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Sulphur content of Tennessee soils

Abram W. Hatcher

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I am submitting herewith a thesis written by Abram W. Hatcher entitled "Sulphur content of Tennessee soils." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agronomy.

Lloyd F. Seatz, Major Professor

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Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

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I am submitting herewith a thesis written by Abram W. Hatcher entitled "Sulfur Content of Tennessee Soils." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Agronomy.

Ray J. Seatz
Major Professor

We have read this thesis
and recommend its acceptance:

E. Winters

Wm. J. Smith, Jr.

Accepted for the Council:

P. H. Waters
Dean of the Graduate School

SULFUR CONTENT OF TENNESSEE SOILS

A THESIS

Submitted to
The Committee on Graduate Study
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the degree of
Master of Science

by

Abram W. Hatcher

August 1950

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Abram W. Hatcher

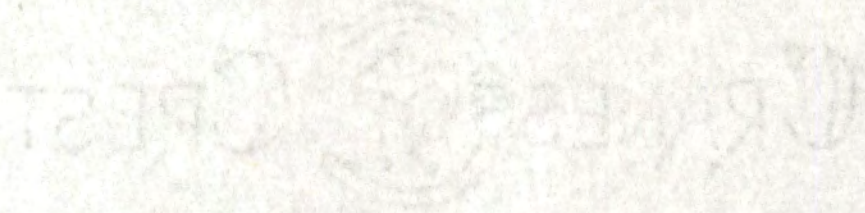
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INTRODUCTION

The study of sulfur in soils has been neglected in recent years except in arid regions. The possibility of a sulfur deficiency, however, is becoming of increasing interest in Tennessee due to the use of larger amounts of high analysis fertilizers and triple superphosphate, which do not contain any significant amount of sulfur. Increasingly higher yields require larger amounts of sulfur. There may not be enough sulfate in the soil or supplied by rain for such heavy yielding crops rich in albuminoid as alfalfa, either for the production of greatest yield or highest feeding value (13)¹. For such crops perhaps a sulfate should be included in the soil amendments. MacIntire (36), in 1917, stated that a continued loss of sulfates, in amounts approximating those which he had measured, would effect a speedy depletion of the soil organic sulfur content. Tests with cotton, conducted by Williamson, Bertram, and Richardson (56), showed that sulfur became deficient in many soils in Alabama when triple superphosphate, sodium nitrate, and muriate of potash were used as sources of phosphorus, nitrogen, and potassium, respectively.

¹Numbers in parentheses refer to references in the bibliography, page 45.

Results with cotton on three soil types in two widely separated parts of Florida indicated that sulfur was deficient and that sulfur nutrition merited greater consideration (23). Fried (21) obtained increases in yield of alfalfa from sulfur fertilization in greenhouses in Indiana. Shedd (48) found soils of Kentucky much poorer in sulfur than phosphorus and was inclined to place sulfur in the same class with phosphorus, nitrogen, and potassium as one of the chief limiting factors in crop production.

In view of the demonstrated sulfur deficiency in certain southeastern states and the lysimeter and rainfall studies made in and near Knoxville indicating possible sulfur deficiencies, it was thought advisable to make a study of the sulfur status of Tennessee soils. The purposes of this study were: (1) to determine the sulfur content of representative Tennessee soils, (2) to correlate the total sulfur content with the organic matter content, and (3) to predict the possibility of a sulfur shortage in some areas of the state.

LITERATURE REVIEW

The available form of sulfur for plants is the sulfate ion (29,57). The sulfate ion is absorbed by plants and assimilated into complex organic compounds. These organic compounds include proteins (chiefly albuminoids), cystine (an amino acid), glutathione (a tripeptide containing cysteine), methionine, vitamin B₁ or thiamine, biotin, jenkolic acid, and the glucoside, sinigrin (12,21, 44,52,57). In addition to being important as a nutrient element itself, sulfur may influence the availability of phosphorus, potassium, and calcium (31,40). Kevorkov (30) found that gypsum was effective in increasing the yields of clover and alfalfa, primarily by serving as a source of sulfur for the plants, although he suggested that an indirect effect was an increase in the supply of available potassium. However, MacIntire et al. (34) reported that sulfates were found not to increase the supply of potassium to growing plants where a favorable reaction had been produced by liming. Erdman (17) stated that sulfur additions increased potassium in drainage water. McKibbin (40) reported that calcium and phosphorus, as a result of sulfur addition, became less available and potassium and sulfur more so. Neller (41), on the other hand, found no significant increase in the amount of calcium, potassium, phosphorus, magnesium,

or iron in plants as a result of sulfur fertilization, but did find an increase in yield. Fraps (20) observed an increase in phosphorus uptake but no increase in nitrogen or potassium with sulfur addition. He also found that sulfur additions increased the availability of phosphorus, iron, manganese, and boron. The latter three elements are expected to become more available with an increase in acidity. Another effect of sulfur additions may be a higher nitrogen content of plants. Kelly and Midgley (29) stated that an abundance of sulfur favored nitrification in the soil and root development in legumes.

In several specific regions of the United States definite responses to sulfur fertilization have been found. Among the sulfur deficient areas are western Washington and Oregon, northern Idaho, Montana, Iowa, Arkansas, and a belt through the northern half of Minnesota (4,11,12,14,16; 42,45). Ranges in sulfur content of soils are given as 300 to 760 pounds per acre for Oregon, 719 to 938 pounds per acre for Iowa, and 412 to 800 pounds per acre for Ohio (6,11,42,45). The average for Kansas is 540 pounds per acre and for Wisconsin 400 pounds per acre (24,51).

Fried (21) found that yields were higher in all cases with sulfur fertilization. Volk, Tidmore, and Meadows (56) found that the sulfur concentration in the tissues of plants not fertilized with sulfur varied between 0.089 and 0.34

percent. The addition of sulfur increased the concentration in corn 120 percent, turnips 470 percent, and vetch 1000 percent. Peterson (44) stated that when large quantities of sulfates were added to the soil there were corresponding increases of sulfates in the plant tissue. Rape, radishes, and clover grown in greenhouses on soils low in sulfur but high in nitrogen, potassium, and phosphorus contained no sulfates, and 90 percent of the total sulfur was unoxidized (probably protein sulfur) when no sulfates were added.

When oxidized to sulfuric acid, sulfur becomes a good mineral solvent. Application of gypsum in arid areas results in improved structure and nutrient solubility (7). Ames and Boltz (6) suggested that sulfur additions resulted in increased water-soluble potassium content due to salt formation. MacIntire (35) reported that liming increased the outgo of sulfates as a result of stimulation of sulfonation and of oxidation of additions of elemental sulfur and of pyrite. He further stated that rainfall in humid regions effected substantially complete removal of ordinary additions of fertilizer sulfates within one year.

Volk and Bell (55), in Florida, found the order of appearance of the various ions in lysimeters to indicate that calcium nitrate dominated the soil solution and retarded the movement of sulfates until nitrate nitrogen, due either to leaching or plant utilization, had passed

its crest of concentration. They also found that the leaching of potash was apparently retarded as an indirect effect of the reduction of the solubility of sulfates by the calcium nitrate. These investigators used a standard treatment consisting of 201 pounds of ammonium nitrate, 215 pounds of potassium nitrate, 248 pounds of monocalcium phosphate, and 748 pounds of hydrated calcium sulfate. They confirmed certain findings of MacIntire (35) when they found that the use of lime caused a marked increase in the loss of sulfates by leaching.

