the experiment. Where S was omitted, dry matter yields at the fourth harvest were only 24% of the initial yields.

The presence of the spodic horizon within the profile significantly reduced yields in the third and fourth harvests. The high acidity and soluble Al in this horizon would be expected to inhibit root penetration and proliferation into the unamended subsoil. Soil pH and sodium pyrophosphate-soluble Al in the spodic horizon were comparable to soil pH and citrate-dithionite soluble Al in the argillic horizons of the Orangeburg and Norfolk soils. Citrate-dithionite soluble Fe in the argillic horizons of the Ultisols was much higher in proportion to the soluble Fe levels in the spodic horizon of the Myakka soil (Table 19). A study of six other Myakka soils in Florida showed that BaCl_2 -TEA extractable acidity in the spodic horizons averaged

Table 25. Extractable sulfate sulfur in treated soils used in a greenhouse evaluation of subsoil sulfur availability.

Soil series	Fertilizer S	Extractable soil S
	-----ppm-----	
Myakka	0	4
	20	22
Lakeland	0	3
	0	3 [†]
Orangeburg	0	4
	20	16
Norfolk	0	4
	20	21

[†]The failure to apply S to this treatment is evident in the extractable S level.

17.5 meq/100g with a base saturation of only 4% (Calhoun et al., 1974; Carlisle et al., 1978).

8.2.2.2 Lakeland

The sorghum-sudangrass also responded to S applications on the Lakeland soil at the second harvest; S increased yields over 300% at the third harvest. The yield difference due to horizon sequence was significant at the 0.01 level of probability in the second harvest but not significant in subsequent harvests. As previously mentioned, the C horizons of Entisols are easily penetrated by plant roots. Roots were well-distributed in soil from this horizon when the experiment was terminated. The small quantity of available sulfate S present was inadequate for optimum yields but sufficient to create a significant difference in yield between horizon sequences. Sulfur uptake indicated that this available S was equivalent to 0.5 to 1.1 mg/pot (or 0.08 to 0.17 ppm). The turbidimetric method of determining S in the soil extracts was not sensitive enough to detect such subtle differences which may or may not have been present in the soil. There were no significant yield differences due to horizon sequence in the third and fourth harvests and no S uptake differences; this indicated that available subsoil S was rapidly depleted during the second 4 weeks of growth.

8.2.2.3 Orangeburg and Norfolk

Sulfur fertilization did not increase yields of plants growing in the Orangeburg or Norfolk soils until the third harvest (Tables 22 and 23). In the Orangeburg soil, S fertilization increased the total dry matter yields by 43% where no argillic horizon was present and by only 28% where the B horizon was included in the horizon sequence (Fig. 10). In the Norfolk soil, these differences were 62% without the B horizon

Fig. 10. Total yields of four harvests of sorghum-sudangrass as affected by sulfur and subsurface soil horizons.

and 0% with it. These differences were even larger for the third and fourth harvests.

Where the horizon sequence included the argillic horizon, yields were not improved by S fertilization in any of the four harvests from the Norfolk soil. Total S uptake by plants in pots without added S but with the argillic horizon was almost 15 mg/pot more than by plants growing in pots where washed sand replaced the argillic horizon. This difference was equivalent to 2.6 ppm of available S in the subsoil during the 16-week study--much less than the 15 ppm of extractable sulfate S found before the experiment (Table 20). These data indicated that the surface horizon of the Norfolk soil contained adequate S for a short-term crop but not enough to maintain optimum growth over a long season.

One factor not included in this study which would be of significant consideration under field conditions is the depth to the argillic horizon. The argillic horizon was placed only 24 cm below the surface in the greenhouse pots. Data from the survey of S in Florida soils showed that the mean depth of the B1 horizon in ten Florida Ultisols was 69 cm (Fig. 9). The typifying pedons for the Norfolk and Orangeburg series have the B1 horizons at 36 and 18 cm, respectively. The depth to the B1 in five Orangeburg soils from Florida ranged from 20 to 56 cm with a mean depth of 35 cm (Calhoun et al., 1974). With such variation in depths to adsorbed S in the argillic horizons, predicting the S fertility status of plants growing on certain Ultisols may be difficult. Young seedlings and shallow-rooted plants may require S fertilization whereas long-season and deep-rooted annuals and perennials may obtain adequate S from the subsoil supplies. Anderson and

Futral (1966) found that yields of cotton were not affected by S application during the first 2 years of an experiment on a Norfolk loamy sand from Georgia. This soil had extractable sulfate levels within its profile similar to the Norfolk soil used in this study. By the third year of the experiment, marked deficiency symptoms appeared on the no-S plots early in the season but disappeared as plant size increased. By the fifth year, plants failed to recover from the S deficiency, and there were highly significant yield increases where S was applied. Cotton is a crop that is known to be sensitive to S deficiencies (Lund and Murdock, 1978).

Subsoil S and the depth to this S in Ultisols may create complications in field experiments. This problem will be pointed out in the section entitled "Sulfur in Bahiagrass and Bermudagrass."

8.3 SULFUR CONCENTRATIONS AND N:S RATIOS

The application of 20 ppm of S to these soils significantly increased the S concentrations in the tissue, reduced the N:S ratios, and resulted in increased S uptake by the plants in almost every series, harvest, and horizon sequence (Tables 21, 22, 23, and 24). These data indicated a close relationship between S concentration in the tissues and dry matter yield of the plant. Relative yields were calculated within each series and harvest and plotted against S concentration (Fig. 11). A critical S concentration of 0.12% was identified for sorghum-sudangrass tops using a segmented model and the non-linear least squares method provided by SAS (Statistical Analysis System, 1979). Data fit a model described by two linear relationships:

Fig. 11. The effect of herbage sulfur concentration on relative yield of 4-week old sorghum-sudangrass tops.

$$(1) \quad y = a + bx$$

$$(2) \quad y = c$$

where y represents relative yield and x represents S concentration in the tissue; a , b , and c are constants. The value of x at the intersection of the two lines ($x = 0.12\%$) is predicted and is considered to be the critical value. This value is within the critical range reported by other workers for grasses (Table 6). These plants were harvested at 4-week intervals under uniform greenhouse conditions. Therefore, the wide variability in S concentration due to type of tissue and plant age was not a problem in this experiment.

