AVAILABLE SULFUR IN SOME MANITOBA SOILS

AS ESTIMATED BY PLANT GROWTH

AND CHEMICAL ANALYSES

A Thesis

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ABSTRACT

Measurement of the water soluble sulfate content of several Manitoba soils indicated that most of the soils contained adequate amounts of sulfur. The lowest water soluble sulfate contents encountered were in the soils of the Stockton association. A more detailed study involving 9 sampling sites within the Stockton association showed that these soils are generally much lower in water soluble sulfate and soil sulfur content than other Manitoba soils.

In a greenhouse experiment the yield of rape was significantly increased by sulfur fertilization on 7 of 11 surface soils involved. All those soils that yielded significant responses to sulfur fertilizer contained less than 2.0 p.p.m. water soluble sulfate. Sulfur uptake by rape was significantly correlated with the amount of water soluble sulfate, heat soluble sulfate and sulfate present after mineralization. The soil sulfur, HCl soluble sulfur, and organic matter contents of the soils were not correlated with sulfur uptake.

A second greenhouse experiment determined the critical level of sulfur in rape as .10% total sulfur, and 200 p.p.m. water soluble sulfate sulfur.

Studies of the sulfate adsorption characteristics of Manitoba soils indicated that adsorbed sulfate is not an important sulfur fraction in these soils. Water soluble sulfate should be a good measure of the sulfate that is available to plants.

In a field experiment, consistent but not statistically significant increases in yield of rape seed were obtained by broadcasting 20 to 40 pounds of sulfur fertilizer on a Stockton soil. This soil contained 252 pounds of water soluble sulfate in the upper 48 inches. Most of the

Stockton soils studied contain less than that amount of water soluble sulfate.

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I   INTRODUCTION

Sulfur is an essential plant nutrient. In plants sulfur is an essential component of proteins, and is thought to be associated with the production of chlorophyll, the development of the root system, and nodulation in legumes (20). The occurrence of sulfur deficient soils in several areas of the world has resulted in an increased interest in the soil chemistry of sulfur. Detailed investigations into methods of analysis for plant available sulfur, the nature of the various sulfur fractions, and the adsorption chemistry of the sulfate ion, have been reported in the last two decades.

In North America soil sulfur deficiencies may be encountered on strongly leached, acid soils such as the Podzols of Eastern United States, or the Grey Wooded soils of Alberta. Sulfur deficiencies are not restricted to degraded soils. Some well drained Chernozemic soils in Washington and Oregon have been shown to contain insufficient amounts of sulfur (23). Little is known of the sulfur fraction of Manitoba soils. This study is an attempt at assessing the sulfur status of these soils, determining the nature of this sulfur, and devising a means of estimating the plant available fraction.

Soils that contain large amounts of water soluble sulfate were considered to be sulfur sufficient, and few investigations were made on these soils. Since preliminary analyses indicated that the coarse textured, well drained Chernozemic soils of the Stockton association contained small amounts of water soluble sulfate, a more detailed study was made of these soils. In devising a chemical soil test for plant available sulfate, several different methods were investigated. The sulfur measured by each method was correlated with uptake of sulfur by rape plants grown on these soils in the greenhouse. A second greenhouse experiment involved

the determination of the critical level of total sulfur, and water extract-
able sulfate sulfur in rape plants. Studies were also conducted on the
adsorption of sulfate ions by several representative Manitoba soils. A
field experiment measured the effect of sulfur fertilizers on rape grown
on a Stockton soil.

II   REVIEW OF LITERATURE

Early workers in Soil Science, although recognizing sulfur as
an essential plant nutrient, made few studies of sulfur in soils. There
were several reasons for this apparent dearth of research on sulfur.
Some of these reasons are: early methods of plant analysis underestimated
the sulfur content of plants, thereby underestimating plant requirements
of sulfur; sulfur was added incidentally to many soils as impurities in
lime and phosphorus fertilizers; and, sulfur deficiencies are not gen-
eral and widespread, as are nitrogen deficiencies, but more localized
and specific to certain areas and soils. However, responses to sulfur
fertilizer in many areas of the world, new methods of plant analysis
and the removal of sulfur impurities from phosphorus fertilizers, has
shown workers that supplies of soil sulfur are not always adequate for
maximum plant growth. Consequently an increased interest in the soil
chemistry of sulfur has developed within the past two decades.

A. NATURE OF SULFUR IN SOIL

The total sulfur fraction in soils comprises both organic
and inorganic forms. Organic sulfur, generally estimated as the diff-
erence between total sulfur and inorganic sulfate, accounts for nearly
all the sulfur present in the surface horizons of most soils (18). Sev-
eral workers have estimated amounts of organic sulfur in soils, and re-
lated the amount of organic sulfur to amounts of other soil constituents.
Evans and Rost (15) working with Chernozemic soils in Minnesota, report
organic sulfur contents ranging from 216 to 428 p.p.m. Nelson (32) re-
ports that most of the sulfur of the surface horizons of soils is in
the organic form. He measured the sulfur content of some surface soils

of Mississippi, which varied in texture from sandy loam to clay, and in
pH from 5.2 to 7.4. These soils contained 127 to 564 p.p.m. total sulfur,
of which 64 to 353 p.p.m. was present in the organic form. The soils had
an average C:N:S ratio of 126:10:1, and amounts of organic carbon, total
nitrogen and total sulfur were positively correlated. Work by Harward
et al.(22) shows that the bulk of the sulfur of surface soils is in the
organic fraction. The organic sulfur levels ranged from 77 to 765 p.p.m.
The amounts of organic carbon and organic S were positively correlated.
The average C:N:S ratio was 145:10:1. Lowe (29), working with soils of
Quebec reports that 53 to 90 per cent of the sulfur is organic. His
more recent work on soils of Alberta reports a mean value of 435 p.p.m.
total sulfur in the Ah, and 273 p.p.m. in the Bm of Chemozemic soils.
The mineral horizons of the Grey Wooded soils contained much less total
sulfur than did equivalent horizons in the Chernozemic soils (28).

Little is known about the compounds of the organic sulfur frac-
tion. The sulfur compounds of plants, such as proteins, polypeptides
and amino acids are assumed to be present, but it is not known how long
they persist. Lowe and Delong (30) and others (16,40) suggest that a
considerable amount of the soil sulfur is covalently bound to the poly-
saccharides, or sulfate esters of phenol. Small amounts of amino acids
methionine and cysteine have been detected in hydrolyzates of soil (18).

Most soils contain significant amounts of inorganic sulfur.
In the lower horizons, especially where soils are imperfectly drained,
calcareous or gypsiferous, inorganic sulfates constitute nearly all the
total sulfur. The sulfate may be present in the soil solution as sul-
fate ions, or occur as relatively soluble salts such as gypsum or

$MgSO_4$ (18). This sulfur fraction is readily available to plants, and consequently on many soils, chemical soil tests which employ water or dilute electrolytes as extractants are suitable for measuring plant available sulfur. In other soils, especially those which are strongly acid and contain appreciable amounts of clay and sesquioxides significant amounts of sulfate may be retained by processes of adsorption (14,21,26). A third form of inorganic sulfate is that sulfate which is coprecipitated with $CaCO_3$. Williams and Steinbergs (40) have shown that in calcareous soils of Australia this fraction comprises an important portion of the total sulfur. This soil sulfur fraction, generally extracted with N HCl is thought to be relatively unavailable to plants. Sulfur may also be present as very insoluble forms such as $BaSO_4$ or pyrite, FeS_2 (18,7).

B. MINERALIZATION OF SULFUR

Soil microorganisms convert the organic sulfur of soil to inorganic sulfate by a process similar to the mineralization of organic nitrogen to nitrate. Although one would expect the release of nitrate and sulfate to be in a ratio of their content in the soil organic matter, several studies have shown that this often does not occur. Barrow (3,4) found that some sulfur deficient soils did not release sulfate although nitrate was mineralized. Nelson (32) reports that mineralization of nitrogen and sulfur are related, but that release of sulfate lags behind release of nitrate. The addition of materials of high organic carbon: organic sulfur ratio may result in fixation of sulfate (32). Incubation studies have estimated the amount of sulfate mineralized as 1.2 pounds per acre per month (32), 9.8 pounds in a 4 week period (22), and 24 pounds in a 100 day period (4). These findings indicate the variable

nature of sulfur mineralization. It is difficult to apply results from studies with various soils under laboratory and greenhouse conditions to particular soils under field conditions.

C. SULFUR BALANCE IN SOILS

The amount of plant available sulfate in soils depends upon the relative rates of addition and loss of sulfate. Where losses of sulfate exceed the amounts released or supplied, sulfur deficiencies result.

On imperfectly drained soils, especially under conditions of low rainfall, soluble sulfate, salts of calcium, magnesium and sodium contribute to the supply of sulfate (18). The mineralization of the sulfur of the organic fraction is an important source of sulfate in many soils. Significant amounts of sulfate are added in rainwater. Workers in the southern United States estimate yearly additions of an average of 12.7 pounds sulfur per acre near industrial areas, and 5.4 pounds sulfur per acre in rural areas (24). Yearly additions of a mean of 27 pounds sulfur per acre per year are reported for Indiana (6). In western Australia about 1 pound per acre per year is added in rainwater (18). It has been shown that plants can adsorb SO_2 from the atmosphere (24). Very little of a crop's requirement is realized from this source. Small amounts of sulfate are added in insecticides and as impurities in some fertilizers. The most common sulfur fertilizers are gypsum and ammonium sulfate.

Removal of sulfate from the soil is principally by two processes; crop removal and leaching. Removal by crops has been estimated at forty pounds per acre per year for members of the Brassica family, twenty pounds per acre per year for legumes, and ten pounds per acre per

year for cereals and grasses (6). Loss of sulfate by leaching may be extensive. Studies with lysimeters have shown that as much as 55 pounds per acre per year may be leached from sandy soils (23). Since sulfate adsorption is negligible at pH greater than 6.0 (26,14), sulfate is easily leached from most neutral or alkaline coarse textured soils.

D. SULFATE ADSORPTION

Many soils have the ability to retain sulfate ions by processes of adsorption. Kamprath et al.(26)found that soils have the capacity to adsorb significant amounts of sulfate ions. Greater amounts of sulfate are adsorbed by soils that are strongly acid than are adsorbed by soils that are less acid or neutral. Clay minerals, sesquioxides and organic matter appear to be the soil constituents responsible for the sulfate ad- sorption phenomena. The species of clay mineral is important. Aluminium saturated kaolinitic clays with a 1:1 type lattice are able to adsorb a great deal more sulfate than 2:1 lattice type clay minerals such as montmorillonite. The amount of adsorbed sulfate increases with increasing concentration of sulfate ions in the soil solution. Phosphate ions can replace adsorbed sulfate, and phosphate is adsorbed preferentially to sulfate.

Work by Chao et al.(8,9) at Oregon indicates that a kinetic equilibrium exists between sulfate retained by soil, and the sulfate in solution. These adsorption phenomena can be described by the Freundlich adsorption equation which considers the relationship between the concentra- tion of an adsorbate, and the amount of its adsorption by an adsorbent. The good fit of adsorption of sulfates by soils suggest that there are no adsorption maxima, and therefore no definite anion exchange capacity.