In order to determine whether enough sulfur is present in the soil to maintain high yields of Tennessee crops it is necessary to present a balance sheet showing the sources as well as the ways of loss (table I and table II). Sources include rainfall, snowfall, and smoke; manures and crop residues, and fertilizers. Losses are incurred through erosion, leaching, and crop removal. Sulfur from rainfall and snowfall is added in varying amounts, depending on, in addition to the annual total precipitation, the proximity to large industrial areas. Alway (3) reported a range of from 120 pounds of sulfur per acre per year at the edge of St. Paul, Minnesota to 5 pounds of sulfur per acre per year in northern Minnesota. Other figures listed for rainfall sulfur content in pounds per acre per year are 25

TABLE I

DATA ON SULFUR ADDITIONS TO THE SOIL

Source	Pounds Per Acre
Plant and Animal Residue (Organic Matter) (57)	5
Rainfall and Snowfall (3,37)	10-20
Fertilizers 500# 20% Super 200# $(\text{NH}_4)_2\text{SO}_4$ 200# K_2SO_4 (21)	40 50 36
Minerals	?
SO_2 in Air (2)	1-30
Total Sulfur Reserves in Soil (21)	720

TABLE II

DATA ON SULFUR LOSSES FROM THE SOIL

Source	Pounds Per Acre
Crop Removal (21)	8-50
Leaching (10,32)	30-50
Erosion (32)	1-10

to 100 (Fried in Indiana), 30 (Lyon and Bizzell in New York), and 15 (Erdman in Iowa) (21,10,15). In Alabama, Volk, Tidmore, and Meadows (56) gave rural figures as 7 to 16 pounds per acre per year at Kinston and Belle Mina, respectively, and the Birmingham figure as 76 pounds per acre per year. In Tennessee, MacIntire and Young (37) gave values (1923) of 52 pounds per acre per year at the University of Tennessee farm at the edge of Knoxville, 95 pounds per acre per year at the heart of Knoxville, and 19 pounds per acre per year seven miles from Knoxville (8-year averages). All of these figures suggest a bountiful supply of sulfur from rainfall near large cities but small amounts in many rural areas.

Alway (2) reported the sulfur dioxide absorbed by lead peroxide-coated fabric as from 100 pounds per acre per year in Minneapolis to less than 5 pounds per acre per year near the Mississippi River headwaters. He stated, however, that only about 22 percent of this amount was absorbed by soils and used this factor to calculate the amount of sulfur added to the soil by the sulfur dioxide present in the air. Pounds per acre per year were reported as 30 for the University Farm, 1.6 for rural Page and Crow Wing, and 1.1 for Bemidji in northern Minnesota. Kelly and Midgley (29) gave ranges of 32.7 to 109, 25 to 250, and 60 to 375 for pounds of sulfur trioxide absorbed by plants in Vermont,

Minnesota, and Indiana, respectively.

Other sources of sulfur include manure and crop residues and commercial fertilizers. Plant and animal residues contain 0.1 to 0.5 percent sulfur (57). Sulfates may also be brought back to the surface horizons through plant roots. After absorption by the roots, they are assimilated by the plants and are left in the crop residues. An annual application of four tons of manure per acre supplies approximately 15 pounds of sulfur (50). Five hundred pounds of 20 percent superphosphate adds 40 pounds of sulfur, 200 pounds of ammonium sulfate 50 pounds, and 200 pounds of potassium sulfate 36 pounds (21). Mineralization is responsible for the conversion of small amounts of sulfur to the soluble sulfate form each year (29). Fried (21) gives the total sulfur reserve in Indiana soils as 720 pounds per acre.

Crop removal of sulfur varies from 8.4 to 45.9 pounds per acre per year, depending upon the individual crop grown (21). Leaching losses vary from 30 to 50 pounds per acre per year (table II). Stewart estimated a similar loss as from 20 to 803 pounds of sulfur per acre annually in Illinois (50). The loss by leaching in Arkansas was estimated at 6 pounds per acre per year. MacIntire, Willis, and Holding (36) found 13 to 64 pounds of sulfur in drainage

water from lysimeters receiving various amounts of calcium and magnesium fertilizers. Lyon and Bizzell (10), in lysimeter studies showed that, when the sulfur in crops was added to that in the drainage water, the sulfur losses from the planted and unplanted soils did not differ greatly. They found that when they allowed for the sulfur added in manure (15.5 pounds per acre per year), the net annual loss of sulfur, where rotation of crops was practiced and manure used, varied from 16 to 28.4 pounds per acre per year. Shedd showed that virgin soils in Kentucky generally had a higher content of sulfur than cropped soils (table III). Erosion, which removes large quantities of organic matter rich in sulfur from the topsoil, takes an average of 6 pounds per acre per year, according to Lipman and Conybeare (32).

Most of the sulfur in soils comes from the organic matter (29). Sulfur oxidizes more rapidly in soils receiving green manure or stable manure than in untreated soils poor in organic matter, according to Waksman (57). Increased microbiological activity and sulfonation result. Sulfur reserves in humid region soils occur chiefly as organic residues from which sulfates are generated (49). Organic matter, by the action of heterotrophic bacteria, fungi, or actinomycetes, is first converted into a sulfur-bearing fraction (57). This sulfur-bearing fraction is either assimilated by microorganisms or decomposed by autotrophic

TABLE III

SULFUR AND PHOSPHORUS CONTENTS OF CERTAIN
VIRGIN AND CULTIVATED SOILS OF KENTUCKY (48)

Geologic Region	Virgin		Cultivated		% Loss Due to Cultivation	#P
	#S	#P	#S	#P		
Eastern Coal Fields	368	964	220	886	40	8
St. Louis -- Chester	1080	680	480	520	56	24
Cincinnati	---	---	---	---	---	---
Western Coal Fields	353	787	313	720	11	9
Keokuk-Waverly	213	460	167	387	22	16
Quaternary	230	760	160	760	30	0
Trenton	587	5,860	560	7,240	5	24 (gain)
Oevonian	220	320	180	320	18	0
Silurian	430	800	370	770	14	4
River Alluvial	700	1,290	450	1,390	36	8 (gain)

bacteria to elemental sulfur, which is further oxidized to sulfuric acid.

Until recent years sulfur in rain and air was given most attention as a source of replenishing our sulfur resources, but now organic matter and fertilizers are more often considered. In 1923 Erdman (16) stated that, due to annual leaching of high amounts of sulfate, a permanent farming program must add sulfur in some form. He suggested that additions may be accomplished by using manure, gypsum, or acid phosphate. Swanson and Miller (51) mentioned that the supply of sulfur was closely related to the supply of organic matter. They further stated that the addition of organic matter to a certain point increased sulfonation and that the loss of sulfur because of cultivation approximately paralleled that of the organic matter loss. In 1922 Erdman (15) concluded that under actual farm conditions the sulfur in annual rainfall was not sufficient to overbalance the loss by drainage and crop removal.

Starkey (49) concluded that much of the sulfur in soils was in organic compounds from which the sulfur was released by microbiological attack. He further stated that the persistence of sulfur in soils of humid areas was due primarily to the presence of organic compounds of sulfur.

Ames and Boltz (5), in Ohio, found that the sulfur content was associated with the amount of organic matter in the soil.

According to Hart and Peterson (24), the original Wolff ash analysis methods for determining plant sulfur, first thought adequate, were found to be low due to volatilization during ignition. In table IV, alfalfa hay, by the old method, contained 0.170 percent sulfur, but by the newer Osborne peroxide method it contained 0.287 percent sulfur. An even wider variation, from 0.034 percent to 0.341 percent, was shown for soybeans.