Nitrogen:sulfur ratios were also closely related to relative yields (Fig. 12). Relative yields were calculated within each soil series and harvest. The mean N:S ratio of the 100% yields was 16. This is the value that Dijkshoorn et al. (1960) found for the N:S ratio in protein of perennial ryegrass foliage, and other researchers have confirmed to be an optimum value for the total N:S ratio in grasses (Woodhouse, 1969; Cowling and Jones, 1971; Metson, 1973; Terman et al., 1973). There did not appear to be any differences in the critical S concentration or the optimum N:S ratio due to soil series or horizon sequence.

9. SULFUR IN BAHIAGRASS AND BERMUDAGRASS IN THE FIELD

9.1 SULFUR IN BAHIAGRASS ON A MYAKKA FINE SAND

The site of this experiment was adjacent to the site where the Myakka soil was collected for the previous experiment. However, responses to S by bahiagrass were not as dramatic as the response to S by sorghum-sudangrass in the greenhouse.

Fig. 12. The effect of herbage N:S ratio on relative yield of 4-week old sorghum-sudangrass tops.

Sulfur had no effect on yields in 1978 (Table 26). The 400 kg/ha N rate increased yields by 42% over the 200 kg/ha rate after the first harvest (Fig. 13). Even though applied S did not increase yields, S concentrations in the harvested forage and total S uptake increased with increased S rates. Where S was omitted, an average of 14.2 and 17.6 kg/ha/yr of S was removed at low and high N rates, respectively. At the highest rate of S, these values were 23.4 and 30.6 kg/ha/yr at the two N rates (Table 27).

Trends toward increased yields with S fertilization were evident during the second year of the experiment (Table 28). Sulfur had no effect on dry matter yields at the lower rate of N at any harvest. At the high N rate, the 10-kg/ha S rate increased yields at all harvests. Additional N increased yields by 20% without S and almost 40% with applied S (Fig. 13). Additional S beyond the 10 kg/ha rate did not significantly increase yields. No noticeable symptoms of S deficiency were observed in the field.

Applying S in split applications throughout the season had no apparent benefit. Even the fourth harvest in late September, 6 months after gypsum application, showed significant increases in S concentration in the tissues with increasing S rates. Rhue and Kamprath (1973) showed that 56 kg/ha of S as gypsum was completely leached from the surface 45 cm of a Wagram loamy sand during 180 days. This experiment was conducted during the winter months in North Carolina. One would expect an even higher rate of leaching during a Florida growing season where heavy summer rainfall occurs. There were no detectable differences in extractable sulfate S in samples from the plots taken in the fall of 1978 and again in the fall of 1979 (Table 29). Bahiagrass

Table 26. The effect of nitrogen and sulfur fertilization on bahiagrass in a Myakka fine sand--1978.

Fertilizer		Dry matter yield [†]	Herbage			
N	S		S [†]	N	N:S ratio	S uptake
-----kg/ha-----			-----%-----			-kg/ha-
<u>Harvest 1</u>						
200	0	950ab	0.199 d	1.65	8.3	1.89
	10	900ab	0.234 cd	1.74	7.6	2.14
	20	910ab	0.263 bc	1.69	6.5	2.34
	40	850 b	0.344a	1.82	5.3	2.88
400	0	1380ab	0.181 d	2.06	11.5	2.47
	10	1590a	0.239 cd	1.88	7.9	3.86
	20	1010ab	0.296ab	2.05	7.0	2.97
	40 [‡]	1400ab	0.350a	1.92	5.5	4.57
	20 [‡]	1320ab	0.200 d	1.96	10.0	2.52
<u>Harvest 2</u>						
200	0	2800 b	0.140 de	1.32	9.5	3.90
	10	2980 b	0.150 de	1.24	8.4	4.45
	20	2820 b	0.171 bc	1.28	7.6	4.77
	40	2860 b	0.214a	1.26	5.9	6.09
400	0	4560a	0.137 e	1.50	11.0	6.22
	10	4420a	0.152 cde	1.51	10.0	6.70
	20	4090a	0.176 b	1.46	8.3	7.13
	40 [‡]	4340a	0.216a	1.50	7.0	9.38
	20 [‡]	4380a	0.159 bcd	1.47	9.3	6.97
<u>Harvest 3</u>						
200	0	3270 b	0.134 c	1.21	9.0	4.39
	10	3530 b	0.148 bc	1.19	8.1	5.28
	20	3280 b	0.170ab	1.18	6.9	5.62
	40	3340 b	0.183a	1.21	6.7	6.12
400	0	4550a	0.135 c	1.42	11.0	6.12
	10	4630a	0.147 bc	1.41	9.8	6.79
	20	4760a	0.147 bc	1.37	9.3	7.02
	40 [‡]	4540a	0.177ab	1.35	7.7	8.06
	20 [‡]	5000a	0.170ab	1.38	8.1	8.48

Table 26. (Continued)

Fertilizer		Dry matter yield [†]	Herbage			
N	S		S [†]	N	N:S ratio	S uptake
-----kg/ha-----			-----%-----			-kg/ha-
<u>Harvest 4</u>						
200	0	3170 b	0.101 bc	0.95	9.6	3.21
	10	3090 b	0.110abc	0.94	8.6	3.51
	20	3260 b	0.120abc	0.95	8.0	3.90
	40	3330 b	0.128a	0.96	7.6	4.28
400	0	4160a	0.099 c	1.12	11.5	4.16
	10	4350a	0.109abc	1.10	10.2	4.74
	20	4350a	0.110abc	1.14	10.4	4.75
	40 [‡]	4290a	0.125ab	1.14	9.2	5.38
	20 [‡]	4380a	0.127a	1.11	8.9	5.54
<u>Harvest 5</u>						
200	0	130 e	0.129 b	1.10	8.5	0.17
	10	190 cde	0.131 b	1.06	8.0	0.24
	20	100 e	0.144ab	1.04	7.3	0.15
	40	150 de	0.153ab	1.06	7.0	0.23
400	0	230 bcd	0.141ab	1.40	10.0	0.33
	10	280abc	0.152ab	1.35	8.9	0.41
	20	290ab	0.141ab	1.30	9.2	0.40
	40 [‡]	280ab	0.166a	1.34	8.2	0.47
	20 [‡]	330a	0.148ab	1.28	8.6	0.49

[†]Values followed by the same letter are not statistically different within harvest at the 0.05 level of significance using Duncan's new multiple range test.

[‡]S rate was split and applied in four equal applications during the season.

*Split S applications

Letters indicate significant differences at 0.05 level using Duncan's New Multiple Range Test.

Fig. 13. The effect of sulfur and nitrogen rates on the annual yield of bahiagrass in a Myakka fine sand.

Table 27. Sulfur removed in herbage.