This discounts the role of anion exchange in sulfate adsorption. Sulfate is easily desorbed; as much as 45 per cent of the sulfate adsorbed by soils from soil-sulfate solution suspensions can be removed by one extraction treatment with water. The exchange reactions are rapid; from 87 to 93 per cent of the exchange has taken place after one minute.

Harvard et al.(21) used soil column chromatographic techniques to demonstrate sulfate retention by soils. They report that S^{35} tagged sulfate ions were much less mobile, and hence adsorbed to a greater degree in those soils of low reaction, especially where aluminum saturated clays were present. The destruction of organic matter in these soils resulted in the sulfate adsorption capacity being reduced by one-third to one-half. The removal of iron and aluminum oxides also reduced the amount of sulfate adsorbed. They postulate that the mechanisms of sulfate adsorption are:

1. Anion exchange involving hydrous oxides of iron and aluminum, and the crystal edges of clay as positively charged sites capable of attracting sulfate ions.

2. Retention of sulfate ions by coördination with hydroxy-aluminum complexes.

3. Salt or molecular adsorption, resulting from attraction between the soil colloids and salts of sulfate.

4. Retention by amphoteric organic compounds. That is, at acid pH, positively charged sites are available on organic matter components for the adsorption of sulfate ions.

E. CHEMICAL SOIL TESTS FOR SULFUR

The development of a chemical soil test to measure supplies of plant available sulfur has been investigated in several areas in

recent years. The main problem associated with many soil tests for sulfur is that the relatively small amounts of sulfate sulfur extracted in most techniques cannot be accurately measured by methods of sulfate analysis which are suited to routine analysis. Most soil tests for sulfur involve measurement of sulfate ions by the turbidimetric method of Chesnin and Yien (10), or modifications of that method (19,2).

Several different extracting solutions have been used, with moderate success, in removing plant available sulfate from soils. A large number of soil tests use water, or dilute electrolytes as extracting solutions. Spencer and Freney (37) were able to obtain good correlations between sulfur uptake by plants and cold water extractable sulfate. Williams and Steinbergs (41) used solutions of dilute electrolyte (0.15% $CaCl_2$ and 0.2 to 6.0% $NaCl$) and found that sulfate sulfur was moderately correlated ($r = 0.78$) to plant uptake of sulfur in a greenhouse experiment. Baidsley and Lancaster (2) report that sulfate extractable by dilute acetic acid solutions was not significantly correlated with sulfur uptake by white clover grown in the greenhouse. Sanford and Lancaster (35) found that sulfur uptake by turnips agreed consistently with the sulfate sulfur contents of soils ($r = 0.87$).

On those soils that contain appreciable amounts of adsorbed sulfate, extractions with phosphate solutions has been shown to more effectively estimate plant available sulfate. Phosphate ions are able to replace the sulfate ions adsorbed to soil constituents. Spencer and Freney (36) found that on a wide range of sulfur deficient soils, extractions with phosphate solutions removed quantities of sulfate that correlated well with sulfur uptake by plants.

Several workers have used "heat soluble" sulfur or sulfate

extractable in hot water as an index of available sulfur supplies (37,41). Heat soluble sulfur, or the sulfate present in soils after mild hydrolysis at $50^{\circ}C$, and drying at $100^{\circ}C$ is thought to consist of the easily soluble sulfate plus the more labile organic sulfate, which is released by the mild hydrolysis. Williams and Steinbergs (41) found that the heat soluble sulfate content of soils was significantly correlated with sulfur uptake by plants in the greenhouse.

Kilmer and Nearpass (27) were able to obtain good correlations between sulfate extractable by 0.5 M $NaHCO_3$ at pH 8.5, and sulfur up‑ take by plants. This method measures the easily soluble sulfate plus the more labile portion of the organic sulfur fraction.

The total sulfur content of a soil does not normally correlate well with sulfur uptake by plants (2,41). Bardsley and Lancaster report that reserve sulfur (largely organic sulfur) was significantly correlated to plant sulfur uptake (2). The "r" values reported are 0.79 for a green‑ house study; and 0.55 for field experiments in which the reserve sulfur content was correlated with per cent yield of the check as compared to the fertilized treatment.

Many chemical soil tests for plant available sulfur are able to separate soils into two broad groups: those that are sulfur suffic‑ ient and those that may be deficient. There is no soil test which con‑ sistently distinguishes between soils that are just able to supply sulfur in adequate amounts for maximum plant growth, and those which are only slightly deficient.

II ANALYTICAL PROCEDURES

A. TURBIDIMETRIC DETERMINATION OF SULFATE IN CLEAR SOIL AND PLANT MATERIAL EXTRACTS

Sulfate was measured by the turbidimetric method. This method involves the precipitation of sulfate as $BaSO_4$, stirring to keep the $BaSO_4$ crystals in suspension, and transmittance measurements of the turbid suspension. Since work by Rossum and Villarruz (34) has shown that such factors as amount and size of $BaCl_2$ crystals used, stirring period, and time before reading affect results, a standardized procedure was adopted.

Twenty-five ml of clear extract was pipetted into a 100 ml beaker. Three ml of acid seed solution (50 p.p.m. S in 6N HCl) was added. The beaker was placed on a magnetic stirrer. After the stirring action had begun a constant weight of 20-30 mesh $BaCl_2$ crystals was added. Stirring was continued for 1 minute. The samples were allowed to stand for an additional 4 minutes. The samples were then placed in a Coleman Junior Spectrophotometer and the per cent transmittance at 400 mu was measured. All samples (including the blank) were read using distilled water as a reference at 100 per cent transmittance. The actual per cent transmittance of each sample was calculated from these values. The per cent transmittance values were converted to optical density, and sulfate concentration was calculated using a standard curve. Standard curves should include optical density values for 0 to 60 p.p.m. sulfate sulfur. Standard curves were prepared for each extractant, since the pH and cation content of the extractant might affect the results.

B. WATER SOLUBLE SULFATE

Twenty-five grams of air dry soil was placed in a 250 ml Erlenmeyer flask and 50 ml of distilled water was added. This suspension was shaken on a reciprocal shaker for thirty minutes. One teaspoon of charcoal (treated to remove water soluble sulfate) was then added. 0.25 gram of NaCl was added to flocculate the colloids and facilitate filtration. Shaking was continued for an additional five minutes. The contents of the flasks were filtered using a Whatman #42 filter paper. 25 ml of the filtrate was pipetted into a 100 ml beaker and the sulfate concentration was measured using the standardized procedure of Part A. 0.15 gram of $BaCl_2$ was used. Blank determinations were made with each set of samples.

C. HEAT SOLUBLE SULFATE

This method is an adaptation of the procedure described by Williams and Steinbergs (41). Twenty-five grams of air dry soil were placed in a 250 ml beaker with 25 ml of water. The beaker was then placed on a steam bath and evaporated until the soil was near dryness. The beaker was then heated for two hours in an oven at $100^{\circ}C$. The beaker was removed from the oven and allowed to cool. The dry soil was then transferred to shaking flasks. Fifty ml of water was used in the transfer. The water soluble sulfate content of the heat treated soil was measured using the method outlined in Part B.

D. N HCl SOLUBLE SULFATES

Twenty-five grams of air dry soil were placed in a 500 ml shaking bottle and 50 ml of 1N HCl was added. After the vigorous reaction of the HCl and $CaCO_3$ of the soil had subsided the bottles

were stoppered. They were shaken on a rotary shaker for 30 minutes. The bottles were removed from the shaker and 2 teaspoons of sulfate free charcoal were added. The bottles were then shaken by hand for 30 seconds, and filtered using a Whatman #42 filter paper. The filtrate is usually a light yellow color, due to the iron removed from the soil by the HCl. To remove the source of this color 10 Ml. of 2.5N NaOH was added to 25 ml. of filtrate in a 100 ml. beaker. The iron is precipitated as the hydroxide. This suspension was then filtered, and 15 ml. of the clear filtrate was pipetted into a 100 ml. beaker. Ten ml. of 1.0 N HCl was added to restore acidity for the $BaSO_4$ precipitation. Three ml. of acid seed solution was then added. The standardized procedure for the determination of sulfate (Part A) was followed. Blank determinations were made with each set of samples.

E. SOIL SULFUR

This method of sulfur analysis was developed by Bardsley and Lancaster (2). It involves the conversion of organic sulfur and reduced inorganic sulfur to sulfates by ignition of a soil-sodium bicarbonate mixture at $500^{\circ}C$. The converted sulfates, and the sulfates already present in the soil are extracted and measured turbidometrically by precipitation as $BaSO_4$. Although this method measures organic sulfur, reduced inorganic sulfur and the sulfates present in soil, the developers do not designate the measured sulfur content as total sulfur. They use the term soil sulfur. A comparison of the soil sulfur content and the total sulfur content of the surface horizons of ten Manitoba soils (Appendix 1) indicates that soil sulfur and total sulfur values are roughly equivalent.

The procedure used was similar to that developed by Bardsley

and Lancaster (2), except that the sulfate contents of the extracts were measured using the standardized turbidometric technique (Part A) in favor of the method described by the developers.

F. PREPARATION OF SOIL SAMPLES

When drying soil samples in preparation for analysis for water soluble sulfates the samples should not be heated. It was found that heating moist samples to 50°C. greatly increased the amount of water soluble sulfate.

TABLE I

THE EFFECT OF DRYING SOILS AT 50°C ON
THE WATER SOLUBLE SULFATE CONTENT.

Soil		p.p.m. SO_4-S Air dry soils	p.p.m. SO_4-S Soils dried at 50°C.
Van Koughnett	0-6	2.9	10.0
Kitching	0-6	5.3	26.4
Braun	0-6	0.8	18.2
McCutcheon	0-6	5.3	8.90
McDonald	0-6	15.2	22.2
Stow	0-6	0.8	10.0

Table I presents a comparison of water soluble sulfate levels in soils that were air dried and soils dried at 50°C.

G. TOTAL SULFUR IN PLANT MATERIAL

The dry ignition procedure described by Sanford and Lancaster (35) was employed. It involves the ignition of a plant material-ignition

powder mixture at $500^{\circ}C$. The ignition powder consists of 9 parts Na_2CO_3, 1 part $NaHCO_3$, 0.6 parts $NaNO_3$ and 0.2 parts $KMnO_4$. Sanford and Lancaster report that this mixture effectively oxidizes organic sulfur to sulfate. Results are comparable to those obtained with the magnesium nitrate method (1,35).

The sulfate present in the extracts from the ignited plant material--ignition powder mixture was measured using the standardized procedure outlined in Part A.

IV THE SULFUR STATUS OF SOME MANITOBA SOILS

A. WATER SOLUBLE AND N HCl SOLUBLE SULFATE IN SEVERAL
MANITOBA SOIL ASSOCIATIONS

The first step in assessing the sulfur status of Manitoba soils
involved measuring the water soluble sulfate content of several different
soil associations. Little was known about the amount of water soluble
sulfate necessary to supply crops. However, by measuring the water solu-
ble sulfate content it was possible to separate the soil associations into
two general groups. The soils with large amounts of water soluble sulfate
constituted one group. Since these soil associations probably contained
adequate supplies of sulfur, no further investigations were made. The
second group was those soils of low water soluble sulfate content. It
was considered that these soils may be deficient, and further investiga-
tions were necessary.

Materials and Methods.