A new interest in sulfur, created about 1910, in part because plants were found to contain considerably more than originally thought, led to additional soil sulfur tests. Shedd (48), in Kentucky, compared the average number of pounds per acre of sulfur and phosphorus in virgin and cultivated soils of the geologic areas of Kentucky (table III). He found the sulfur in virgin soils to range from 213 to 1080 pounds per acre and in cultivated soils from 160 to 560 pounds per acre. This again suggests that most of the sulfur is contained in the organic matter of the soil. Shedd reported that the loss of sulfur due to cultivation ranged from 5 to 56 percent of the total amount present. Swanson and Miller (51) also stated that the greater part of sulfur in most soils occurred in complex organic compounds. They further stated that if the relative soil

TABLE IV

COMPARISON OF OLD ASH METHOD
FOR SULFUR IN PLANT ANALYSIS
WITH NEW METHOD (24)

Crop	%S (New)	%S (Old)
Alfalfa Hay	.287	.170
Red Clover	.164	.089
Barley	.153	.024
Rape Tops	.988	.453
Soybeans	.341	.034

supply of sulfur was not larger than that of some other essential elements, notably phosphorus, sulfur might become a limiting factor in crop production. These workers gave a comparison of the percentage of sulfur in two pairs of soil samples from Russell and Greenwood counties of Kansas (table V), concluding that, whether or not sulfur was a limiting element in production of crops on Kansas soils, it was apparent that the supply of this essential element was closely related to the supply of organic matter.

One of the most complete analyses of the sulfur problem was made in Illinois, where, in the 1920's, the sulfur content was reported along with the nitrogen, phosphorus, and potassium content of representative samples in county soil survey bulletins of the University of Illinois Agricultural Experiment Station. The Peoria County Bulletin (1921) (26) gives the cycle of transformation of sulfur in nature, commonly known as the "sulfur cycle". Sulfur thus becomes largely self-renewing, in spite of considerable loss by leaching. The main idea here, however, as well as in practically every sulfur survey in the literature, is that, under circumstances where the natural stock of sulfur is not so high and where the amount returned through rainfall is small, sulfur soon becomes a limiting element in crop production.

TABLE V

PERCENT SULFUR IN TWO PAIRS OF SOIL SAMPLES
FROM RUSSELL AND GREENWOOD COUNTIES
OF KANSAS (51)

Soil Number		%S		% Loss
Virgin	Cropped	Virgin	Cropped	
1031	1032	0.044	0.027	38
1037	1036	0.062	0.036	41

The sulfur content of representative Illinois soils is given in Illinois Soil Report #20 (1921) (27) (table VI). Four main groups are included, viz. the upland prairie soils, upland timber soils, terrace soils, and swamp and bottom-land soils. The total sulfur and the total nitrogen content are closely correlated. Figures for sulfur and nitrogen content of Piatt County soils again show the close relationship between the amount of sulfur and the amount of nitrogen (table VII) (25).

In 1936 the Illinois annual report stated that an investigation of the sulfur content of soils in relation to organic matter content indicated the strong probability that the portion of sulfur which was retained against leaching was combined largely with the soil organic matter (28). Figure 1 shows in graphic form the organic carbon and the sulfur content of the upland surface soils of twenty-eight counties widely distributed throughout Illinois. The sulfur/carbon ratio is shown to be about 1/50 in soils containing up to about 40,000 pounds of organic carbon in 2,000,000 pounds of soil and to become wider in certain soils which are richer in organic matter. This correlation implies that sulfur, as well as carbon, is chiefly combined with the organic matter of the soil.

Eaton (14) showed the phosphorus, sulfur, and organic matter contents of soils in graphic form for

TABLE VI

TOTAL NITROGEN AND TOTAL SULFUR IN TYPICAL ILLINOIS SOILS (27)

Soil Type Number	Soil Type	Physiographic Position	Vegetation	Total N (Pounds)	Total S (Pounds)
20	Black Clay Loam	Upland	Prairie	7760	1620
25	Black Silt Loam	Upland	Prairie	9340	1780
60	Brown Sandy Loam	Upland	Prairie	2390	580
34	Yellow-gray Silt Loam	Upland	Timber	3910	700
35	Yellow Silt Loam	Upland	Timber	2320	560
64	Yellow-gray Silt Loam	Upland	Timber	1440	380
64	Yellow-gray Silt Loam	Terrace	Unknown	2160	640
20, 1420	Black Clay Loam	Terrace	Unknown	7240	1360
54	Mixed Loam	Bottom	Unknown	5170	810
25	Black Silt Loam	Bottom	Unknown	13960	2860
61	Deep Peat	Bottom	Unknown	22650	3250

TABLE VII

NITROGEN AND SULFUR CONTENT OF PIATT COUNTY (ILLINOIS) SOILS (25)

Soil Type Number	Soil Type	Total N (Pounds)*	Total S (Pounds)*
36	Light Brown Silt Loam	4,230	670
41	Brown Silt Loam	4,710	700
66	Black Clay Loam on Drab Clay	6,940	1,050
64	Black Clay Loam on Calcareous Drift	6,310	910
18	Brownish Yellow-Gray Silt Loam	2,100	520
17	Brownish Yellow-Gray Silt Loam on Compact Medium Plastic Clay	2,230	440
134	Brownish Yellow-Gray Silt Loam Over Sand or Gravel	2,270	420

*Average Pounds Per Two Million Pounds of Soil -- 0 to 6 2/3 Inches

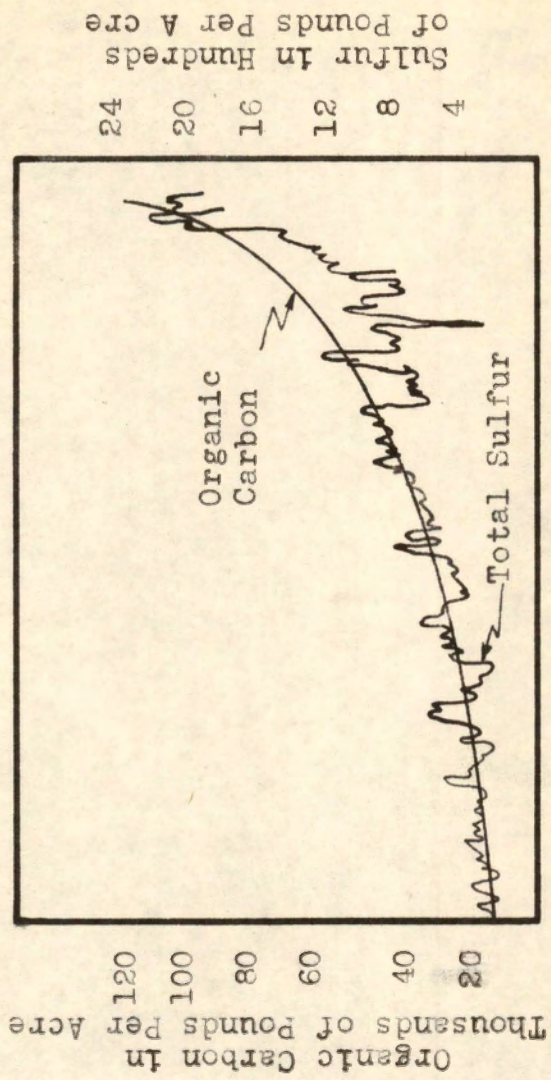


Figure 1
Relative Amounts of Sulfur and
Organic Carbon in Illinois
Surface Soils (28)

Alabama, Maryland, Oklahoma, the Central States, and Chicago (figure 2). Here again was shown a tendency for the total sulfur content to follow closely the total organic matter content of the soil.