Fertilizer		Herbage S			
		Bahia grass		Bermudagrass	
		1978	1979	1978	1979
N		S			
		kg/ha			
200	0	13.6	14.9 c*	11.1 d	16.4 e
200	10	15.6	18.6 c	14.5 c	21.0 cde
200	20	16.8	22.8 bc	16.3 bc	21.1 cd
200	40	19.6	27.3 b	18.1ab	22.9 bcd
400	0	19.3	15.9 c	14.1 c	20.1 de
400	10	22.5	24.3 b	16.5 bc	25.8 bcd
400	20	22.3	25.5 b	17.5 b	30.1ab
400	40	27.9	33.2a	20.5a	35.2a
400	20 [†]	24.0	24.8 b	17.7 b	25.2 bc

* Values followed by the same letter are not statistically different within harvest at the 0.05 level of significance using Duncan's new multiple range test.

[†] S rate was split and applied in four equal applications during the season. All other S rates were applied in early spring.

Table 28. The effect of nitrogen and sulfur fertilization on bahiagrass in a Myakka fine sand--1979.

Fertilizer		Dry		Herbage				
N	S	matter		S [†]	N	N:S	S	
-----kg/ha-----		yield [†]		-----%-----		ratio	uptake	
-----kg/ha-----								
<u>Harvest 1</u>								
200	0	1820	d	0.130	ef	1.38	2.36	
	10	2100	d	0.200	c	1.55	4.23	
	20	2280	cd	0.250	b	1.34	5.71	
	40	2180	d	0.285a		1.26	6.18	
400	0	2770	bc	0.117	f	1.49	3.26	
	10	3500a		0.175	d	1.50	6.12	
	20	2780	bc	0.222	c	1.53	6.19	
	40	3090ab		0.305a		1.44	9.36	
	20 [‡]	2960ab		0.142	e	1.75	4.21	
<u>Harvest 2</u>								
200	0	2880	d	0.107	de	1.23	3.14	
	10	2670	d	0.137	c	1.42	3.62	
	20	2660	d	0.177	b	1.29	4.72	
	40	3100	d	0.222a		1.25	6.92	
400	0	3600	c	0.100	e	1.51	3.60	
	10	4530a		0.127	cd	1.52	5.80	
	20	4400a		0.140	c	1.42	6.16	
	40	4120ab		0.187	b	1.43	7.75	
	20 [‡]	3830	bc	0.137	c	1.62	5.24	
<u>Harvest 3</u>								
200	0	4600	c	0.115	cd	1.13	5.29	
	10	4910	c	0.115	cd	1.08	5.63	
	20	4600	c	0.145	b	1.10	6.67	
	40	4780	c	0.177a		1.05	8.51	
400	0	4960	c	0.097	d	1.38	4.83	
	10	5650	b	0.117	cd	1.34	6.62	
	20	5870ab		0.120	cd	1.34	7.03	
	40	6030ab		0.145	b	1.29	9.70	
	20 [‡]	6340a		0.125	bc	1.30	7.95	

Table 28. (Continued)

Fertilizer		Dry matter yield [†]	Herbage			
N	S		S [‡]	N	N:S ratio	S uptake
-----kg/ha-----			-----%-----			-kg/ha-
<u>Harvest 4</u>						
200	0	3280 d	0.125 bc	1.33	10.7	4.09
	10	3360 d	0.145 b	1.39	9.7	4.89
	20	3530 cd	0.170a	1.31	7.7	6.00
	40	3500 d	0.182a	1.34	7.4	6.33
400	0	3760 bcd	0.115 c	1.58	13.8	4.33
	10	4520a	0.127 bc	1.54	12.1	5.78
	20	4190abc	0.140 b	1.53	11.0	6.00
	40 _‡	4480a	0.165a	1.50	9.2	7.34
	20 [‡]	4360ab	0.170a	1.50	8.8	7.40

[†]Values followed by the same letter are not statistically different within harvest at the 0.05 level of significance using Duncan's new multiple range test.

[‡]S rate was split and applied in four equal applications during the season.

Table 29. Extractable and total sulfur in bahiagrass plots from the Beef Research Unit.

Fertilizer S	Depth or horizon	Extractable soil S [†]		Total soil S (1978) [†]
		1978	1979	
-kg/ha-	-----cm-----	-----ppm-----		
<u>200 kg/ha N</u>				
0	0-15	2	2	78
	15-30	3	1	60
	above spodic	3	2	66
	spodic	7	3	132
10	0-15	2	2	98
	15-30	1	0	75
20	0-15	3	2	85
	15-30	2	1	37
40	0-15	2	3	97
	15-30	5	1	56
	above spodic	4	1	42
	spodic	10	3	72
<u>400 kg/ha N</u>				
0	0-15	2	2	100
	15-30	2	3	62
10	0-15	2	3	110
	15-30	1	1	47
20	0-15	2	2	82
	15-30	2	2	50
40	0-15	2	2	115
	15-30	2	0	53
20 [‡]	0-15	1	3	110
	15-30	2	2	46

[†] Each value is the mean of samples from four plots.

[‡] S rate was split and applied in four equal applications during the season.

produces a large stolon-root mass which is capable of retaining significant quantities of nutrients. While there were no differences in the total mass of the stolon-root system, significant differences were found in the S concentration of the tissues (Table 30). Plots which had no S applied accumulated an average of 30 kg/ha of S while those which received 40 kg/ha/yr of fertilizer S accumulated over 42 kg/ha of S during the 2-year study. These values would have been somewhat higher if the root system below the sampling depth had been collected and analyzed.

The N:S ratio was surprisingly low in both the bahiagrass and bermudagrass tissues during both years of the study. The highest ratios were associated with the high N and no S plots in 1979. These values averaged 14.0 and 12.9, respectively, for the bahiagrass and bermudagrass. The low N:S ratios indicated an accumulation of sulfate although sulfate S in the tissues was not determined. All of the values reported in Tables 26, 27, 31, and 32 were below or near the critical N:S ratio of 14 reported by Metson (1973) for gramineous plants and within or below the normal N:S ratio of 12 to 17 reported by Woodhouse (1969) for bermudagrass. The stolon-root system also contained similar N:S ratios.

9.2 SULFUR IN BERMUDAGRASS ON A KENDRICK FINE SAND

Bermudagrass yields on a Kendrick fine sand averaged 68% of the bahiagrass yields on the Myakka soil in 1978. However, yields in 1979 varied less than 10% between the sites (15,400 kg/ha of bahiagrass and 14,400 kg/ha of bermudagrass). The Kendrick fine sand is a better-drained soil than the Myakka. The Coastcross I bermudagrass suffered severe damage during the winter months, initiated growth later in the

Table 30. Stolon-root mass from bahiagrass plots at the Beef Research Unit.