Soil samples were obtained during the summer of 1963. Some
of the soils were sampled at the 0-6, 6-12, 12-24, 24-36 and 36-48 inch
depths. Others were sampled in each soil horizon. The soils were air
dried and ground to less than 1 m.m. in preparation for analyses.

Texture was estimated by hand texturing. Organic matter was
determined by the Walkley-Black method (39). Water soluble and N HCl
soluble sulfate were measured using a procedure similar to those out-
lined in Section B and D of Chapter III.

Results and Discussion.

The measurement of water soluble sulfate contents indicated
that the soils of several associations contained adequate amounts of
sulfur (Table II and Table III). The highest sulfate contents were
encountered in the Plum Ridge, Lundar and Balmoral soils. These soils,

TABLE 2

WATER SOLUBLE SULFATE SULFUR CONTENT AND OTHER
CHARACTERISTICS OF SOME MANITOBA SOILS

Soil Association or Series	Texture 0 - 6"	% Organic Matter 0-6"	Water Soluble S 0-24" lb/acre	Water Soluble S 0-48" lb/acre
Stockton A	LS	1.6	3	6
Stockton B	LS	2.6	6	12
Miniota A	LS	2.4	7	19
Gilbert B	LFS	5.3	197	288
Plum Ridge A	FSL	4.7	21	195
Plum Ridge B	FSL	6.1	50	117
Plum Ridge C	FSL	12.3	397	1286
Plum Ridge D	FSL	5.6	64	2569
Almasippi A	LS	4.5	13	88
Almasippi B	FSL	3.7	9	44
Newdale A	CL	5.1	22	1564
Newdale B	CL	6.4	12	55
Erickson	L	2.9	10	32
Waitville	SL	3.1	17	195
Poppleton A	LS	2.9	26	87
Poppleton B	LS	1.7	10	109
Wellwood A	L	4.6	51	79
Wellwood B	L	4.9	55	66
Lundar	SiC	5.5	449	—

TABLE 3

N HCl SOLUBLE SULFUR, AND WATER SOLUBLE SULFATE
IN SEVERAL SOIL ASSOCIATIONS

Soil Association or Series	Horizon	Water Soluble Sulfate S p.p.m.	N HCl Soluble Sulfur p.p.m.
Erickson - Orthic Dark Grey	Ah	2	2
	B	1	2
	Cca	1	7
	C	3	24
	C	3	28
Newdale A - Orthic Black	Ap	4	5
	Bm	2	3
	Cca	2	41
	C	6	53
	C	38	168
Stockton A Orthic Black	0 - 6	0.7	5
	6 - 12	0.4	2
	12 - 24	0.4	2
	24 - 36	0.4	4
	36 - 48	0.4	10
Lundar	Ap	28	222
	AC	58	250
	C	144	198
Plum Ridge A Gleyed Carbonated Rego Black	Ah	6	84
	AC	26	160
	Cca	73	129
	C	72	135
	II C	118	144

Cont'd.

TABLE 3 (continued)

Soil Association or Series	Horizon	Water Soluble Sulfate S p.p.m.	N HCl Soluble Sulfur p.p.m.
Plum Ridge B	Ap	8	100
Ste. Rose	AC	8	100
	Cca	24	99
Gleyed Carbonated	C	9	26
Rego Black	II C	15	51
Wellwood A	C	2	7
Stockton B	C	1	4
Poppleton A	C	14	40
Poppleton B	C	12	111
Wellwood B	C	5	26
Newdale B	C	8	53
Almasippi A	C	16	34
Almasippi B	C	7	40
Gilbert A	C	2	19
Gilbert B	C	9	25
Plum Ridge A	C	20	42
Plum Ridge B	C	8	30
Balmoral	Ap	11	291
Limestones		3	27

released by mineralization; sulfate is easily lost from these coarse textured, slightly acid soils by leaching; and $CaCO_3$ and soluble salts have been leached from the solum. The low water soluble sulfate contents measured in the Stockton soils resulted in more intensive investigations on these soils. These investigations are reported in Part B of this chapter.

Some soil associations and series that are similar to Stockton in morphology and composition, and which should be investigated as to their sulfur supplies, are:

Miniota Association

Almasippi Association   ⸱ Orthic Black members

Souris Association   ⸱ Orthic Black members.

The data presented in Table III indicate the presence of water insoluble sulfates. The HCl soluble sulfate contents of the soils are higher than the water soluble sulfate contents. The increase in sulfate extracted by HCl is probably due to the dissolution of $CaCO_3$ and the subsequent release of the sulfate coprecipitated with it. Williams and Steinbergs (41) found that all calcium carbonate samples analyzed contained water insoluble sulfate which could be extracted with hydrochloric acid. The highest HCl soluble sulfate contents were measured in the calcareous soils.

B. DETAILED STUDY OF THE STOCKTON SOILS

The assessment of the water soluble sulfate content of several soil associations in Manitoba indicated that the soils of the Stockton association contained little water soluble sulfate. In order to investigate the sulfur status of these soils more thoroughly a de-

tailed study was made of them.

Materials and Methods.

Soils Involved

The soils of the Stockton association are developed on the deep sandy deposits of the upper Assiniboine Delta. Surface texture varies from very fine sandy loam to sand. Approximately 530,000 acres of Stockton soils have been mapped (11,12,13). The association has been divided into two textural types. The Stockton Loamy Sands range in texture from sand to loamy sand, are excessively drained and droughty. They are not generally suitable for cultivation. Sand dunes occupy large portions of this soil area. The other type, the Stockton Fine Sandy Loams, ranges in texture from loamy fine sand to very fine sandy loam. The topography is generally level to slightly undulating. Nearly all the soils of this type are cultivated.

The dominant profile type in the Stockton association is the Orthic Black. A representative Orthic Black profile may be described as follows:[1,2]

Stockton Orthic Black

Location	= Southwest quarter of Section 28, Township 10, Range 12 West.
Vegetation	= Cultivated. Common native vegetation is a mixture of upland prairie grasses and

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1. Field description based on National Soil Survey Committee of Canada Proceedings, Winnipeg, 1963.

2. Colors described using Munsell Soil Color Charts.

                      - aspen and burr oak groves.

Drainage   - Well drained.

Parent Materials   - Moderately coarse textured weakly cal-

                         careous deltaic material.

Topography   - Level to slightly undulating.

Horizon	Depth-inches	Description
Ap	0-5	Very dark greyish brown to dark grey loamy fine sand. Slightly acid in reaction. Very weakly developed fine granular structure. Very friable when moist, loose when dry.
AB	5-10	Dark greyish brown to greyish brown loamy fine sand. Slightly acid in reaction. Structureless to weakly developed fine granular structure. Very friable when moist, loose when dry.
BM	10-27	Dark brown to greyish brown loamy fine sand. Neutral in reaction. Structureless. Very friable when moist, loose when dry.
C1	27-38	Yellowish brown to brownish yellow fine sand. Effervesces with dilute HCl. Moderately alkaline in reaction. Structureless and loose.
C2	38-48	Yellow fine sand. Effervesces with dilute HCl. Moderately alkaline. Structureless and loose.

Sampling Procedure:

The Stockton soils were sampled at nine sites. The samples were obtained from cultivated soils. The Ap, Bm and C horizons were sampled at each location.

Methods of Analyses.

The texture of each sample was estimated by hand texturing, pH determinations were done on a 1:1 suspension of soil and distilled water. Organic matter was determined by the Walkley-Black method (39). The water soluble sulfate content, and the "soil sulfur" contents employed the methods described in Chapter III, Analytical Procedures.

Results and Discussion.

Table 4 presents the results in this study. The water soluble sulfate content was low at all nine sites. This indicates that the low sulfate content encountered in those Stockton soils sampled in the Sidney area is not a local characteristic, but a general characteristic of the entire association. Less than 1 p.p.m. water soluble sulfate was measured in the Ap horizon at seven of the nine sites.

There are several factors which may have contributed to the low sulfate content of these soils. The low organic matter contents and the low soil sulfur contents indicate that there is little organic sulfur in these soils. Organic sulfur compounds are converted to sulfate forms by mineralization processes. Therefore low organic sulfur contents result in little sulfate being released in the soil. Barrow (3,4) found that soils deficient in sulfur did not mineralize sulfate upon incubation, while soils of significant sulfur content mineralized sulfate upon incubation. The second factor affecting supplies of sulfate in these soils, concerns the texture of the soils and the nature of the under-

TABLE 4

THE pH, ORGANIC MATTER CONTENT, SOIL SULFUR CONTENT, AND WATER SOLUBLE SULFATE CONTENT OF 9 STOCKTON SOILS.

Soil Type and Location	Horizon	Texture	pH	Organic Matter %	p.p.m. Soil Sulfur	p.p.m. Water Soluble Sulfate
Stockton FSL	Ah	LFS	6.60	1.80	60.0	0.4
S.W. 32-10-12 W	Bm	FS	6.78	1.25	75.0	0.8
	C	FS	6.80	0.26	33.0	1.2
Stockton FSL	Ap	VFSL	6.90	3.39	96.3	1.7
S.E. 32-10-12 W	Bm	LVFS	7.55	1.16	64.7	2.4
	C	LVFS	7.80	0.58	51.4	1.6
Stockton FSL	Ap	VFSL	6.80	4.23	156.0	0.4
S.E. 28-10-12 W	Bm	VFSL	7.25	1.23	80.1	0
	C	VFSL	7.82	0.44	66.8	0.4
Stockton FSL	Ap	LFS	6.65	2.77	81.3	1.4
N.W. 9-10-12 W	Bm	FS	6.75	0.82	53.1	1.8
	C	FS	7.02	0.79	51.4	0.8
Stockton LS	Ap	VFS	7.38	1.83	75.0	0.4
S.W. 20-10-11 W	Bm	VFS	7.40	0.77	52.5	0.8
	C	VFS	7.78	0.53	45.0	1.3
Stockton FSL	Ap	VFSL	6.32	3.67	130	0.6
N.E. 15-8-11 W	Bm	LVFS	6.72	1.48	87.0	1.3
	C	VFS	7.80	0.86	63.3	1.1
Stockton LS	Ap	MS	7.18	1.70	67.5	0
N.W. 6-8-13 W	Bm	MS	7.08	0.62	32.5	0.4
	C	MS	7.30	0.27	30.0	0.9
Stockton FSL	Ap	LFS	6.98	1.86	67.0	0.4
S.E. 17-10-14 W	Bm	FS	7.01	0.83	63.3	0.4
	C	FS	7.32	0.35	35.0	0
Stockton FSL	Ap	VFS	6.92	2.84	88.3	0.8
S.W. 21-10-13 W	Bm	VFS	6.82	1.03	67.0	0
	C	VFS	6.78	0.72	60.0	0.4

lying material. Downward percolation of water is rapid in these coarse textured soils. There are no impermeable layers to restric the downward movement of water and ions that may be in solution. The third factor is the pH of the soil. It is known (26,14) that little sulfate is adsorbed at pH greater than 6.0. Therefore in the Stockton soils, sulfate released in the surface horizons could be readily leached beyond rooting depths. Both the pH and high permeability of these soils contribute to the rapid removal of sulfate by leaching.