In recent years even more precise investigations of the relationship of sulfur to organic matter content of the soil have been made by Evans and Rost (18) of Minnesota (1945) and Madanov (38) of Russia (1946). Evans and Rost, in view of so many variations in the literature figures on sulfate sulfur and atmospheric sulfur, made an analysis of the total organic matter, humus sulfur, sulfate sulfur, and total sulfur of typical chernozems, black prairie, and podzol soils of Minnesota. By analyzing representative figures (table VIII), these authors concluded that the nitrogen to organic sulfur ratios of chernozems and black prairie soils varied only within narrow limits, but that this ratio in podzols had a wider range. A direct relationship between the carbon and nitrogen and organic sulfur content of Minnesota soils was shown. However, Evans and Rost (18) reported that their data were not in general agreement with Vinokurov, possibly due to different methods of leaching. Vinokurov (54) claimed that the amounts of organic sulfur were insignificant. Figures showed the

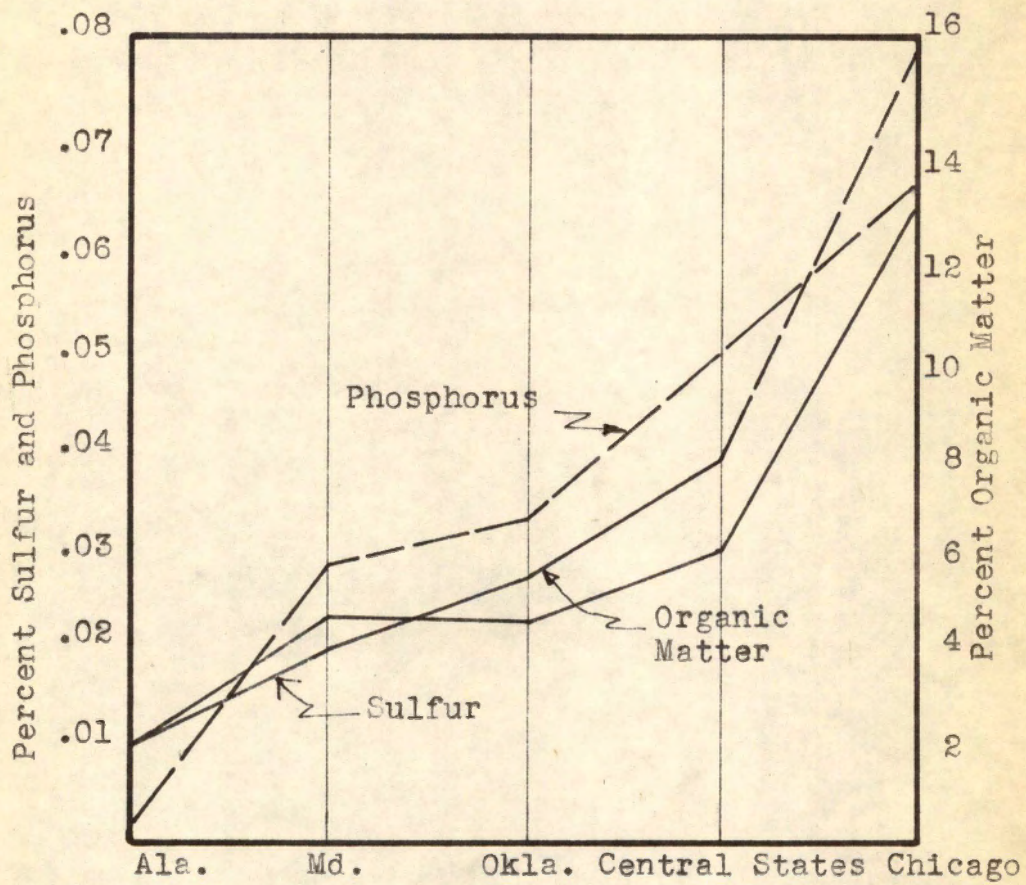


Figure 2
 Sulfur, Phosphorus, and
 Organic Matter Contents
 of Five Groups of Soil
 (14)

TABLE VIII

SULFUR, NITROGEN, AND ORGANIC MATTER RELATIONS OF CERTAIN MINNESOTA SOILS (18)

Soil Classification	C/N	C/Organic S	N/Organic S	N/Humus S	SO ₄ ²⁻ NonSO ₄ ²⁻	% Organic		
						Inorganic	Total	
Average Chernozem	11.4	99.1	8.7	546	2.8	23.9	73.3	11.9
Black Prairie	11.8	103.1	8.7	46.6	4.9	24.4	71.0	13.4
Northeastern Podzols	15.1	265.8	17.6	38.2	7.9	41.6	49.5	22.7
Northcentral Podzols	11.8	204	17.2	69.0	6.8	48.8	45.4	11.3

greatest amount for Russian soils as 23 parts per million for a solonetz, but, even in Minnesota, according to Evans and Rost, for podzols with low organic sulfur, this was 20 percent of the total sulfur.

Madanov (38), in 1946, made a similar study of Russian soils. His aim was to study the protein part of humus as to its saturation by sulfur. Samples of chernozem and chestnut soils were chosen and analyzed for total nitrogen, and organic and mineral forms of sulfur. It was shown (table IX) that the content of organic sulfur in the A, A₁, and B horizons closely paralleled the content of total nitrogen and, consequently, was compounded with the proteins of the soil. Madanov differed from Vinokurov but came nearer to agreement with Evans and Rost, who gave the organic sulfur minimum in chernozems and black prairie soils as 64 percent of the total sulfur (table X). He stated that in chernozems rich in humus, the organic sulfur constituted 70 to 80 percent of the total amount of sulfur, and that in soils poor in humus nearly equal amounts of organic and mineral sulfur made up the soil's total content of sulfur.

TABLE IX

ORGANIC AND MINERAL SULFUR CONTENT AND HUMUS
CONTENT OF FOUR CHERNOZEM PROFILES (38)

Soil Name	Soil No.	Horizon	% Humus	Organic S ₀₃ In 100 g. Soil	% from Humus	% Mineral S ₀₃	% Total S ₀₃	Organic S		Mineral S	Total S
								Total S	Mineral S		
First Type Chernozem	51	A	15.45	.1817	1.17	.0404	.2221	82	18	100	
		A1	13.01	.1625	1.24	.0404	.2029	80	20	100	
		AB	11.80	.1543	1.30	.0411	.1954	79	21	100	
		B1	1.15	.0281	2.44	.0445	.0726	39	61	100	
Second Type Chernozem	47	A	10.73	.1564	1.45	.0308	.1872	83	17	100	
		A1	7.70	.1042	1.35	.0390	.1430	73	27	100	
		AB	3.33	.0583	1.75	.0425	.1008	57	43	100	
		B1	0.87	.0226	2.59	.0425	.0651	35	65	100	
Second Type Chernozem	4	A1	5.44	.0528	0.96	.0397	.0925	57	43	100	
		B1	4.15	.0392	0.94	.0404	.0796	50	50	100	
		B	2.47	.0260	1.05	.0452	.0712	36	64	100	
		C	1.42	.0157	1.10	—	—	—	—	—	100
Second Type Chernozem	9	A2	0.46	.0248	1.04	.0541	.0589	8	92	100	
		B1	1.75	.0315	1.80	.0219	.0534	59	41	100	
		B2	0.71	.0233	3.28	.0220	.0453	52	48	100	
		C	0.28	.0082	2.92	.0220	.0302	27	73	100	
			0.00	—	—	.0304	—	—	100		

TABLE X

ORGANIC MATTER, CARBON, NITROGEN, AND SULFUR CONTENTS
OF CERTAIN MINNESOTA SOILS (18)

Soil Classification	% Organic Matter		% Carbon		% Nitrogen		Sulfur (ppm)		
	Total	Humus	Sulfate	NonSulfate	Total	Sulfate	NonSulfate	Humus	
Average Chernozem	4.316	3.583	.314	.468	360	14	115	58	
Average Black Prairie	3.769	3.207	.270	440	309	20	110	59	
Podzols Northeastern	1.312	1.329	.088	101	50	8	42	23	
Podzols Northcentral	0.824	0.819	.069	88	40	6	43	10	

MATERIALS AND METHODS

In this study samples of representative soil types from the major physiographic regions of Tennessee were chosen. Each sample represented a composite of several sub-samples taken from the identified area. Table XI gives certain information about the 24 Tennessee surface soil samples studied.