Fertilizer		Stolon-root mass [†]	Nutrient concentration [†]		N:S ratio
N	S		S	N	
-----kg/ha-----			-----%-----		
200	0	24,400a*	0.138a	0.78a	5.6 b
200	40	24,600a	0.170 b	0.76a	4.5 c
400	0	20,700a	0.125a	1.37 b	11.0a
400	40	23,200a	0.185 b	1.14 b	6.2 b

[†] Each value is the mean of four replications.

* Values followed by the same letter are not statistically different at the 0.05 level of significance using Duncan's new multiple range test.

Table 31. The effect of nitrogen and sulfur fertilization on bermudagrass in a Kendrick fine sand--1978.

Fertilizer		Dry matter yield [†]	Herbage			
N	S		S ⁺	N	N:S ratio	S uptake
-----kg/ha-----			-----%-----			-----kg/ha-----
<u>Harvest 1</u>						
200	0	950 b	0.127 c	1.49	11.8	1.23
	10	1220ab	0.172 bc	1.56	9.0	2.13
	20	1230ab	0.195abc	1.52	7.8	2.39
	40	1290ab	0.277a	1.49	6.3	3.54
400	0	1210ab	0.150 bc	2.10	14.1	1.86
	10	1660ab	0.167 bc	1.99	12.1	2.62
	20	1030ab	0.212abc	2.22	10.4	2.09
	40	1610ab	0.240ab	2.09	9.1	3.74
	20 [‡]	1760a	0.155 bc	1.92	12.5	2.68
<u>Harvest 2</u>						
200	0	1340ab	0.130 f	1.57	12.4	1.71
	10	1200ab	0.170 de	1.69	9.9	2.04
	20	1300ab	0.190 cd	1.65	8.7	2.47
	40	1370a	0.222 b	1.75	7.9	3.04
400	0	1130ab	0.157 ef	2.30	14.7	1.77
	10	1130ab	0.182 cde	2.30	12.7	2.05
	20	1250ab	0.210 bc	2.40	11.5	2.62
	40	1080 b	0.267a	2.36	8.9	2.88
	20 [‡]	1240ab	0.170 de	2.21	13.2	2.08
<u>Harvest 3</u>						
200	0	3190a	0.165 d	1.43	8.7	5.23
	10	3600a	0.185 cd	1.46	7.9	6.53
	20	3820a	0.182 cd	1.39	7.6	7.01
	40	3280a	0.225 b	1.38	6.2	7.40
400	0	3530a	0.182 cd	1.92	10.6	6.44
	10	3580a	0.217 bc	1.85	8.9	7.40
	20	3720a	0.210 bc	1.84	8.8	7.81
	40	3400a	0.262a	1.89	7.2	8.95
	20 [‡]	3570a	0.222 b	1.77	8.0	7.94

Table 31. (Continued)

Fertilizer		Dry matter yield [†]	Herbage			
N	S		S [‡]	N	N:S ratio	S uptake
-----kg/ha-----			-----%-----			
<u>Harvest 4</u>						
200	0	2250a	0.145 b	1.32	8.3	3.46
	10	2590a	0.150 b	1.22	8.1	3.86
	20	2670a	0.165ab	1.28	7.9	4.44
	40	2590a	0.166ab	1.27	7.7	4.28
400	0	2440a	0.167ab	1.98	11.8	4.08
	10	2720a	0.165ab	1.82	11.0	4.48
	20	2880a	0.175ab	1.82	10.3	4.96
	40	2640a	0.187a	1.90	10.1	4.96
	20 [‡]	2890a	0.172ab	1.68	9.9	5.03

[†]Values followed by the same letter are not statistically different within harvest at the 0.05 level of significance using Duncan's new multiple range test.

[‡]S rate was split and applied in four equal applications during the season.

Table 32. The effect of nitrogen and sulfur fertilization on bermudagrass in a Kendrick fine sand--1979.

Fertilizer		Dry matter yield [†]	Herbage			
N	S		S [†]	N	N:S ratio	S uptake
-----kg/ha-----			-----%-----			
Harvest 1						
200	0	2380 c	0.130 e	1.09	8.4	3.13
	10	2510 c	0.167 cd	1.09	6.5	4.29
	20	2830 bc	0.170 cd	1.06	6.2	4.90
	40	2200 c	0.177 cd	1.02	5.8	3.95
400	0	3880a	0.152 de	1.52	10.1	5.96
	10	3810ab	0.197 bc	1.49	7.6	7.56
	20	3740ab	0.227ab	1.66	7.3	8.46
	40	4490a	0.250a	1.60	6.6	11.10
	20 [‡]	3760ab	0.157 de	1.38	8.7	5.92
Harvest 2						
200	0	2620 d	0.112 e	1.21	10.9	2.93
	10	2880 cd	0.127 de	1.16	9.2	3.68
	20	2560 d	0.142 cd	1.23	8.7	3.64
	40	2790 d	0.157 bc	1.12	7.1	4.39
400	0	3380 bc	0.130 de	1.86	14.4	4.39
	10	3760ab	0.147 bcd	1.74	11.8	5.53
	20	4230a	0.167 b	1.74	10.5	6.93
	40	3700ab	0.215a	1.76	8.2	7.93
	20 [‡]	4190a	0.160 bc	1.66	10.4	6.73
Harvest 3						
200	0	4290abc	0.115 e	1.13	9.9	4.93
	10	4410ab	0.150 d	1.15	7.7	6.59
	20	3790 c	0.165 cd	1.14	7.0	6.27
	40	3840 c	0.190 b	1.15	6.1	7.2
400	0	4000 bc	0.122 e	1.69	14.0	4.86
	10	3920 bc	0.162 cd	1.68	10.5	6.34
	20	4740a	0.180 bc	1.62	9.1	9.54
	40	4620a	0.227a	1.74	7.7	10.10
	20 [‡]	4600a	0.165 cd	1.57	9.6	7.64

Table 32. (Continued)

Fertilizer		Dry matter yield [†]	Herbage			
N	S		S [†]	N	N:S ratio	S uptake
-----kg/ha-----			-----%-----			
			Harvest 4			
200	0	3640a	0.147 bc	1.30	8.8	5.40
	10	3800a	0.170 b	1.30	7.7	6.47
	20	3850a	0.165 b	1.28	7.8	6.33
	40	3770a	0.195a	1.28	6.6	7.36
400	0	3380a	0.142 c	1.83	13.0	4.82
	10	4090a	0.162 bc	1.78	10.9	6.68
	20	3320a	0.167 b	1.76	10.6	5.54
	40	3440a	0.195a	1.77	9.1	6.65
	20 [‡]	2500 b	0.197a	1.80	9.1	4.90

[†]Values followed by the same letter are not statistically different within harvest at the 0.05 level of significance using Duncan's new multiple range test.