The soil sulfur content of the Ap horizon of the Stockton soils ranges from 60 to 156 p.p.m. The soil sulfur contents of the Ap of several other soils were: Newdale 247 p.p.m., Waitville 73 p.p.m., Almasippi 98-268 p.p.m., Wellwood 272 p.p.m., Firdale 242 p.p.m., Plum Ridge 450 p.p.m., Lundar 810 p.p.m. The Stockton soils contain less total sulfur (soil sulfur is an approximate measure of total sulfur) than many other Manitoba soils. The low soil sulfur content of the soils is probably related to the low organic matter contents. Soil sulfur is a measure of the organic sulfur content, and the inorganic sulfates.

The soil sulfur content of a sulfur responsive soil of Southeastern United States was 58 p.p.m. in the 0-6" depth, and 79 p.p.m. in the 6-12" depth (24). Many of the Stockton soils have similar soil sulfur contents. However, a direct comparison should not be drawn. Adsorbed sulfate is an important fraction in the more acid soils of southern United States, and it is source of plant available sulfate. The soils of southern United States probably receive larger amounts of sulfur in rainwater than do the Stockton soils. Both these points would suggest that the Stockton soils are less adequately supplied with available sulfate than some deficient soils of Southeastern United States.

Generally, the results of this study indicate that sulfur supplies in the Stockton soils are less than the sulfur supplies in most Manitoba soils. All the soils sampled in the Stockton association were low in water soluble sulfate.

V   GREENHOUSE EXPERIMENT I

The purpose of this experiment was to assess the sulfur supplying capacities of several Manitoba soils and to evaluate the worth of some chemical soil tests for plant available sulfur.

A. MATERIALS AND METHODS

Soils.

There were eleven soils studied in this experiment. They were selected to include a range in sulfur content. Preliminary analyses indicated that the Plum Ridge soils were well supplied with plant available sulfur; that the Wellwood, Firdale and Almasippi soils were moderately supplied; and that the Stockton soils might be deficient; and, that the Sandilands soil was almost definitely deficient.

One soil (Plum Ridge X) was obtained from the Plum Ridge series. These soils are developed on strongly calcareous, moderately coarse textured lacustrine deposits. Drainage is generally imperfect, and the dominant profile type is the Gleyed Carbonated Rego Black (33). Gypsum crystals are often encountered in the upper portion of the C horizon. This soil has more than adequate supplies of sulfur.

Two soils were sampled in the Wellwood association, the Wellwood VI soil and the Wellwood XI soil. The Wellwood soils are moderately well drained Orthic Black developed on moderately calcareous, medium textured lacustrine sediments (11). These sediments overlie the deep sand deposits of the Upper Assiniboine Delta. Generally calcium carbonate has been leached beyond the solum of these soils, and gypsum crystals are never encountered. Organic matter serves as the main

supplier of plant available sulfur in these soils.

One sample (Firdale VIII) was collected from the Firdale association. Firdale soils are moderately well drained Dark Grey soils. They were developed on moderately calcareous, medium textured deposits at the eastern edge of the Upper Assiniboine Delta (11). Calcium carbonate has generally leached beyond the solum, and gypsum crystals are a rare occurrence in the parent material. The bulk of the sulfur used in plant growth must be derived from the organic matter.

There were three sites sampled in the Almasippi soil association, the Almasippi I, II and III soils. These soils were developed on the moderately calcareous, moderately coarse textured deltaic sediments of the Lower Assiniboine Delta (11). These soils were developed under imperfect drainage and the dominant profile types are Gleyed Carbonated Rego Blacks and Gleyed Blacks. Gypsum crystals are often encountered in the parent material. On the better drained sites, $CaCO_3$ and other more soluble salts have leached beyond the solum. Where this has occurred, and the soils are low in organic matter, sulfur deficiencies would be plausible.

Three sites were sampled (Stockton IV, V, VII) in the Stockton association (11). Stockton soils were developed on the weakly calcareous, deep sand deposits of the Upper Assiniboine Delta. These soils are well to rapidly drained, and the dominant profile type is the Orthic Black. Where these soils are coarse textured and low in organic matter, the occurrence of sulfur deficiencies is a distinct possibility.

There was one sample from the Sandiland series (36), the Sandilands IX soil. Sandilands soils are well drained Minimal Podzol soils developed in coarse textured siliceous sand deposits in South-

eastern Manitoba. They are extremely low in natural fertility and almost certainly deficient in sulfur.

Table V lists some characteristics of the soils.

Experimental Design.

There were three treatments for each soil. Treatment A received no sulfur fertilizer, and four rape plants were grown. Treatment B received 25 p.p.m. sulfate sulfur, and four rape plants were grown. Treatment C received no sulfur fertilizer, and there were no plants grown on this soil. The purpose of treatment C was to measure the amount of sulfate released by mineralization during the period of growth for plants on treatments A and B. Each treatment was replicated three times for each soil.

Procedure.

The soils were obtained in October. The Ap horizon of a cultivated soil was sampled for all soils except the Sandilands where the Ae horizon of a virgin soil was sampled. The soils were air dried in the greenhouse, then mixed, and sieved to remove roots and plant residues. A representative sample was then taken for chemical analyses. The soils were stored in the greenhouse for about two months prior to planting. One gallon glazed porcelain pots were used. Two kilograms of soil was placed in each pot. One hundred p.p.m. K and 41 p.p.m. P were added as K_2HPO_4 in dilute solution in a band $1\frac{1}{2}$ inches below the soil surface. In one treatment 25 p.p.m. S, as Na_2SO_4 in dilute solution was added in a band one inch below the soil surface. Thirty p.p.m. N, as NH_4NO_3 in dilute solution, and 2 p.p.m. Boron, as $Na_2B_4O_7$ in dilute solution, was added to the surface of the soil. Eight to ten seeds of Tanka rape were sown in each pot on February 1. After emergence the plants were thinned to four plants per pot. Dis-

TABLE V

SOME CHARACTERISTICS OF THE SOILS USED
IN GREENHOUSE EXPERIMENT I

Soil		Texture	pH	% O.M.
Almasippi	I	LFS	7.85	1.95
Almasippi	II	VFSL	7.20	5.91
Almasippi	III	FSL	7.70	2.59
Stockton	IV	LFS	6.85	2.51
Stockton	V	LS	6.87	2.68
Wellwood	VI	VFSL	7.25	5.42
Stockton	VII	LFS	6.85	1.64
Firdale	VIII	VFSL	7.00	4.27
Sandilands	IX	MS	5.95	0.73
Plum Ridge	X	LUFS	7.80	6.77
Wellwood	XI	VFSL	5.70	6.49

tilled water was used for watering. On March 7 all the pots were fertilized with NH_4NO_3 in dilute solution. All the soils were fertilized to contain 100 p.p.m. N, according to the content of NO_3-N at seeding, as measured by a soil test. The above ground portion of the plants was harvested on March 26, dried at $50^\circ C$. for two days and weighed. The soil in treatment C was removed from the pots at this time, and air dried. The soils were then ground to pass a 1 m.m. sieve, and the water soluble sulfate content was measured.

The experiment was arranged in a split plot design. A statistical analysis was made of the results for yields of rape plants. Values for linear correlation of mgs. sulfur uptake by the plants of the check treatments versus sulfur content of the soils as estimated by various soil tests were calculated. Regression lines were drawn to indicate the relationship between sulfur uptake by the plants of the check treatments and those soil tests that were significantly correlated with sulfur uptake.

The methods of soil and plant analyses used are described in Chapter II, Analytical Procedures.

B. RESULTS AND DISCUSSION

Table VI lists the results of the various chemical soil tests used to assess the sulfur supplying capacity of the 11 soils. The yield and sulfur content of rape grown at 2 levels of sulfur supply in the soils is presented in Table VII. A statistical analysis of the yields is summarized in the ANOV table presented in Table VIII.

The application of sulfur fertilizer resulted in increases in yield of plant material on nine of the eleven soils studied. The in-

creases were statistically significant at the .01 level on the
Almasippi I, Stockton IV, Stockton V and Wellwood VI soils. The in-
creases on the Almasippi III, Firdale VIII and Sandilands IX soils were
significantly different from the check yields, at the .05 level. Substan-
tial, but not significant increases were realized on the Almasippi II
and Stockton VII soils. The Wellwood XI and Plum Ridge X soils did not
yield substantial increases due to sulfur fertilization. These data in-
dicate that the surface horizons of several Manitoba soils are not able
to supply sufficient sulfur for maximum growth of rape under the optimum
conditions of the greenhouse.

Significant differences between soils were noted in the yields
of the check treatments. This is expected, since these soils were select-
ed to include a range in sulfur supplying capacity. One would expect the
yields of the sulfur treatment to be similar for all soils, since it was
assumed that adequate amounts of sulfur, nitrogen, phosphorous, potassium
and boron were supplied. It was noted that the yields of the sulfur
treatment on 9 of the 11 soils were quite similar. The Sandilands IX and
Plum Ridge X soils yielded significantly less than did the other 9 soils.
Since all the major nutrients were in adequate supply this reduced yield
could be due to a minor or secondary (e.g. Calcium) element deficiency
or some factor of nutrient imbalance. Investigations into the minor
element status of the Plum Ridge and Sandilands soils should be consider-
ed.

Table IX lists r values for simple linear correlations of the
various soil tests and sulfur uptake. The relation between water soluble
sulfate and sulfur uptake is illustrated in Figure 1. Figures 2 and 3
show similar relations between heat soluble sulfate and sulfur uptake;

TABLE 6

A COMPARISON OF SEVERAL METHODS OF EVALUATING
PLANT AVAILABLE SULFUR IN SOILS

Soil	Organic Matter %	Soil Sulfur p.p.m.	H$_2$O Soluble Sulfate-S p.p.m.	1.0N HCl Soluble Sulfate p.p.m.	Heat Soluble Sulfate-S p.p.m.	Sulfate After Mineralization p.p.m.
Almasippi I	1.95	100	0.6	3.9	4.8	2.4
Almasippi II	5.91	268	1.5	7.6	5.6	1.6
Almasippi III	2.59	175	1.5	10.0	2.2	2.2
Stockton IV	2.56	116	0.0	6.2	3.2	0.0
Stockton V	2.68	85	0.0	8.2	4.0	0.0
Wellwood VI	5.42	255	0.0	18.0	5.6	3.8
Stockton VII	1.64	60	0.4	6.3	5.0	0.5
Firdale VIII	4.27	242	1.3	18.0	6.0	1.8
Sandilands IX	0.73	27	0.0	2.0	0.0	0.0
Plum Ridge X	6.77	450	9.2	55.0	20.0	9.0
Wellwood XI	6.49	290	2.0	6.2	9.6	6.6

TABLE 7

YIELD AND SULFUR CONTENT OF RAPE GROWN
UNDER 2 LEVELS OF SULFUR SUPPLY.