A rapid and accurate method was desired for the determination of sulfur content of soils. The first step was a complete oxidation of the sulfur contained in the organic matter of the soil. Two wet digestion procedures were tried, the nitric acid-perchloric acid method of Evans and St. John (19) and the hydrogen peroxide method, originally used by W. O. Robinson (46) in the determination of the total organic matter content of soils. A modification of the former method for testing for sulfur in feeds was found to be time-consuming. Difficulties with this method included: (1) a minimum of three days required to run one series of samples, (2) the necessity of using care in handling the hot perchloric acid, (3) excessively large amounts of sodium hydroxide required for neutralization, (4) discrepant results in sulfur content due to interference by iron and aluminum, even after their elimination by precipitation with ammonium hydroxide, (5) the formation of gels which were difficult to filter, even using a 10-cm. Buchner funnel with suction, and

TABLE XI

CERTAIN CHARACTERISTICS OF 24 TENNESSEE SURFACE SOIL SAMPLES

Sample Number	Soil Series	Area	Physio-graphic Position	Parent Rock	Color		Major Profile Number
					Surface	Subsoil	
4	Paden	West	Terrace	Alluvium	Brown Gray	Yellow Mottled	3
10	Dewey	East	Upland	Limestone	Gray Brown	Red	4
15	Fullerton	East	Upland	Limestone	Brown Gray	Yellow Red	4
17	Sequoia	East	Upland	Shale	Brown Gray	Red Yellow	4-3
18	Decatur	East	Upland	Limestone	Brown	Dark Red	4
21	Emory	East	Colluvial	Limestone	Brown	Brown	4
28	Loring	West	Upland	Loess	Brown Gray	Brown Yellow	4-3
40	Obion	West	Bottom	Alluvium	Gray	Gray	3
49	Memphis	West	Upland	Loess	Brown Gray	Brown	4
51	Loring	West	Upland	Loess	Brown Gray	Brown Yellow	4-3
53	Grenada	West	Upland	Loess	Brown Gray	Yellow Mottled	3
56	Grenada	West	Upland	Loess	Brown Gray	Yellow Mottled	3
60	Hagerstown	Middle	Upland	Limestone	Brown	Dark Red	4
62	Hartsells	East	Upland	Sandstone	Brown Gray	Brown Yellow	4
63	Hartsells	East	Upland	Sandstone	Brown Gray	Brown Yellow	4
64	Hartsells	East	Upland	Sandstone	Brown Gray	Brown Yellow	4
66	Cumberland	East	Terrace	Limestone	Brown	Dark Red	4
67	Tyler	East	Terrace	Sandstone	Gray	Mottled	2
68	Elk	Middle	Terrace	Alluvium	Brown	Brown	4
74	Baxter	Middle	Upland	Limestone	Brown Gray	Brown to Yellow	4
78	Mercer	Middle	Upland	Limestone	Brown Gray	Gray Yellow	4
80	Godwin	Middle	Colluvial	Limestone	Dark Brown	Brown	4
82	Bodine	Middle	Upland	Limestone	Gray	Yellow	4(6)
85	Dickson	Middle	Upland	Limestone	Brown Gray	Yellow	3

(6) inconsistent results in the percentage of sulfur. As a result, this method was discarded.

W. O. Robinson (46) found the hydrogen peroxide digestion suitable for quantitative work in organic matter determinations. This method, he stated, offered an advantage in rapidity of organic matter determination over the combustion method when a large number of analyses were to be made. Evans and Rost (18) used hydrogen peroxide for the determination of organic sulfur, after removing the inorganic fraction by extraction with hydrochloric acid. In the opinion of these writers, the sulfur fraction of the organic matter was the easiest to oxidize. Madanov (38), in 1946, determined organic sulfur by oxidation with hydrogen peroxide.

The nitric acid-hydrochloric acid digestion of Marsden and Pollard (39) required many evaporations to dryness and the use of two reagents. According to Shaw and MacIntire (47), there was still no assurance that complete oxidation of native sulfur materials was effected by this method.

The hydrogen peroxide method seemed most satisfactory for the purposes desired. Advantages included the use of only one reagent, since organic and inorganic sulfur were being determined together, and a minimum time of an hour required for complete oxidation.

Three titrimetric methods subsequent to hydrogen peroxide oxidation were given considerable time and study due to their ease of performance and rapidity as compared to gravimetric procedures. The THQ (tetrahydroxyquinone) indicator method, suggested by W. H. Betz and Company (21), gave a difficultly reproducible end point and was therefore discarded after several variations in procedure were tried.

The Marsden and Pollard benzidine hydrochloride procedure (39) provides for the oxidation of benzidine sulfate by potassium permanganate. It was rejected due to the time-consuming factor, the necessity of the use of several reagents containing minute amounts of sulfur, and the inconsistent results. Thomson (53) reported it as least accurate of all sulfur methods.

The Belcher and Goelbert method, with slight modifications, was tried as a relatively rapid titrimetric oxidation-reduction procedure. After precipitation of barium sulfate, tenth-normal potassium dichromate is added to precipitate barium chromate. The barium chromate precipitate is dissolved in acid and titrated with ferrous ammonium sulfate. Discrepant results were obtained due to the inclusion of iron in the barium chromate precipitate. This caused an indistinct end point. The procedure was

eliminated because of its lengthiness and the difficulty of duplication of results.

The quickest and most accurate method proved to be the standard gravimetric procedure in which the sulfur is precipitated as barium sulfate, ignited in a muffle furnace, and weighed (8).

A combination of the hydrogen peroxide digestion and the gravimetric barium chloride precipitation methods was found to have the following four major advantages over any others considered for a large number of samples:

(1) speed, (2) simplicity, (3) use of a limited number of reagents, and (4) reasonable accuracy.

The official A. O. A. C. Kjeldahl method (18) was used in the determination of total nitrogen content of the 24 soil samples tested. The wet oxidation method cited in U. S. D. A. Circular #757 (43) was used for the organic matter determination.

RESULTS AND DISCUSSION

Table XII gives the amount of barium sulfate precipitated from each of the 24 samples in each of the several determinations; also, the average values are given, together with the average percentage of sulfur for each sample. Blanks were used to account for any sulfur in the hydrogen peroxide. The range in sulfur content of the 24 samples is 0.007 to 0.030 percent. The average value is 0.015 percent. The very low value of 0.007 percent sulfur for the Decatur soil may be due to incomplete oxidation of the sulfur in the organic matter due to a high soil manganese content. The range in percent sulfur for mineral soils of the United States is given as 0.008 to 0.20 by Lyon and Buckman (33).