[‡]S rate was split and applied in 4 equal applications during the season.

spring, and tolerated drought less than the Pensacola bahiagrass. The 1978 season had an unusually dry spring and fall. During both years, the first harvest in May consisted of 50 to 80% broadleaf weeds at Green Acres. Subsequent harvests were dominantly bermudagrass.

Neither S nor N had any effect on dry matter production during 1978, although there were significant differences in the S and N concentrations in the plant tissues (Table 31). These differences were also obvious in decreasing N:S ratios with increasing S rates.

Harvest data from 1979 showed that higher N rates increased yield by 19% (Table 32, Fig. 14). Sulfur fertilization produced a significant difference in total dry matter yield for the season. The 20 and 40 kg/ha S rate increased yields by 10% over the check plot at high N rates. No significant differences were observed between S treatments at the low N rate.

The previous experiments as well as research by others (Ensminger, 1958; Neller, 1959; Anderson and Futral, 1966; Lund and Murdock, 1978; Mitchell and Gallaher, 1980) have pointed out the significance of subsoil S on crop nutrition in Ultisols. Extractable and total S with depth in selected plots in this experiment show that extractable S in the surface horizons are comparable to that in the Myakka soil while total S is generally less (Table 33). Extractable and total S increases sharply at the argillic horizon. Because of the sandy, well-drained nature of this soil, one would expect roots of the bermudagrass to reach this large source of available S.

In the process of sampling selected plots for subsoil material, the author noted considerable variation in depth to the argillic horizon. The depth to the argillic horizon was measured in each plot to

* Split S applications

Letters indicate significant differences at 0.05 level using Duncan's New Multiple Range Test.

Fig. 14. The effect of sulfur and nitrogen rates on the annual yield of bermudagrass on a Kendrick fine sand.

Table 33. Extractable and total sulfur in bermuda-grass plots from Green Acres Agronomy Farm.

Fertilizer S	Depth or horizon	Extractable soil S ⁺		Total soil S _t (1978)
		1978	1979	
--kg/ha---	-----cm-----	-----ppm-----		
<u>200 kg/ha N</u>				
0	0-15	2	2	58
	15-30	3	2	22
	above argillic	4	7	12
	argillic	20	19	70
10	0-15	3	2	57
	15-30	3	2	21
20	0-15	3	2	59
	15-30	4	1	28
40	0-15	3	4	60
	15-30	3	2	24
	above argillic	4	4	10
	argillic	21	18	76
<u>400 kg/ha N</u>				
0	0-15	2	2	59
	15-30	3	1	30
10	0-15	3	3	59
	15-30	3	2	30
20	0-15	4	3	53
	15-30	3	2	28
40	0-15	3	4	62
	15-30	3	2	29
20 [‡]	0-15	3	4	56
	15-30	3	2	24

⁺ Each value is the mean of samples from four plots.

[‡] S rate was split and applied in four equal applications during the season.

determine if there were any correlations with depth and the S nutrition of the bermudagrass. Although the topography of the experimental area was quite uniform with less than a 2% slope, the depth to the argillic horizon varied from near 60 cm to over 200 cm (Fig. 15). The area was mapped as Kendrick fine sand, but because of this large variation in depth to the argillic horizon, part of the plot area would probably be considered Arredondo fine sand. At some of the deeper points, the upper argillic horizon was very moist with some mottling in contrast to the well-drained condition of the shallow argillic horizons. While the direction of the blocks was parallel to the slope of the soil surface, it was perpendicular to the slope of the argillic horizon. This situation created a source of variation within the experiment that could not be evaluated. The S concentration in the forage was significantly correlated with depth to the argillic horizon at the 0.05 level of significance, but the correlation coefficient was only 0.20. Total yield was significantly correlated with N uptake ($r = 0.91$), N concentration in the forage ($r = 0.80$), S uptake ($r = 0.76$), and S concentration in the forage ($r = 0.45$) but not with depth to the argillic horizon.

9.3 FORAGE SULFUR CONCENTRATIONS AND N:S RATIOS

There were few observations with S concentrations below what would be considered to be a critical level. Bremer (1976) reported a critical plant S concentration for 'Midland' bermudagrass of 0.10 to 0.15%. There is a trend toward lower yields below a S concentration of 0.12%, but a critical level cannot be established with these data (Fig. 16).

Fig. 15. A contour plot of the depth to the argillic horizon (cm) in the experimental area on a Kendrick fine sand at Green Acres Agronomy Farm.

Fig. 16. The effect of S concentration in bahiagrass and bermudagrass on relative yields at high N rates.

The same trend was observed with the N:S ratios in bermudagrass as with bahiagrass (Tables 27 and 31). The highest mean ratio, 12.8, was from the treatment without S but with a high rate of N. Most of the N:S ratios were much less than this and well within the optimum range for plant protein.

As previously mentioned, S uptake was highly correlated with forage yield (Table 28). There were significant differences in S uptake with S fertilization. Even where no S was applied, 16.4 kg/ha of S were removed at low N rates. At high S and N rates, more than twice this amount was removed in the forage. Assuming a bulk density of 1.3 g/cm^3 , and using mean total S levels from Table 33, the author found that the upper 30 cm of this soil contains 164 kg/ha of S of which only 6 kg/ha were available to plants at any one time.

10. SOURCES AND CYCLING OF SULFUR IN THE FIELD

Data from these experiments and from other research have been combined to estimate the sources and cycling of S in a Florida Spodosol with a bahiagrass sward (Fig. 17). Estimates of sources of plant available S have been made wherever possible. Most values are quite variable but all have come from reliable data collected in the southeastern United States from soils or conditions similar to rural north Florida. No attempt was made to balance the input and uptake of S by bahiagrass because of the lack of certain essential values such as annual leaching losses of S and S mineralization rates for Florida soils.