Soil	Yield of Treatment A (check) in gms.	Yield of Treatment B (25 p.p.m. S) in gms.	Percent Yield Treatment A/ Treatment B	S % in Check	Mgs S Uptake in Check	S % Treatment B	Mgs S Uptake Treatment B
Almasippi I	3.04	7.50	40.5	.06	1.82	.30	22.50
Almasippi II	4.95	6.97	71.0	.06	3.12	.31	21.60
Almasippi III	4.14	7.63	54.2	.07	2.90	.30	23.11
Stockton IV	2.85	7.40	38.5	.07	2.00	.30	22.42
Stockton V	3.66	7.68	47.6	.05	1.83	.27	20.73
Wellwood VI	4.20	8.24	50.9	.06	2.52	.29	23.89
Stockton VII	5.17	7.80	66.0	.06	2.90	.28	21.84
Firdale VIII	4.30	8.01	53.6	.06	2.70	.29	22.90
Sandilands IX	1.90	5.59	29.3	.07	1.33	.38	21.24
Plum Ridge X	6.75	6.02	110.1	.15	10.12	.40	24.08
Wellwood XI	6.80	7.63	86.6	.08	5.23	.29	21.74

TABLE 8

ANOV TABLE OF THE YIELDS OF RAPE GROWN ON 11
SOILS UNDER 2 LEVELS OF SULFUR SUPPLY

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Square	F Value	Tabled F Value	
					.05	.01
Replicates	2	0.158	.076	.197		
Soils	10	50.15	5.02	13.088**	2.35	3.37
Error A	20	7.70	.385			
Soils + Replicates (main plots)	32	58.01				
Treatments	1	150.88	150.88	50.126**	4.30	7.95
Soils x Treatment Interaction	10	39.52	3.952	1.31		
Error B	22	66.24	3.01			
Total	65	256.56				

Least Significant Difference Values. a. Soils $L.S.D._{.01} = 1.43$ gm.

$L.S.D._{.05} = 1.06$ gm.

b. Treatments $L.S.D._{.01} = 4.00$ gm.

$L.S.D._{.05} = 2.95$ gm.

TABLE 9

VALUES FOR LINEAR CORRELATION (r) BETWEEN MGS SULFUR UPTAKE
AND SULFUR SUPPLY AS INDICATED BY VARIOUS SOIL TESTS.

	r
Sulfur Uptake mgs vs. 1.0 N HCl Soluble Sulfate, P.P.M.	0.28
Sulfur Uptake mgs vs. Soil Sulfur P.P.M.	0.24
Sulfur Uptake mgs vs. % Organic Matter	0.53
Sulfur Uptake mgs vs. Water Soluble Sulfate P.P.M.	0.75[*]
Sulfur Uptake mgs vs. Water Soluble Sulfate After Mineralization, P.P.M.	0.89[**]
Sulfur Uptake mgs vs. Heat Soluble Sulfate P.P.M.	0.96[**]

[*] Significant correlation at the .05 level.

[**] Significant correlation at the .01 level.
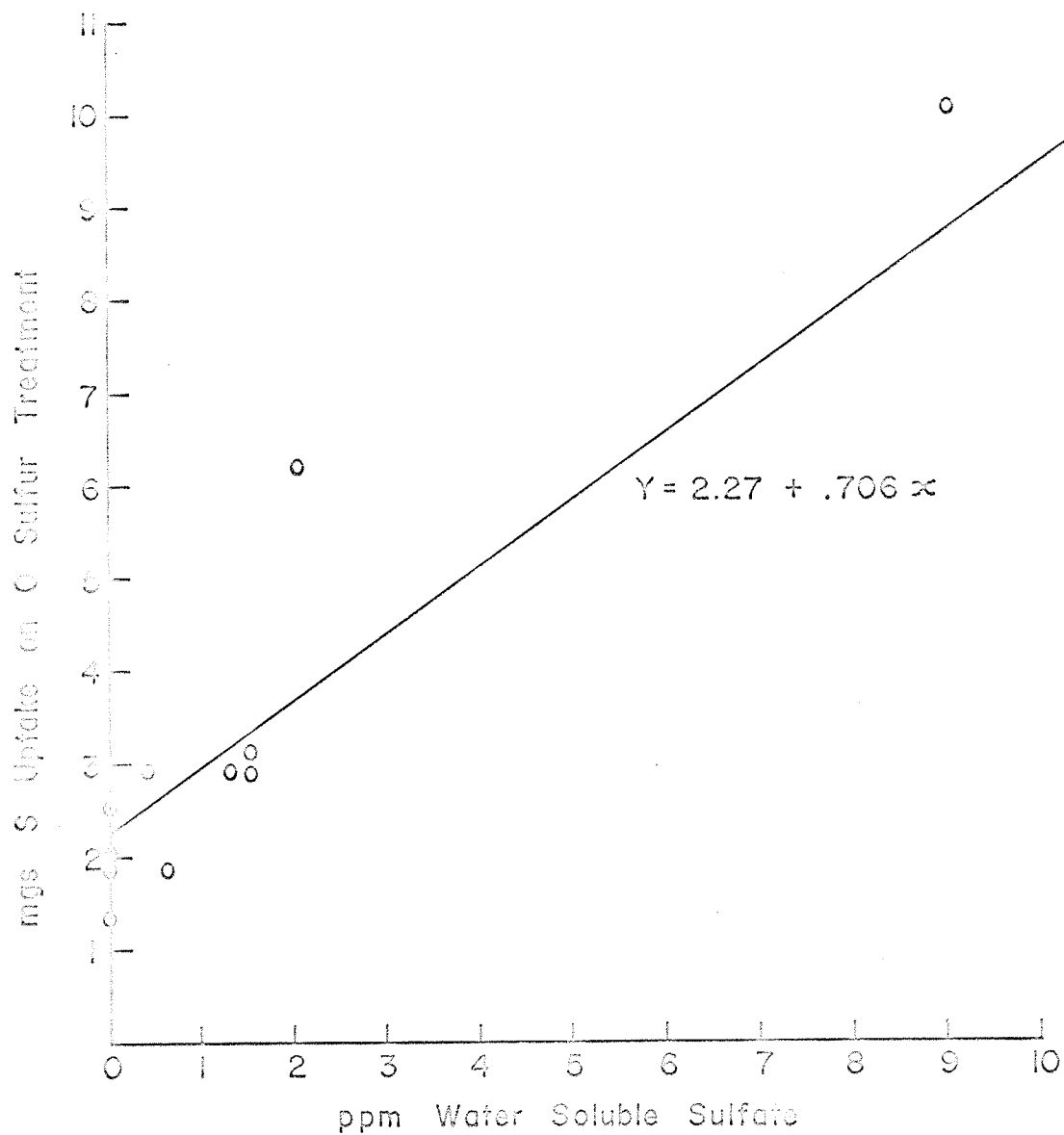
Figure 1 Regression Line for Water Soluble Sulfate
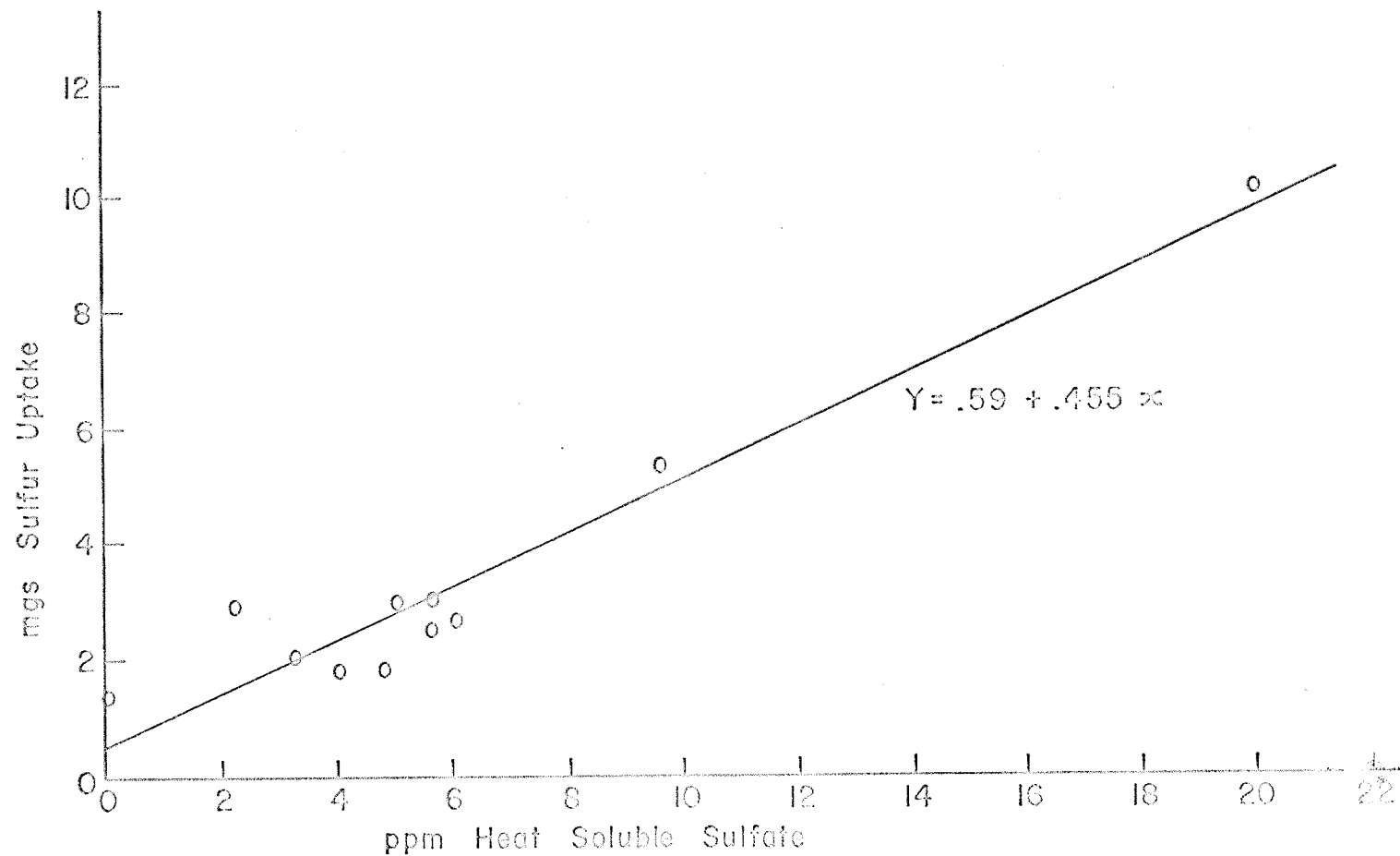Versus mgs Sulfur Uptake by Rape.