Table XIII gives the percent sulfur, percent nitrogen, percent organic matter by the Kjeldahl (NX20) method, and the percent organic matter by the wet oxidation method. The range in nitrogen content for mineral soils of the United States is 0.02 percent to 0.50 percent (33) compared to the range for the 24 Tennessee samples of 0.043 percent to 0.186 percent. The average for these 24 samples is 0.086 percent. Waksman gives a nitrogen value of 0.048 percent for Colbert clay (0 to 30 cm.), a soil typical of this region of the United States. Lyon and

TABLE XII

SULFUR CONTENT OF 24
TENNESSEE SURFACE SOIL SAMPLES

Sample Number	Milligrams of BaSO ₄							Ave.	%S*
	Determination Number								
	1	2	3	4	5	6	7		
4	5.8	4.9	5.4	5.5				5.4	.015
10	8.4	7.6	6.9	6.6	6.0	7.1	6.8	7.1	.019
15	4.7	6.1	4.5	4.1				4.8	.013
17	4.6	5.5	5.5	5.1				5.2	.014
18	2.5	2.1	2.4	2.9				2.5	.007
21	4.0	4.2	2.7	2.7	9.1	8.3	9.8	5.8	.016
28	4.7	6.4	5.6	5.1				5.4	.015
40	5.2	6.0	7.5	7.8	7.3	7.1	6.3	6.7	.018
49	0.6**	2.8	3.8	3.5	4.7	4.5	2.7	3.7	.010
51	3.7	5.0	3.5	3.7				4.0	.011
53	5.3	4.5	6.5	3.6	4.8	5.5	5.7	5.1	.014
56	3.7	5.0	4.4	3.4				4.1	.011
60	7.2	—	6.9	6.0				6.7	.018
62	6.6	6.7	6.3	4.3				6.0	.016
63	7.6	4.3	6.7	3.3	4.6	5.2	7.6	5.6	.015
64	7.2	4.1	7.8	5.0	6.1	5.4	6.5	6.0	.016
66	9.2	4.6	9.3	5.5	6.0	7.6	8.9	5.1	.020
67	14.6**	3.7	5.1	5.2				4.7	.013
68	7.7	3.9	1.9	7.0	9.3	5.0		5.8	.016
74	5.4	3.7	4.0	2.5	3.6	3.9	.03**	3.8	.011
78	6.3	4.4	3.3	3.6	4.7	4.8	5.8	4.7	.013
80	12.4	11.8	9.3	10.9	6.7**	1.0	10.1	11.1	.030
82	5.1	3.7	4.0	3.1				4.0	.011
85	5.5	2.7	6.1	3.5				4.5	.012

$$*\%S = \frac{\text{Milligrams BaSO}_4 \times .01373}{5}$$

**Value not included in average

TABLE XIII

CONTENT OF SULFUR, NITROGEN, AND ORGANIC
MATTER IN 24 TENNESSEE
SURFACE SOIL SAMPLES

Soil Number	Soil Series	%S	%N	%O.M.* (NK ₂ O)	%O.M.* (Wet Oxidation)
4	Paden	.015	.058	1.2	1.2
10	Dewey	.019	.096	1.9	1.9
15	Fullerton	.013	.048	1.0	1.2
17	Sequoia	.014	.073	1.5	1.4
18	Decatur	.007	.082	1.6	1.8
21	Emory	.016	.100	2.0	1.6
28	Loring	.015	.067	1.3	1.2
40	Obion	.018	.145	2.9	2.6
49	Memphis	.010	.070	1.4	1.5
51	Loring	.011	.098	2.0	1.7
53	Grenada	.014	.100	2.0	2.4
56	Grenada	.011	.067	1.3	1.0
60	Hagerstown	.018	.067	1.3	1.2
62	Hartsells	.016	.060	1.2	1.7
63	Hartsells	.015	.075	1.5	2.6
64	Hartsells	.016	.089	1.8	2.3
66	Cumberland	.020	.082	1.6	1.6
67	Tyler	.013	.126	2.5	2.9
68	Elk	.016	.119	2.4	1.9
74	Baxter	.011	.043	0.9	0.7
78	Mercer	.013	.081	1.6	1.6
80	Godwin	.030	.186	3.7	3.7
82	Bodine	.011	.059	1.2	1.7
85	Dickson	.012	.062	1.2	1.8
Ave.		.015	.086	1.7	1.8

*O.M. - Organic Matter

Buckman (33) give percent nitrogen values of 0.048 for Cecil soils of North Carolina, 0.039 for Norfolk soils of North Carolina, and 0.120 for Kentucky soils. The values obtained in this study compare favorably to these values in the literature.

In table XIV the 24 Tennessee soil samples are grouped according to geographic regions. The nitrogen-to-sulfur ratio for the 24 soil samples studied and the average nitrogen-to-sulfur ratio for each region of the state are also given. The average nitrogen-to-sulfur ratio for the state is 5.7, excluding the Decatur sample. The nitrogen-to-sulfur ratios for East, Middle, and West Tennessee soils are 5.4, 5.4, and 6.5, respectively. (The Decatur sample was not included in the calculation of the East Tennessee nitrogen-to-sulfur ratio.) This suggests a possible tendency for less sulfur in the organic matter of West Tennessee soils, but the difference shown by this limited number of soil samples is probably not significant.

The range in percent sulfur, comparatively narrow for Tennessee, corresponds closely to the narrow range in percent nitrogen; thus, the average low sulfur content of Tennessee soils has a close relationship to the typical low nitrogen content of soils of this section of the United States. A tendency for the sulfur content to follow

TABLE XIV

PERCENT SULFUR, PERCENT NITROGEN, AND
NITROGEN-TO-SULFUR RATIOS OF 24
TENNESSEE SURFACE SOIL SAMPLES

<u>Location</u>				
<u>East Tennessee</u>				
Sample Number	Soil Series	%S	%N	N/S
10	Dewey	.019	.096	5.0
15	Fullerton	.013	.048	3.7
17	Sequoia	.014	.073	5.2
18	Decatur*	.007	.082	11.7*
21	Emory	.016	.100	6.2
66	Cumberland	.020	.082	4.1
67	Tyler	.013	.126	9.7
Ave.		.015	.087	5.6
<u>Cumberland Plateau</u>				
Sample Number				
62	Hartsells	.016	.060	3.8
63	Hartsells	.015	.075	5.0
64	Hartsells	.016	.089	5.6
Ave.		.016	.075	4.8
<u>East Tenn. Ave.</u>				
		.015	.083	5.4
<u>Highland Rim</u>				
Sample Number				
74	Baxter	.011	.043	3.9
82	Bodine	.011	.059	5.4
85	Dickson	.012	.062	5.2
Ave.		.011	.055	4.8
<u>Outer Basin</u>				
Sample Number				
68	Elk	.016	.119	7.4
80	Godwin	.030	.186	6.2
Ave.		.023	.152	6.8

-continued

TABLE XIV

PERCENT SULFUR, PERCENT NITROGEN, AND
NITROGEN-TO-SULFUR RATIOS OF 24
TENNESSEE SURFACE SOIL SAMPLES

Location	Soil Series	%S	%N	N/S
Inner Basin				
<u>Sample Number</u>				
60	Hagerstown	.018	.067	3.7
73	Mercer	.013	.081	6.2
Ave.		.016	.074	5.0
Middle Tenn. Ave.		.016	.088	5.4
West Tennessee				
<u>Sample Number</u>				
4	Paden	.015	.058	3.9
28	Loring	.015	.067	4.5
40	Obion	.018	.145	8.1
49	Memphis	.010	.070	7.0
51	Loring	.011	.098	8.9
53	Grenada	.014	.100	7.1
56	Grenada	.011	.067	6.1
West Tenn. Ave.		.013	.086	6.5

*Not included in averages

the nitrogen content is shown in figure 3. In this graph the percent sulfur is plotted as a function of the percent nitrogen. The regression coefficient and the correlation coefficient were calculated according to the method of Snedecor (22). The 0.64 correlation coefficient is highly significant. The formula for the regression line is $y = .088 x + .0073$. Several apparent contradictions to the above correlation are exceptions rather than the general rule.