Edgerton et al. (1980) found a mean of 2.6 kg/ha of sulfate S was deposited in northern Florida during the winter months and 5.8 kg/ha during the summer months. These values were an average from 12

* This value is quite variable and has not been determined on an annual basis. Nelson (1964) found an average of 10 kg/ha of S mineralized from 12 Mississippi soils during 6 months.

** Extractable sulfate S in Florida Spodosols averaged 7 kg/ha at any one time.

Fig. 17. Annual sources and cycling of sulfur (kg/ha/yr) in the surface (0-15 cm) of a north Florida Spodosol.

locations. At a Gainesville, Florida, collecting station, they reported that bulk precipitation (open rainfall collectors) for 1978-79 contained a volume-weighted concentration of 0.0352 meq of sulfate S/liter. Rainfall data from the Beef Research Unit from 1976 through 1979 showed a mean annual rainfall of 120 cm. Of this, 65% or 78.3 cm fell from April through September, the period of active growth of bahiagrass. If the rainfall at the Beef Research Unit contained the same S concentration as that in Gainesville (it would probably be less), we would expect approximately 4.4 kg/ha of S deposited during the growing season.

Estimated evapotranspiration for the Jacksonville, Florida, area is 69.3 cm for April through September (0.385 cm/day) and 100 cm annually (L. C. Hammond, personal communication). Therefore, 88.5% of the natural rainfall during the growing season was removed by evapotranspiration. Specific evapotranspiration data were not available for a well-fertilized actively growing bahiagrass sward, but, no doubt, it would be higher than the values presented here. Using these data, we can estimate that approximately 3.9 kg/ha of rainfall S would remain in the surface soil or be taken up by the plant through mass flow. The remainder would probably be leached beyond the rooting zone or immobilized by microorganisms.

Jones et al. (1979) estimated that an average of 8.4 kg/ha/yr of atmospheric S was absorbed directly by the soil in South Carolina from 1973 to 1977. This value was based on data from 15 locations, and it continually increased from 2.8 kg/ha in 1973 to 13.0 kg/ha in 1977. Atmospheric S varied significantly with season of the year in South Carolina as it does in Florida. Specific atmospheric data are not

available by seasons; therefore, a value of 4.2 kg/ha of S will be used as an estimate of S absorbed directly by the soil during the 6-month growing season.

No values are available on the amount of S that may be absorbed directly through the bahiagrass foliage. Olsen's estimate of 30% of the total plant's S needs was a function of the effective leaf surface of healthy cotton plants (Olsen, 1957). Bahiagrass forms a dense mat of stolons and roots that cover the soil surface. Foliage at harvest rarely exceeds 60 cm in height. Much of the estimated 4.2 kg/ha of S that would be absorbed by the soil might, in fact, be absorbed by the plant before reaching the soil--particularly if the plant is growing under S-deficient conditions. Any SO_2 absorbed by the soil surface during the winter months would likely be leached through the rooting zone.

The plant S that cannot be accounted for by the above values comes from mineralization of organic S (total S) or from stolon-root S carried over from the previous season. Nelson (1964) found an average of 10 kg/ha of S was mineralized from 12 Mississippi soils during a 6-month period under controlled conditions. This value varied widely with different soils. Mineralization is known to be affected by so many variables that convenient field estimations of this value have not been achieved.

From the greenhouse experiment with subsoil S, we found that approximately 15 mg of S/pot was removed in the tops of the sorghum-sudangrass growing in surface soil of a Myakka fine sand during 16 weeks with no added S. If we assume that the roots contained about 0.10% S, then 6.5 mg S/pot remained in the roots for a total of

approximately 21 mg/pot of S. This value should represent total available and mineralized S during the 16-week period of the experiment. It would be equivalent to approximately 9 kg/ha of S in the top 15 cm of soil in the field. This value was used in Fig. 17 but would probably be higher during an entire growing season under field conditions.

SECTION V SUMMARY AND CONCLUSIONS

The experiments discussed in this study complement the S fertility work done in the 1950's by Bartlett, Neller, and others. Their work pointed out that most Florida soils were low in available S, and many crops, particularly legumes, would respond to S applications in the field. Even though available soil S may be inadequate for many crops in Florida soils, data from this study and recent studies of atmospheric S showed that S from rainfall, direct absorption of SO_2 by the soil and plant leaves, and available soil S may be adequate for low to moderate crop yields. Non-fertilizer sources of S account for an estimated minimum of 21 kg/ha of plant-available S. With an average of 15 to 39 kg of S applied in fertilizers per harvested hectare in Florida, S deficiencies among field crops are unlikely. However, where high-analysis fertilizers containing little or no S are used and high yields are maintained, S deficiencies are likely to appear.

The following are additional conclusions which may be made from the experiments reported in this work:

1. The surface 15 cm of most Florida soils contain less than 5 ppm of extractable sulfate S and are unable to provide adequate S to a growing crop for more than 4 to 8 weeks without additional sources of S.
2. Total S in the surface horizons (0-15 cm) of Florida Spodosols, Entisols, and Ultisols averaged 74 ppm and was highly correlated with organic C ($r=0.89$) and total N ($r=0.95$).
3. C:N:S ratios in the surface horizons of selected Florida Spodosols, Entisols, and Ultisols averaged 150:6.4:1, 166:5.9:1, and 112:7.1:1, respectively. These ratios are

considerably higher than those reported for soils in other areas and may have important implications for organic S mineralization in these soils.

4. Spodic horizons contained slightly less extractable and total S than the surface (A1) horizons but considerably more than the A2 horizons. This S did not contribute to the S nutrition of sorghum-sudangrass in the greenhouse and actually reduced yields when included in a simulated soil profile.
5. Ultisols contained an average of 33 ppm of extractable S in their argillic horizons. This value represented more than 40% of the total S. Adsorbed sulfate in the argillic horizon in a Norfolk soil was sufficient to meet the needs of a sorghum-sundangrass hybrid in the greenhouse for 16 weeks; adsorbed sulfate in the argillic horizon of an Orangeburg soil from the same area was not sufficient to meet the S needs of the plant beyond 8 weeks.
6. Entisols are uniformly low in adsorbed S in subsurface horizons and contain an average of around 6 ppm of sulfate S. Yields of a sorghum-sudangrass in a Lakeland fine sand were significantly increased by S fertilization after 4 weeks of growth in the greenhouse. Subsoil S contributed to the S nutrition of the plants but not enough to increase yields.
7. A critical concentration of total S in 4-week old sorghum-sudangrass tops was 0.12%. The critical N:S ratio was 16.
8. Yields of Pensacola bahiagrass on Myakka fine sand in the field were not increased by S applications the first year. The lowest rate of S, 10 kg/ha, significantly increased total dry matter production the second year at a high rate of N (400 kg/ha).
9. Yields of Coastcross I bermudagrass on Kendrick fine sand in the field were not increased by S fertilization the first year. Significant yield increases were observed at the 10 and 20 kg/ha S rates the second year at the highest rate of N (400 kg/ha).
10. Spring S applications as gypsum increased the S concentration in the forage and S uptake at every harvest during both years.
11. Applying S in split applications during the season apparently had no benefit over a single application in the early spring.
12. Spring S applications had no apparent effect on extractable S in the soil profile in the fall.