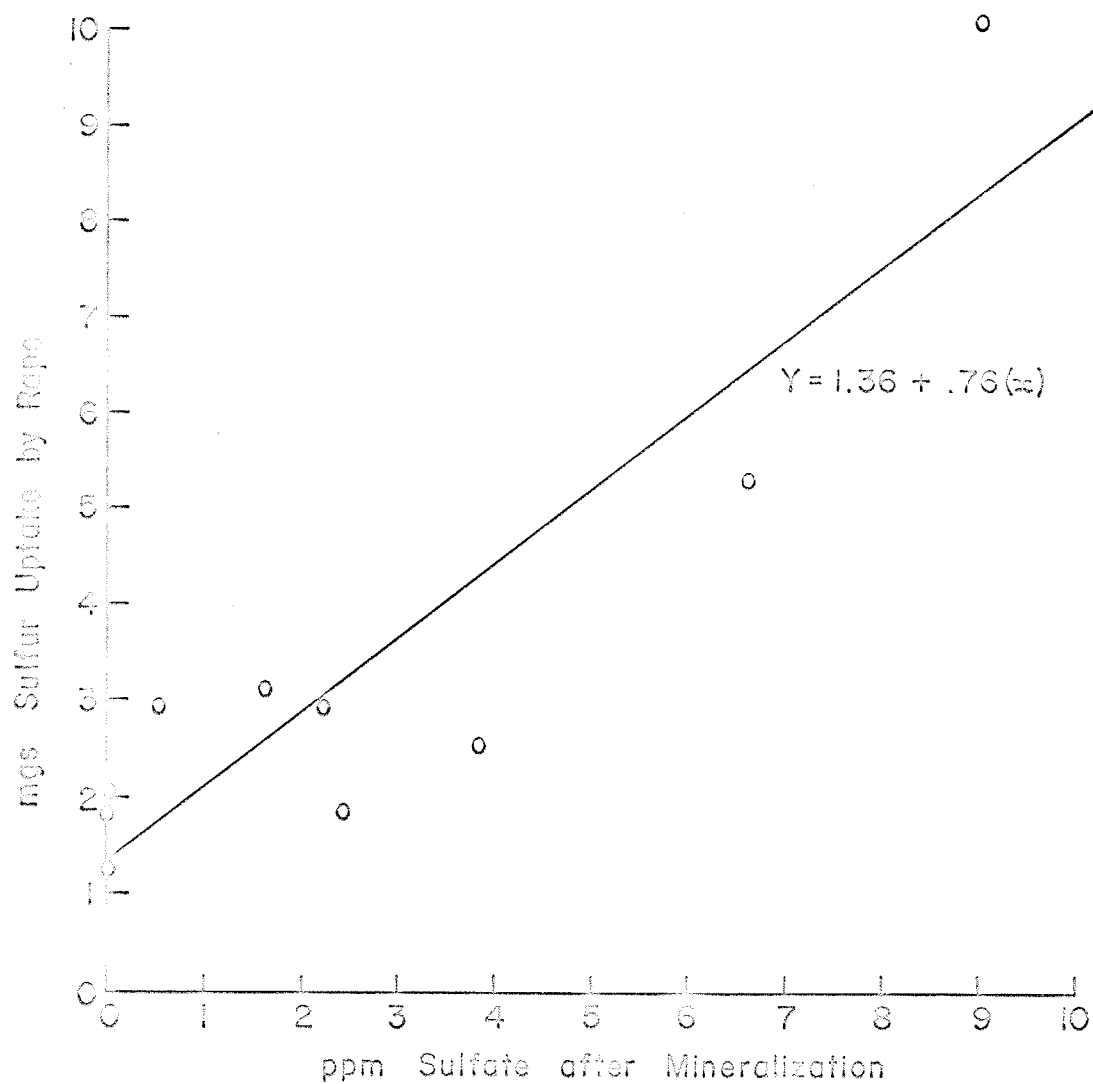Figure 2   Regression Line for Heat Soluble Sulfate Versus mgs Sulfur Uptake
by Rape.

Figure 3   Regression Line for Water Soluble Sulfate
after Mineralization Versus mgs Sulfur
Uptake by Rape

and water soluble sulfate after mineralization and sulfur uptake.

Sulfur uptake was not correlated significantly with the soil sulfur content of the soils. Since soil sulfur is essentially total sulfur (See Appendix 1), it appears as if sulfur may be similar to nitrogen in its behaviour in Manitoba soils. The total nitrogen content of these soils is often not a good index of the supply of available nitrate. The total sulfur content on the basis of these analyses, does not indicate the amount of available sulfate. Bardsley and Lancaster (2) and other workers (24) in the southern United States report a significant correlation (r = 0.79) between reserve sulfur (soil sulfur - easily soluble sulfate) and sulfur uptake under greenhouse conditions. Since the amounts of water soluble sulfate are negligible when compared to the concentration of "soil sulfur" in the soils of this study, it is evident that the "r" value for linear correlation between reserve sulfur (soil sulfur - sulfate sulfur) and sulfur uptake would differ only slightly from the "r" value for soil sulfur versus sulfur uptake. These data involve only eleven soils and it is important to consider that further investigations may show that the "soil sulfur" concentration of Manitoba soils is more important in determining the amount of available sulfate than this study indicates.

The amount of sulfate sulfur soluble in N HCl was not correlated with sulfur uptake. The HCl extraction method measures the easily soluble sulfate plus the sulfate coprecipitated with $CaCO_3$. Since the sulfate present in the $CaCO_3$ is largely unavailable to plants (40), the lack of a significant correlation is to be expected.

The organic matter content of the soils was slightly but not significantly correlated with sulfur uptake (r = 0.53). This illustrates

that the amount of organic matter is of some importance in assessing
the sulfur supplying capacity of a soil.

The amount of water soluble sulfate is significantly correlat-
ed at the 5% level (r = 0.75). Spencer and Freney (37), Williams and
Steinbergs (41) and others have reported significant correlations be-
tween easily soluble sulfate, and sulfur uptake. The amount of water
soluble sulfate in these soils should be a good index of sulfur avail-
ability. The results of another section of this investigation
(Chapter VIII) indicate that the adsorption of sulfates by these soils
is negligible. Therefore, all or nearly all the water soluble sulfate
present in these soils should be available to plants. Consequently
water soluble sulfate should be a good test. The author realizes the
limitations of the water soluble sulfate test. Conclusions are based
on a limited number of observations, and the measurement of sulfate at
low concentrations is somewhat inaccurate using the turbidimetric
technique. However, the water soluble sulfate test should be valuable
in separating those soils which are adequately supplied with sulfate,
from those which may be deficient in available sulfate. In this experi-
ment, all those soils responding to additions of sulfur fertilizer
contained less than 2 p.p.m. water soluble sulfate.

The most significant correlations are between sulfur uptake
and heat soluble sulfate (r = 0.96), and between sulfur uptake and
water soluble sulfate present after incubation (r = 0.89). These data
indicate that the organic sulfur fraction is of some importance in de-
termining supplies of available sulfate. The heat soluble sulfate pro-
cedure measures water soluble sulfate, plus the more labile sulfate of
the organic fraction (41), which is released by gentle hydrolysis and

heating. The significant correlation of sulfate present after incubation, and sulfur uptake indicates that the mineralization of organic sulfur is of some importance in determining supplies of available sulfate. It is noted that the "r" value for sulfur uptake versus water soluble sulfate is 0.75. Since both the heat soluble and incubation procedures measure water soluble sulfate plus a portion of the organic sulfur fraction, the "r" values of 0.96 and 0.89 respectively, indicate that a portion of the organic sulfur fraction did become available to the plants during the growth period.

Two soils, the Wellwood VI and Wellwood XI soils released 3.8 and 4.6 p.p.m. sulfate sulfur respectively during the growth period. If these data are applied to field conditions this would be a release of approximately 8 pounds of sulfate sulfur per acre in nine weeks. Lesser amounts of sulfate were mineralized in the Almasippi I, II and III soils and in the Firdale VIII soil. These soils released the equivalent of .2 to 3.8 pounds of sulfate sulfur per acre in the nine week period. The Stockton IV, V, and VII soils, and the Sandiland IX soil did not mineralize measureable amounts of sulfate. Similar results are reported by Barrow (4). He found that soils deficient in sulfur often did not release sulfate during incubation.

That amount of sulfate mineralized by the soils of treatment C may not have been equal to the amount released by those soils growing plants. Freney and Spencer (17) report that more sulfate is mineralized in soils growing plants, than is mineralized in soils not growing plants.

VI GREENHOUSE EXPERIMENT II

The purpose of this experiment was to establish a critical
level of sulfur content in rape. The critical level, in this instance,
is that level of sulfur content in rape plants at which further additions
of sulfur fertilizer did not yield an increase in total yield of plant
material. This value for the critical level of sulfur in rape plants should
be of some value in assessing the sulfur supplying capacity of soils grow-
ing rape, through plant tissue analysis. This value for the critical
level of sulfur in rape would enable one to evaluate the sulfur require-
ments of rape, as well.

A. EXPERIMENTAL PROCEDURE

The plants were grown on a coarse textured soil which was low
in organic matter, acid in reaction (pH = 6.62), and, which contained
negligible amounts of sulfur. The soil was sampled from the Ae horizon
of a Sandilands soil (36). The supply of plant nutrients, except for
sulfur, was brought to a constant level in all treatments through the
addition of fertilizer materials. This level was such that the plants
would be adequately supplied in all plant nutrients other than sulfur.

The amount of sulfur supplied was the one variable. There
were ten treatments, and two replicates of each treatment. Table X
lists the amount of sulfur supplied in each treatment.

The plants were grown in one-half gallon glazed porcelain
pots. Each pot contained one kilogram of soil. The constant amount
of Nitrogen, phosphorus and potassium fertilizers, and the proper
amount of sulfur fertilizer (added in the form Na_2SO_4) was added in
dilute solution to each pot prior to planting. The plants emerged on

Figure 4

Rape Plants Illustrating Symptoms Characteristic
of Severe Sulfur Deficiency

Figure 5

Rape Plants Illustrating Symptoms of
Sulfur Deficiency Such As One Might
Expect Under Field Conditions.

Figure 6

Rape Plants That Have Received Adequate
Amounts of All Plant Nutrients.

April 24, and were thinned to two plants per pot. The micronutrients were added in the distilled water used for irrigation. The plants were observed for symptons of sulfur deficiency, and the onset and description of these symptons were recorded.

The plants were harvested on May 30. They were dried at $50^{\circ}C$ and weighed. The plant material was ground prior to analyses. The entire above ground portion of the plant was analyzed for total sulfur content, using the method described in Chapter II. Analytical procedures, and for water soluble sulfate using the following procedure.

WATER SOLUBLE SULFATES IN PLANT MATERIAL

Fifty ml of water was added to 0.25 grm of finely ground air dry plant material in a 250 ml Ehrlenmeyer flask, and shaken for 30 minutes on a reciprocal shaker. One-quarter teaspoon of charcoal was added, and shaking continued for an additional five minutes. The suspension was then filtered, using a Whatman #42 filter paper. The sulfate concentration of the filtrate was measured using the standard procedure described in Part A, Chapter III.

B. OBSERVATIONS

Eleven days after emergence the plants in the O treatment showed signs of sulfur deficiency. These symptons were: the plants were smaller than those plants receiving sulfur fertilizer, chlorosis, the leaves had thickened to give a leathery feel, the leaves were cupped upward. The color photographs in Figures 4 and 5, illustrate these deficiency symptons. Similar symptons were noted on the 2 mg treatment 15 days after emergence; on the 4 mg treatment 22 days after emergence;

on the 6 mg treatment 24 days after emergence; and, on the 8 mg treatment 36 days after emergence. It was noted that prior to the appearance of pronounced deficiency symptons, growth was retarded. After the appearance of symptons of severe sulfur deficiency, growth was halted. The most deficient plants (0,2 and 4 mg) did not flower. Treatments 6 mg to 28 mg were in flower at harvest.

C. RESULTS AND DISCUSSION

The data for yield, percentage total sulfur, and p.p.m. water soluble sulfate are presented in Table X. These data are presented graphically in Figure 7.

The addition of 16 mg of sulfur did not result in an increase in yield above the yield of the 12 mg sulfur treatment. The total sulfur concentration of the 12 mg treatment was .10%; and the total sulfur concentration of the 16 mg treatment was .11%. It appears as if the critical level of total sulfur in rape is .10% sulfur. Plants with greater than .10% sulfur at this stage of growth should not respond to additions of sulfur fertilizer.