In figure 3 the relative amounts of sulfur and nitrogen in the 24 Tennessee surface soil samples are given in graphical form with the samples arranged according to increasing nitrogen content. The percentage of sulfur, in general, increases with an increase in the percentage of nitrogen for Tennessee soils, just as for Illinois soils the percentage of sulfur was shown to increase with an increase in the percentage of organic carbon (figure 3).

Maximum variation between percentage of organic matter of individual samples determined by the Kjeldahl (NX20) and wet oxidation methods was 0.6 with one exception (table XIII). The exception was a sample from the Cumberland Plateau for which the difference was 1.1 (from 1.5 to 2.6). The three Cumberland Plateau samples of the same soil series (Hartsells) showed organic matter

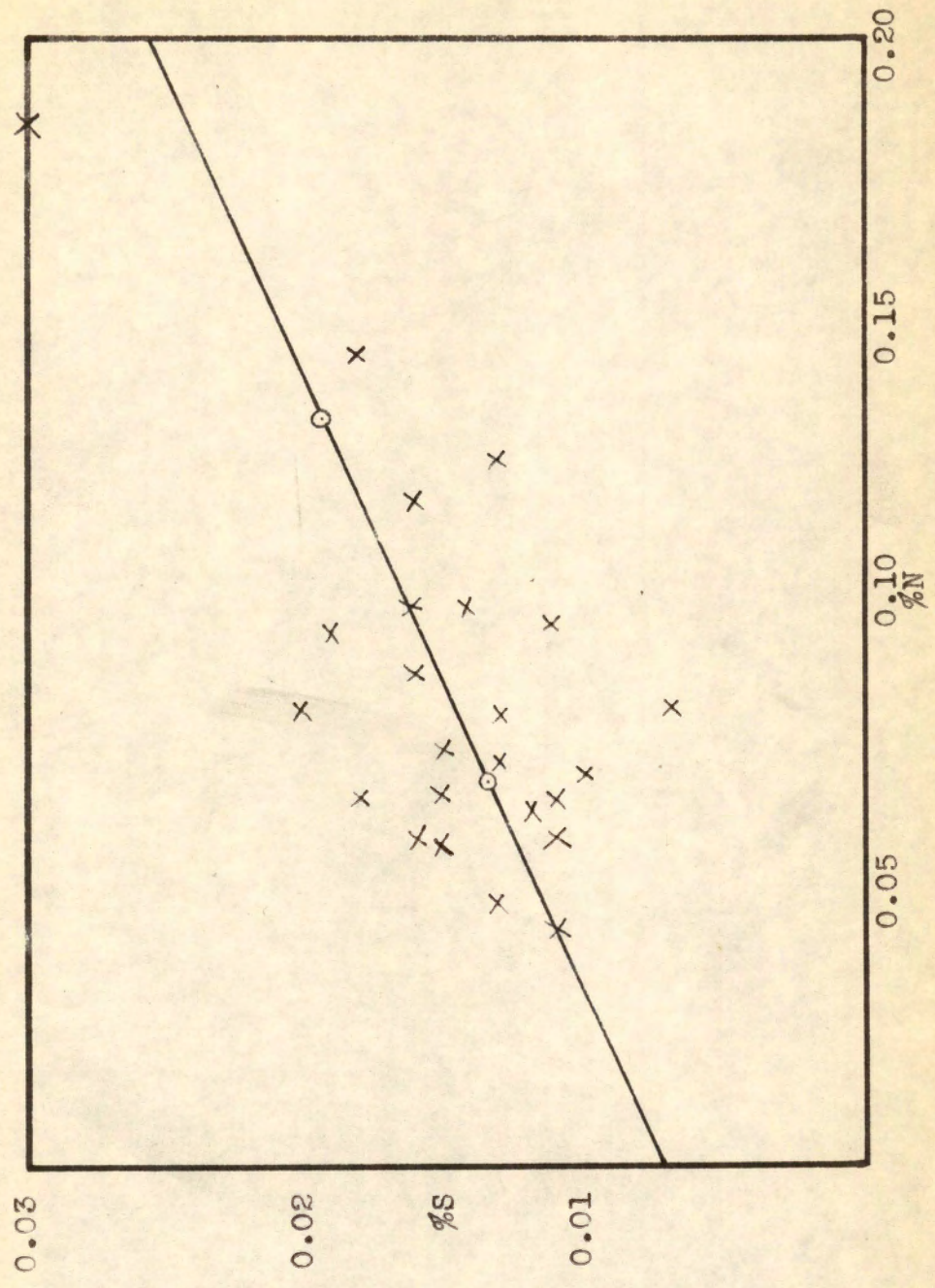


Figure 3
Percent Sulfur as a Function of Percent Nitrogen

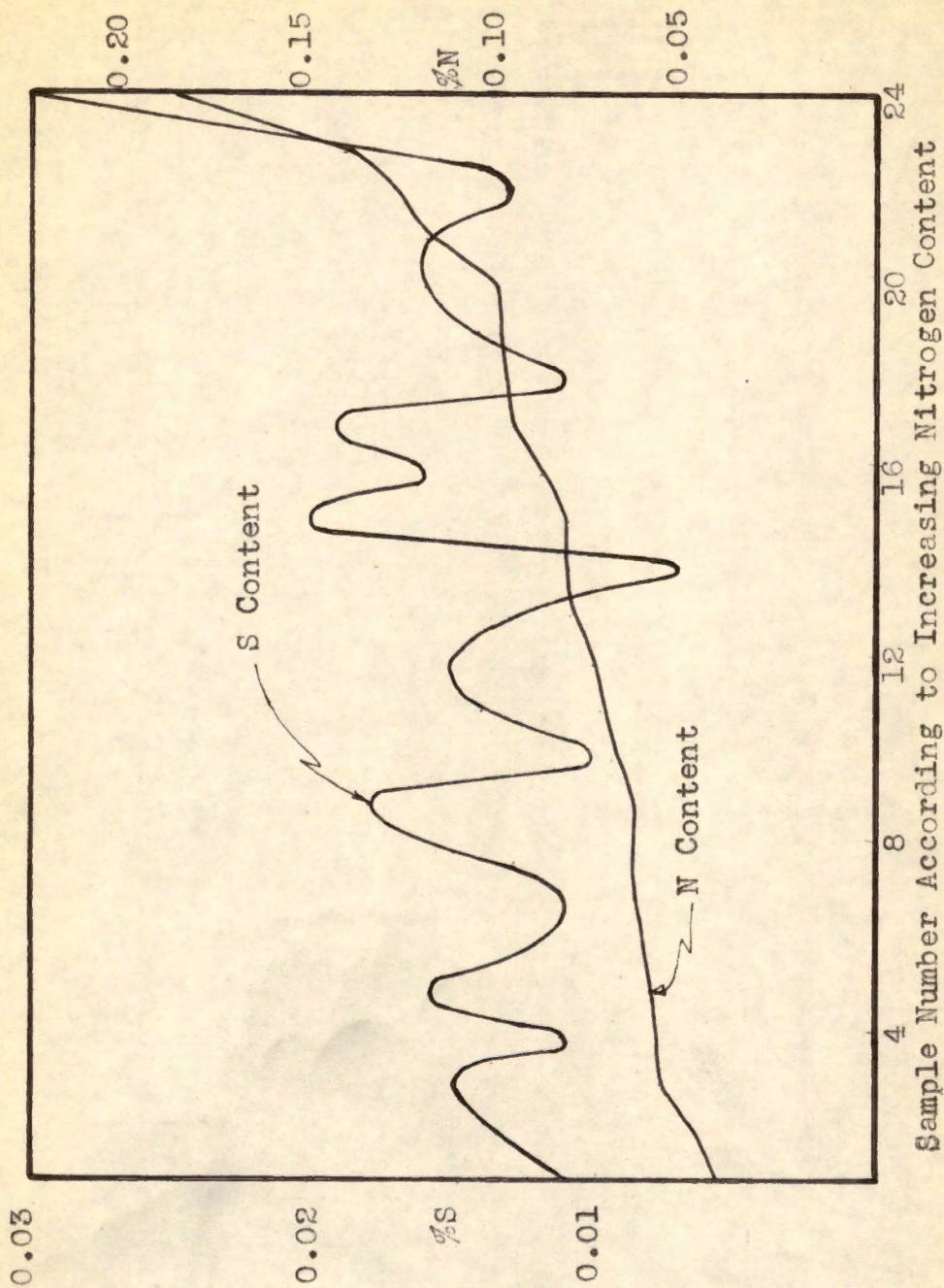


Figure 4

Relative Amounts of Sulfur and Nitrogen in
24 Tennessee Surface Soil Samples

percentages of 1.2, 1.5, and 1.8 by the Kjeldahl (NX₂₀) method and 1.7, 2.6, and 2.3 by the wet oxidation method, yet they showed almost identical total sulfur values of 0.016, 0.015, and 0.016 percent respectively (table XIII). The wider-than-normal variation in organic matter content by the two different methods may be attributed to the fact that Cumberland Plateau soils have a generally higher amount of raw organic matter. Thus, the usual factor of "twenty" required for the conversion of humus nitrogen content to organic matter content is too small. Waksman (53) states that the nitrogen determination as a basis for the determination of organic matter content of soils involves not only the use of an arbitrary factor, which may be considerably different for different humus formations, but also assumes a constant relationship between the carbon and nitrogen content of the humus. Concerning the wet oxidation procedures, he states that they deserve consideration since their results check well with those obtained by dry combustion, even for soils very low in organic matter.

No attempt will be made at this time to suggest any specific area in Tennessee where a shortage of sulfur actually exists. However, in view of the generally low sulfur values for soils of the state and the benefits noted by Volk and Tidmore (56) in cotton fertilization with

gypsum in Alabama, it is suggested that fertilization with sulfur in Tennessee deserves further study, particularly in areas of limited industrial development and limited fuel consumption.

SUMMARY

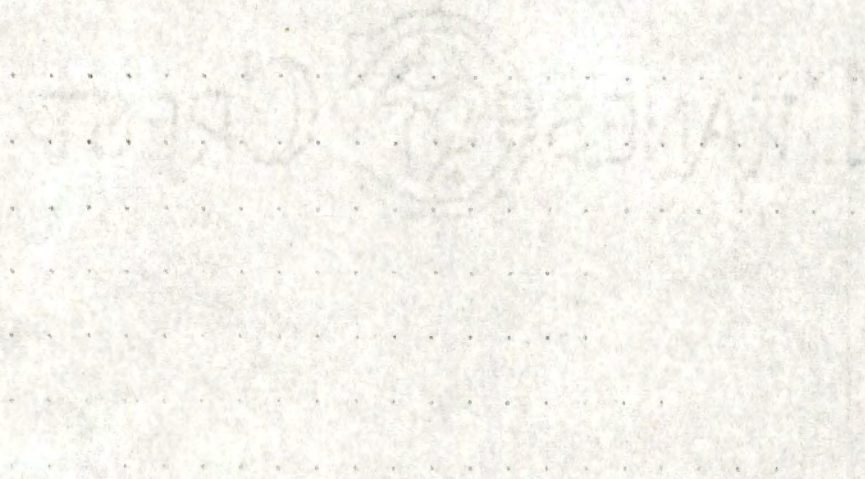
A review of the literature pertaining to soil sulfur additions, losses, and effects on plant growth was made. The following conclusions are drawn:

1. A low sulfur content is characteristic of the highly leached, low organic matter soils of the southeast.
2. Crops respond to sulfur fertilization in sulfur-deficient areas.
3. The soil sulfur content and organic matter content are closely correlated.