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APPENDICES

APPENDIX A
DIGESTION PROCEDURE FOR ESTIMATION OF
TOTAL SULFUR IN PLANT TISSUE

REAGENTS

Magnesium nitrate digestion solution: Place 113 g of MgO in a large Erlenmeyer flask and add 300 ml of demineralized water. Place flask on a magnetic stirrer and insert stirring rod. Very slowly add 465 ml concentrated HNO₃ while stirring (CAUTION--the reaction is strongly exothermic and should be carried out under a hood). Allow 1 to 2 hours for the addition of all of the acid. After cooling, rinse the contents of the flask into a 1-liter volumetric flask and dilute to volume with demineralized water.

6N HCl: Add 500 ml of concentrated HCl to 500 ml of demineralized water. Mix well and allow to cool.

PROCEDURE

1. Accurately weigh 0.50 g of the ground plant tissue into a 50-ml beaker or crucible.
2. Add 5 ml of the Mg(NO₃)₂/HNO₃ solution. Allow to stand a few minutes until all of the plant material is wet.
3. Evaporate to dryness on a hot plate. Sample must be completely dry to prevent frothing of the sample when placed in the muffle furnace.
4. Remove from hot plate and place in a muffle furnace. Heat to 300°C for 1 hour. Increase temperature to 500°C and muffle for 2 additional hours.
5. Allow sample to cool. Moisten with demineralized water, add 10 ml of 6N HCl, and evaporate to dryness slowly on a hot plate. Be careful that samples do not "bump" resulting in loss of the sample.
6. Add 5 ml of 6N HCl, and heat to dissolve all residue. Remove from hot plate. Carefully wash contents into a 50-ml volumetric flask or test tube calibrated to 50 ml.
7. Allow sample to cool and dilute to volume. Stopper with a plastic stopper and shake well.
8. Allow samples to stand overnight and remove an aliquot from the surface or filter through a Whatman no. 42 filter paper.
9. Determine sulfate S turbidimetrically.

APPENDIX B
DIGESTION PROCEDURE FOR ESTIMATION OF
TOTAL SULFUR IN SOILS

REAGENTS

(All reagents are the same as those for plant tissue digestion.)

PROCEDURE

1. Weigh 5 g of air-dried, screened soil into a 50-ml beaker or ceramic crucible.
2. Add 10 ml of the magnesium nitrate digestion solution. Allow to stand a few minutes until the soil is thoroughly moist.
3. Evaporate to dryness on a hot plate. Sample must be completely dry to prevent frothing of the sample when placed in the muffle furnace.
4. Remove from hot plate and place in a muffle furnace. Heat to 300°C for 1 hour. Increase temperature to 500°C and muffle for 3 additional hours.
5. Cool. Add 15 ml of the 6 N HCl and evaporate to dryness on a hot-plate. Be careful that samples do not "bump" resulting in loss of the sample.
6. Add 5 ml of 6 N HCl and dilute to a 50-ml volume.
7. Shake vigorously and allow suspended material to settle overnight. Filter through a Whatman no. 42 filter paper before determining S turbidimetrically.

APPENDIX C
PROCEDURE FOR THE TURBIDIMETRIC DETERMINATION OF
SULFATES IN SOIL EXTRACTS, DIGESTED SOIL
EXTRACTS, AND DIGESTED PLANT TISSUE

REAGENTS

Acetic/phosphoric acid: Mix 900 ml concentrated acetic acid with 300 ml concentrated H_3PO_4 .

Gum acacia solution: Dissolve 5 g gum acacia in 500 ml hot water. Filter hot through a Whatman no. 42 filter paper on a Buchner funnel using suction. Cool and dilute to 1 liter with acetic acid.

Barium sulfate seed suspension: Dissolve 18 g $BaCl_2 \cdot 2H_2O$ in 44 ml hot water. Add 0.5 ml of the 2,000 ppm S standard. Bring to a boil, and cool quickly. Add 4 ml of the gum acacia solution and mix well. Prepare fresh daily.

Barium chloride solution: Add 200 g $BaCl_2 \cdot 2H_2O$ to a 1-liter volumetric flask. Add enough hot water to dissolve. Cool and dilute to volume.

Standard sulfate solution (2,000 ppm S): Dissolve 1.0875 g of oven-dried K_2SO_4 in 0.1 N HCl and dilute to 100 ml. Prepare a 10 ppm S working standard daily by diluting 1 ml of the 2,000 ppm S standard to 200 ml with demineralized water.

PROCEDURE

1. Prepare standards containing 0 to 100 μg S by pipetting appropriate volumes of the 10 ppm S standard into test tubes calibrated at 25 ml. Standards of 0, 20, 40, 60, 80, and 100 μg S are usually adequate to establish a curve.
2. Pipette an aliquot of sample containing 20 to 80 μg S into a test tube. Do not run more than 30 samples with a single set of standards.
3. Add 2 ml of the acetic/phosphoric acid.
4. Add water to a volume of approximately 18 ml; stir on a vortex mixer.
5. Add exactly 0.5 ml of the barium sulfate seed suspension.
6. Add 1 ml of the barium chloride solution.
7. Stopper each tube with a plastic stopper and invert three times. Wait 10 minutes and invert three more times. Wait 5 minutes and invert three more times.

8. Remove stoppers and add 1 ml of the gum acacia solution. Dilute to volume (25 ml) with demineralized water. Stopper again and invert 3 times.
9. Allow samples to stand for 1.5 hours.
10. Invert 10 times and read absorbance or transmittance on spectrophotometer set on a wavelength of 440 nm. The wavelength is not critical since only light blockage by the BaSO_4 precipitate is measured and not absorbance. The standard curve is usually linear from 10 to 80 $\mu\text{g S}$.