The water soluble sulfate sulfur content of the plants of the 12 and 16 mg treatments is 40 p.p.m. and 360 p.p.m. respectively. The critical level of water soluble sulfate might be arbitrarily set at some figure between 40 and 360 p.p.m., perhaps 200 p.p.m. To check these values, a comparison of the total sulfur content and the sulfate sulfur content of rape grown on sulfur deficient and sulfur sufficient soils in Greenhouse Experiment #1 was made.

TABLE 10

YIELD, PERCENT TOTAL SULFUR, AND P.P.M. WATER SOLUBLE SULFATE
SULFUR OF RAPE, AS COMPARED TO MGS OF SULFATE SULFUR SUPPLIED.

Treatment	mg S Supplied	Yield in gms.	% Total S	p.p.m. Water Soluble SO_4-S
Check	0	1.14	.07	40
2	2	2.41	.07	40
4	4	3.44	.06	0
6	6	4.36	.07	0
8	8	5.23	.08	20
12	12	5.81	.10	40
16	16	5.80	.11	360
20	20	6.07	.16	480
24	24	6.34	.20	540
28	28	6.73	.24	730

These data illustrate that the suggested values for the critical level
of total sulfur (.10%) and sulfate sulfur (200 p.p.m.) may be used to
separate soils that are responsive to sulfur fertilizer from those that are
sulfur sufficient. Although these values for the critical level are arbi-
trary, they might be used as a guide in identifying sulfur deficient rape
plants, and hence, sulfur deficient soils, by plant analyses.

Soil	% Yield	% Total S Check	Water soluble SO_4-S - Check	Water soluble SO_4-S - Treatment
Stockton IV	39	.07	40	1700
Wellwood VI	51	.06	0	1025
Wellwood XI	87	.08	117	2350
Plum Ridge X	110	.15	385	2670

Jones (25) reports that subterranean clover plants growing on sulfur
deficient soils contained less than 170 p.p.m. sulfate sulfur. Plants
growing on soils not responding to sulfur fertilization contained greater
than 170 p.p.m. sulfate sulfur. Values of 250 p.p.m. sulfate sulfur in
sugar beet leaves, and of 320 p.p.m. sulfate in rye grass have also been
suggested as critical levels of sulfate sulfur in plants (25). Crimson
clover and ladino clover containing less than .14% total sulfur should
respond to additions of sulfur fertilizer (24). Clover, grown in the
greenhouse, was definitely deficient when the total sulfur content was less
than .1% at half bloom stage (24). It appears as if values of .10% total
sulfur and 200 p.p.m. sulfate sulfur, although somewhat arbitrary, should
enable one to identify sulfur deficient and sulfur sufficient plants.

Figure 7 illustrates some interesting facts about the uptake
of sulfur by rape plants. If organic sulfur (sulfur utilized in plant
tissues is considered to be total sulfur-sulfate sulfur (25, 5), it is

shown that additions of small amounts of sulfur fertilizer to severely deficient plants does not yield an increase in organic sulfur content. An increase in growth does occur, but the sulfur content remains relatively constant at .07 to .08%. There is little or no sulfate sulfur in these plants. As more sulfur is supplied, and less stress is placed on sulfur supply, there is an increase in organic sulfur content, until the apparent critical level is reached at .10 to .11% total sulfur. Additional increments of sulfur fertilizer, after the requirement of sulfur for tissues has been satisfied, results in a rapid, almost linear increase in sulfate sulfur content. It appears as if sulfate sulfur does not accumulate until the requirements for sulfur in plant tissue have been met. Therefore, plants with appreciable amounts of sulfate sulfur must be receiving sulfur in adequate amounts. Deficient plants generally contain less than 200 p.p.m. water soluble sulfate.
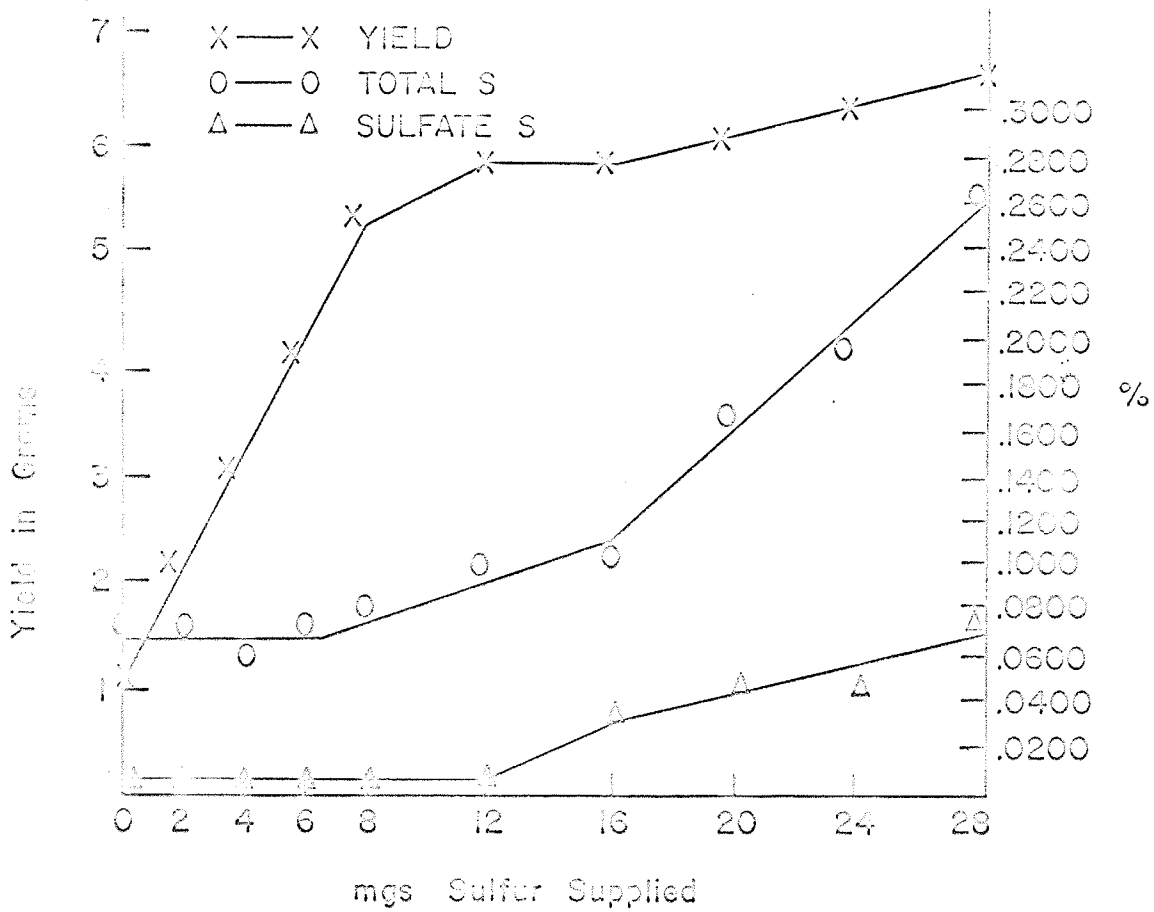
Figure 7 Yield, Total Sulfur and Sulfate Sulfur in
Rape as influenced by Amount of Sulfur
Supplied.

A. INTRODUCTION

The purpose of this study was to determine if sulfate adsorption by soil components is an important process in Manitoba soils. The sulfate adsorption characteristics of some Manitoba soils were investigated by:

1. Measuring the release of sulfate from soils leached with distilled water.

2. Measuring the release of sulfate from soils leached with phosphate solutions.

3. Leaching soils with sulfate solutions containing S^{35} tagged sulfate ions, and estimating the amount of sulfate retained by the soil components.

4. Measuring the amount of sulfate adsorbed by soil components in a suspension of soil and S^{35} tagged sulfate solutions.

Adsorbed sulfate is normally loosely held, and partially available to plants. In soils containing significant amounts of adsorbed sulfate, methods of estimating the plant available fraction usually employ extracting solutions containing an anion capable of displacing the adsorbed sulfate ions (37). The adsorption of appreciable amounts of sulfate ions is associated with a strongly acid pH, the presence of significant amounts of 1:1 lattice type clay minerals, and/or, sesquioxides (14,21,26). At acid pH it has been shown that organic matter is a soil constituent capable of retaining sulfate ions by adsorption processes. The majority of Manitoba soils are not acid. Most of the soils that are strongly acid (eg. Podzols of South-East Area)

do not contain appreciable amounts of clay, or other constituents capable of retaining sulfate ions. One would not expect sulfate adsorption to be an important process in our soils. To corroborate, or disprove, this theory, a study was made of sulfate adsorption in our soils. It was considered that if sulfate adsorption is not an important process in Manitoba soils, then water extracts of the soils should contain the bulk of the sulfate that is readily available to plants.

B. MATERIALS AND METHODS

Design of Columns and Methods of Leaching.

The columns were 40 centimeters long. They were constructed from glass tubing 6 centimeters inside diameter. A one centimeter exit tube was fitted into the lower end of the column. This exit tube was plugged with glass wool prior to filling the columns with soil. The glass wool retained the soil particles while allowing the free passage of leachate. The columns were filled with soil to a depth of 35 centimeters. The soils were air dried, ground to a size less than 1 mm, and well mixed prior to filling the columns. Care was taken during filling to insure a fairly uniform distribution of the various sized particles and aggregates. During leaching a fairly constant head of water was maintained in the column at the upper surface of the soil.

Soils.

Table XI lists come characteristics of the soils involved in the sulfate adsorption study. Texture was estimated by hand texturing. pH measurements were made on a 1:1 suspension of soil and water. Water soluble sulfate was measured using the turbidimetric technique, as described in Chapter II, Analytical Procedures.

TABLE 11

SOME CHARACTERISTICS OF THE SOILS
INVOLVED IN THE ADSORPTION STUDY.

Soil	Texture	pH	Water Soluble Sulfate p.p.m.	Sub-group Designation
Almasippi I	LFS	7.85	0.6	Gleyed Carbonated Rego Black.
Almasippi II	VFSL	7.25	1.5	Gleyed Carbonated Rego Black.
Firdale I	VFSL	7.00	1.3	Orthic Black
Lundar I	L	7.90	7.2	Gleyed Carbonated Rego Black.
Newdale Ah	CL	6.90	3.6	Orthic Black.
Newdale Bm	CL	7.05	4.0	Orthic Black.
Newdale CB	CL	7.70	5.2	Orthic Black.
Sandilands Ae	VFS	6.30	0.0	Minimal Podzol.
Sandilands Bfj	VFS	6.18	0.0	Minimal Podzol.
Sandilands C	VFS	6.55	0.0	Minimal Podzol.
Stockton I	LFS	6.85	0.0	Orthic Black.
Stockton II	LS	6.87	0.0	Orthic Black.
Stockton Ap	LFS	6.60	0.4	Orthic Black.
Stockton Bm	VFS	6.78	0.8	Orthic Black.
Stockton C	FS	6.80	1.2	Orthic Black.
Seven Sisters Ae	C	5.40	8.3	Gleyed Grey Wooded.
Vassar Ae	VFS	6.55	1.2	Bisequa Grey Wooded.
Vassar Bt	CL	6.58	3.0	" " "
Waitville Ae	L	5.90	1.8	Grey Wooded.
Waitville Bt	CL	6.50	2.2	" "
Waitville C	CL	7.79	4.0	" "
Wellwood I	VFSL	7.00	0.0	Orthic Black.
Wellwood II	VFSCL	5.70	2.0	Orthic Black.