4. Soil sulfur additions are higher near industrial areas than in rural areas.

The sulfur, nitrogen, and organic matter content of 24 representative Tennessee surface soil samples was determined. These data show:

1. A comparatively low sulfur content for Tennessee soils, ranging from 0.007 to 0.030 percent.
2. A close correlation between the amount of sulfur and the amount of nitrogen in the soils of Tennessee.
3. The need for work on crop responses to sulfur fertilization in thinly populated areas of Tennessee.

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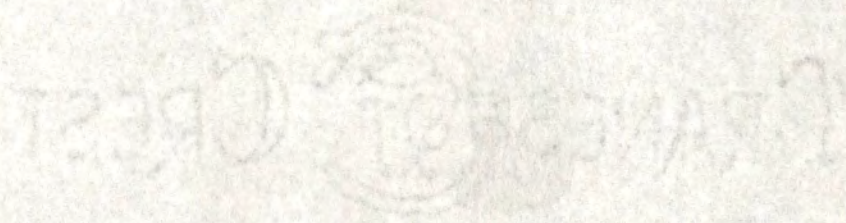
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APPENDIX



PROCEDURE FOR THE DETERMINATION
OF TOTAL S CONTENT OF SOIL:

1. Weigh out a 5-gram sample of soil (ground to pass a 20-mesh sieve) into a 500-ml. Erlenmeyer flask.
2. Add slowly 10 ml. of 30% H_2O_2 (Merck) and place on hot plate.
3. Digest for approximately 15 minutes and then add slowly 10 ml. more of 30% H_2O_2 .
4. Again, after 15 minutes, add slowly 10 ml. of 30% H_2O_2 .
5. Digest for a minimum of one hour, until the supernatant liquid is perfectly clear.
6. Cool and filter through a 10-cm. Buchner funnel, using Whatman #42 filter paper, into a 500 or 1000-ml. suction flask.
7. Wash with distilled water until a volume of 200 ml. is obtained.
8. Transfer filtrate to a 400-ml. beaker.
9. Dilute to 300 ml. with distilled water.
10. Add 2 drops of methyl red indicator.
11. Acidify with 0.1 N. HCl to a point 0.5 ml. beyond the methyl red color change from orange to red.
12. Heat on hot plate to boiling.
13. Precipitate $BaSO_4$ by the addition of 10 ml. of 5% $BaCl_2$.
14. Allow the solution to digest for 5 or 10 minutes on the hot plate.
15. Cool the solution for 4 hours.
16. Filter through a Gooch crucible with an asbestos mat.
17. Wash with distilled H_2O until free of chlorides.
18. Ignite crucible in a muffle to approximately $500^\circ C$ for $\frac{1}{2}$ hr.
19. Weigh on an analytical balance.
20. Calculate as %S by the following formula:
$$\frac{\text{mg. } BaSO_4 \times 0.01373}{5} = \%S$$

Precautions and suggestions:

1. A violent reaction with the evolution of heat shows the presence of MnO_2 or Cr_2O_3 . If less than 0.25% MnO_2 is present it can be destroyed by evaporation with a small excess of oxalic acid before adding the H_2O_2 (1).

2. Run a blank and treat it just like a regular sample.
3. Caution must be used in adding the peroxide to prevent excessive frothing.
4. The samples must not be placed on the hot plate until the reaction has subsided.
5. Do not allow the solution to evaporate to dryness or near dryness, or incorrect results will be obtained.
6. If coarse BaSO_4 crystals are not observed after the four-hour cooling period it is advisable to allow the beaker to stand overnight.
7. The complete procedure should require no more than 12 hours for 24 samples run simultaneously after sufficient proficiency is attained.
8. The Gooch crucibles may be re-used for an indefinite number of times once a good mat is obtained.