APPENDIX D
AN INDIRECT METHOD FOR THE DETERMINATION OF SULFATES
IN SOIL EXTRACTS (FROM HUE AND ADAMS, 1979)

REAGENTS

Barium standard: Dissolve 1.9610 g $\text{BaSO}_4 \cdot 2\text{H}_2\text{O}$ in 0.1 N HCl and dilute to a 1-liter volume. This solution is a 1,000 ppm Ba stock solution. Prepare a 100 ppm Ba working standard by diluting a 10 ml aliquot of the stock solution to 100 ml with demineralized water.

$\text{ClCH}_2\text{COOH/KOH}$ solution: Dissolve 47.25 g ClCH_2COOH and 3.40 g KOH in 250 ml demineralized water.

BaSO_4 seed suspension: Place 0.1 g BaSO_4 powder in 100 ml demineralized water. Shake well before each use.

95% ethanol

PROCEDURE

1. Aliquot 10 ml of a 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ extract containing 1 to 20 ppm sulfate into a 100 ml plastic bottle.
2. Add 3 ml of a 100 ppm Ba standard.
3. Add 2 ml of the $\text{ClCH}_2\text{COOH/KOH}$ solution 0.1 ml of the BaSO_4 seed suspension, and 15 ml of 95% ethanol.
4. Cap and shake for 15 minutes.
5. Transfer to centrifuge tube and centrifuge at 5,000 g for 30 min. at 5°C.
6. Analyze supernatant for Ba by atomic absorption spectroscopy using a N_2O /acetylene flame at an absorption wavelength of 554 nm.

APPENDIX E
MEAN AND TOTAL VALUES FOR FOUR HARVESTS OF A
SORGHUM-SUDANGRASS CROP IN THE GREENHOUSE

Horizon sequence	Fertilizer S ---ppm---	Mean plant height --cm--	Herbage			
					Mean N:S ratio	Total S uptake -mg/pot-
			S	N		
			-----%-----			
<u>Myakka fine sand⁺</u>						
A/sand	0	57	0.096	3.05	33	16.1
A/sand	20	78	0.192	2.67	14	61.9
A/B	0	54	0.095	3.31	38	14.6
A/B	20	72	0.182	2.88	17	48.3
<u>Lakeland fine sand⁺</u>						
A/sand	0	63	0.106	2.90	29	16.8
A/sand	20	83	0.197	2.72	16	73.1
A/C	0	61	0.107	2.91	29	19.6
A/C	20	80	0.192	2.85	16	66.5
<u>Orangeburg fine sand⁺</u>						
A/sand	0	69	0.132	2.80	28	43.9
A/sand	20	83	0.197	2.83	16	77.2
A/B	0	74	0.131	2.78	24	43.2
A/B	20	76	0.178	2.85	18	71.1
<u>Norfolk fine sand⁺</u>						
A/sand	0	64	0.089	2.56	38	22.5
A/sand	20	76	0.161	2.49	16	49.8
A/B	0	75	0.139	2.54	18	40.4
A/B	20	70	0.164	2.62	16	47.0

⁺Plants were harvested every 28 days. Values are the mean or total of four harvests.

APPENDIX F
THE EFFECT OF HORIZON SEQUENCE AND SULFUR
ON ROOT DRY MATTER YIELD AT HARVEST

Horizon sequence	Fertilizer S	Soil series			
		Myakka	Lakeland	Orangeburg	Norfolk
-----g/pot-----					
A/sand	0	6.5	7.3	15.9	8.0
A/sand	40	17.1**	18.3**	19.3	13.1*
A/B or A/C	0	4.9	9.9	18.3	13.2
A/B or A/C	40	12.8**	18.5**	17.9	12.1

*,** Significant at the 0.05 and 0.01 levels, respectively, within horizon sequence.

APPENDIX G
NUTRIENT LEVELS IN COMPOSITE SAMPLES FROM EXPERIMENTAL
AREAS AT THE BEEF RESEARCH UNIT (MYAKKA FINE SAND)
AND AT GREEN ACRES AGRONOMY FARM
(KENDRICK FINE SAND)

Sampling date	Double-acid extractable nutrients [†]				
	pH	P	K	Mg	Ca
	-----ppm-----				
	<u>Myakka fine sand</u>				
Spring, 1978	5.2	9	16	23	452
Fall, 1978	5.5	10	16	44	460
Fall, 1979	5.3	12	32	88	560
	<u>Kendrick fine sand</u>				
Spring, 1978	5.9	50	16	45	228
Fall, 1978	5.9	56	35	48	228
Fall, 1979	5.6	65	24	68	228

[†]Extracted using double-acid (0.01 N HCl + 0.025 N H₂SO₄).

APPENDIX H
 RAINFALL DISTRIBUTION AT THE BEEF RESEARCH UNIT,
 GAINESVILLE, FLORIDA, FOR 1978 AND 1979

VITA

Charles Clifford Mitchell, Jr., son of Charles Clifford and Phebe (Hinson) Mitchell, was born in Selma, Alabama, on 14 March 1948. He attended Marengo County (Alabama) schools and graduated valedictorian from Marengo County High School in 1966.

He attended Birmingham Southern College, Birmingham, Alabama, where he received the Bachelor of Science degree in biology in 1970. He attended graduate school at Auburn University where he received the Master of Science degree in soil fertility in 1973. Prior to receiving the master's degree, he accepted a position of research associate with the Department of Agronomy and Soils at Auburn University and worked with the soil testing program in Alabama for 5 years. For two of those years, he coordinated on-the-farm soil fertility research with farmers in north Alabama and worked out of the Tennessee Valley Substation at Belle Mina, Alabama.

In 1977, he returned to graduate school at the University of Florida on a half-time graduate assistantship with the Extension Soil Testing Laboratory in the Soil Science Department. In September, 1980, he accepted a position with the Department of Agricultural Chemical Services at Clemson University, Clemson, South Carolina, as Laboratory Director and Lecturer in Agronomy and Soils.

He is married to the former Peggy Armstrong of Hamilton, Alabama, and is a member of Theta Chi Fraternity, Gamma Sigma Delta, national

honor society of agriculture, the American Society of Agronomy, the Soil Science Society of America, and the Soil and Crop Science Society of Florida.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

W. G. Blue, Chairman
Professor of Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

T. L. Yuan
Professor of Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

J. B. Sartain
Associate Professor of
Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

R. D. Rhue
Associate Professor of
Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

R. N. Gallaher
Associate Professor of Agronomy

This dissertation was submitted to the Graduate Faculty of the College of Agriculture and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1980

Dean, College of Agriculture

Dean, Graduate School

UNIVERSITY OF FLORIDA

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