C. EXPERIMENT A

In this experiment the surface horizons of some Chernozemic soils were leached in glass columns with distilled water. Measured aliquots of the leachate were collected. The colored leachates were treated with charcoal to remove interfering color. The sulfate concentration of each aliquot was measured using the turbidimetric technique. The soils in the columns were allowed to drain for twenty-four hours, and then leached with a 20 p.p.m. phosphate solution. Aliquots of the leachate were collected, decolorized with charcoal, and the sulfate concentration was determined. Table XI lists some characteristics of the soils studied.

Results and Discussion.

Table XII and Table XIII present the results of this experiment.

The data in Table XII indicate that the amount of sulfate removed from the soils by leaching with water is proportional to the amount of water soluble sulfate present. Nearly all the sulfate removed was contained in the first 100 ml of leachate. Several workers have demonstrated that adsorbed sulfate is not tightly held, and may be partially desorbed by extractions with water (8). If adsorbed sulfate constituted an important portion of the sulfate present in these soils, one would expect a high concentration of sulfate in the initial aliquots of leachate (mainly water soluble sulfate), then smaller, but significant concentrations of sulfate in subsequent aliquots of the leachate. This is not the case in four of the six soils of this study, the Lundar I, Newdale, Almasippi II and Firdale I soils. The sulfate concentration of the 115 - 165 ml aliquot of leachate from these soils contained 0 p.p.m. or nearly 0 p.p.m. sulfate. In the remaining two soils, the Stockton II

TABLE 12

THE RELEASE OF SULFATE IONS FROM
SOILS LEACHED WITH WATER

Soil	p.p.m. SO_4-S in each aliquot (mls)						
	0-12.5	12.5-25	25-37.5	37.5-50	50-100	100-115	115-165ml
Almasippi II	65	62	39	19.3	5.5	2.0	0
Lundar I	67	100	72	50	20.3	0	0
Stockton II	19.3	9.0	13.3	9.0	0	3.0	2.0
Firdale I	60.0	38.0	17.0	2.0	3.6	5.5	0.6
Wellwood II	39.3	55.0	20.3	9.6	0	3.6	3.6
Newdale Ah	18.0	100.0	65	34	8.0	0	0

TABLE 13

THE RELEASE OF SULFATE IONS BY A 20 p.p.m. PHOSPHATE SOLUTION,
FROM SOILS LEACHED FREE OF WATER SOLUBLE SULFATE.

Soil	p.p.m. SO_4-S in Each Aliquot (ml)		
	0-25	25-50	50-75
Almasippi II	0	0	0
Lundar I	0	0	0
Stockton II	0	0	0.4
Firdale I	0	0	0.4
Wellwood II	0.4	0	0.4
Newdale Ah	0	0	0

and Wellwood II, small amounts of sulfate were present in the 115 - 165 ml aliquots. This suggests that a small fraction of the sulfate present in these two soils is slowly water soluble, or held by adsorption processes. Kamprath et al.(26) showed that an acid reaction is necessary for signifi-cant amounts of sulfate to be held by adsorption. The Wellwood II and Stockton II soils are both acid. It is possible that adsorption processes are of some importance in the retention of sulfate by these soils. How-ever, allowing these soils to drain for 24 hours, and then leaching with 20 p.p.m. phosphate solution did not release more sulfate. These data are presented in Table XII. Chao et al.(8) were able to demonstrate that extraction with phosphate solutions removed nearly all adsorbed sulfate from soils. These data suggest that the adsorption of sulfate ions by soil constituents is not an important process in these soils.

D. EXPERIMENT B. LEACHING SOIL COLUMNS WITH S^{35}
TAGGED SULFATE SOLUTIONS

Materials and Methods.

In this study the soils were leached with a 20 p.p.m. sulfate solution containing S^{35} tagged sulfate ions. $MgSO_4$ $2H_2O$ was used to prepare the sulfate solution. Two microcuries of S^{35} was added to each 100 ml of solution. Measured aliquots of the leachate were collected and the amount of sulfate retained by the soil was estimated by measur-ing the radioactivity of the leachates, and comparing this value to the radioactivity of the original solution.

The following procedure was used in measuring the radioactivity of the samples. One ml portions of the solutions were pipetted into ribbed copper planchets, and evaporated at $60^{\circ}C$ on a hot plate. The

planchet was then placed under the thin mica window of a Nuclear

Chicago Geiger-Mueller counter operated at 1000 kilovolts, and counted.

Each sample was counted for 10 minutes. The counts per 10 minutes for

a sample of the leachate was compared to the counts per 10 minutes for

the original solution, or standard. The amount of sulfate retained by

the soils was inferred from the per cent recovery, of added sulfate,

in the leachate.

In a further study, using this technique the soils were first

leached with a 20 p.p.m. sulfate solution, allowed to drain, then leached

with distilled water. The amount of sulfate adsorbed by these soils,

and the manner of release of adsorbed sulfate was inferred from measure-

ments of the activity of the leachates.

Table XI lists some of the characteristics of the soils in-

volved in this study.

Results and Discussion.

The results of this study are presented in Table XIV and

Table XV.

Those results presented in Table XIV indicate that the Sandi-

lands, Vassar, and to a lesser extent, the Stockton soils have the

ability to adsorb small amounts of sulfate ions. Approximate calculations

indicate the small amount of sulfate adsorbed. The columns contained

800 $\neq$ 100 gms of soil. Fifty ml of 20 p.p.m. sulfate solution contain

0.1 mg of sulfate sulfur. The Vassar Ae horizon adsorbed 100% - 37.4% =

62.8% of the sulfate supplied in the first 50 ml of solution. This is

.0628 mgm of sulfate adsorbed by 800 gms of soil, which is less than 1

p.p.m. SO_4 adsorbed.

In all soils, the amount of S^{35} present in the 50-75 ml

TABLE 14

RECOVERY OF S^{35} TAGGED SULFATE IONS IN THE LEACHATE FROM SOILS
LEACHED WITH 20 P.P.M. S^{35} TAGGED SULFATE SOLUTION.

Soil	0-25 ml aliquot		25-50 ml aliquot		50-75 ml aliquot	
	counts /10 min.	% recovery.	counts /10 min.	% recovery.	counts /10 min.	% recovery.
Sandilands Bfj	3349	41.2[*]	7029	86.6[*]	7413	91.3[*]
Stockton Bm	7115	87.6[*]	8459	104.2[*]	8031	98.9[*]
Newdale Bm	9461	116.5[*]	9077	114.6[*]	8981	120.8[*]
Vassar Bt	6181	76.1[*]	7221	88.9[*]	8250	101.6[*]
Waitville Bt	9445	116 [*]				

	0-50 ml aliquot	
Waitville Ae	9664	107.4[**]
Newdale Ah	7798	88.7[**]
Sandilands Ae	4981	56.7[**]
Vassar Ae	3285	37.4[**]
Stockton Ap	6816	74.9[**]

[*] Standard Count/10 min. = 8117

[**] Standard Count/10 min. = 8789

TABLE 15

RELEASE OF ADSORBED S^{35} TAGGED SULFATE IONS
BY LEACHING WITH DISTILLED WATER

Soil	Counts/10 Minutes in Aliquot of Leachate				
	100-150 ml	150-250 ml	250-300 ml	300-350 ml	350-400 ml
Sandilands Ae	8055	8211	2968	186	< 10
Vassar Ae	7413	6495	181	20	< 10
Stockton Ap	7893	6453	533	21	< 10

aliquot of the leachate is nearly equivalent to the S^{35} content of the original solution. This indicates that the sites available for sulfate adsorption are satisfied by small amounts of sulfate ions. These data are in accord with the findings of Kamprath et al.(26) and Chao et al.(8,9), who report the importance of an acid pH in the adsorption of sulfate by soils. The most retentive soils are the most acid. The more neutral Newdale, Waitville and Stockton soils adsorbed little, or no sulfate. The Vassar and Sandilands soils adsorbed some sulfate. Swoboda and Thomas (38) used a similar soil column technique to study the adsorption of sulfate by soils. They found that nearly all the sulfate added to the surface of these soils was retained by the soils. Greater than 200 inches of water were required to leach appreciable amounts of sulfate through a 14 cm soil column. Those soils studied by Swoboda and Thomas appear to be a great deal more sulfate retentive than the soils of this study.

Table XV lists the results of the second part of this experiment. Three soils containing appreciable amounts of adsorbed sulfate were leached with water, and the release of adsorbed sulfate was inferred from measurements of the radioactivity of the effluent. The radioactivity of the 100 - 150 ml aliquot and the 150 - 200 ml aliquot is nearly equivalent to the radioactivity of the original sulfate solution. This is expected, since these soils were saturated with sulfate solution. In the successive aliquots 250 - 300, 300 - 350 and 350 - 400 the amount of $S^{35}O_4$ ions present in the effluent reduces rapidly. The radioactivity of the 350 - 400 ml aliquot was less than 10 counts per 10 minutes. This suggests, that once the sulfate concentration of the

solution in the soil was reduced, that any adsorbed sulfate was quickly and easily desorbed. Chao et al.(8) found that 35 - 45% of the sulfate adsorbed to soil could be removed with one extraction with water. Lesser amounts of sulfate were removed by subsequent extractions. In this study, any adsorbed sulfate must have been quickly and easily removed, since the radioactivity of the effluent was nearly 0, after 400 ml of water had passed through the soil column.

These data suggest that the most acid soils in this study can adsorb small quantities of sulfate from sulfate solutions. Neutral and alkaline soils did not retain sulfate ions. The adsorbed sulfate is not tightly held since extractions with water quickly desorbed this adsorbed sulfate.

E. EXPERIMENT C. THE ADSORPTION OF SULFATE IONS BY SOILS IN A 1:5
SUSPENSION OF SOIL AND 20 p.p.m. SULFATE SOLUTION

Materials and Methods.

Twenty grams of air dry soil was shaken with 100 ml of 20 p.p.m. sulfate solution. The sulfate solution contained sulfate ions tagged with S^{35}. Two microcuries of S^{35} were added to each 100 ml of solution. $MgSO_4$ $2H_2O$ was used to prepare the sulfate solution. The suspensions were shaken on a rotary shaker in one pint glass bottles equipped with poly-ethylene covered rubber stoppers. In section B the soils were shaken for two hours, allowed to stand for 48 hours, then shaken for an additional two hours prior to filtering. In section A the soils were shaken for two hours, then filtered. Whatman #42 filter papers were used. The radioactivity of the clear filtrates was measured. One ml portions of the filtrate were evaporated in ribbed copper planchets, then counted.

A counting procedure similar to the method outlined in Experiment B, Adsorption Study, was employed. The activity of the filtrate was compared to the activity of the original sulfate solution to determine the per cent recovery of added sulfate ions in the filtrate. It was considered that a reduction in activity of the filtrate, as compared to the original solution is a result of retention of sulfate ions by the soils, or exchange with sulfate ions in the soil.

Those data presented in Table XVI indicate that none of the soils studied were able to adsorb appreciable amounts of sulfate. The values for per cent recovery are all greater than 90%, indicating that the soils were able to remove little, or no sulfate from the solution. These results are not unexpected. Several workers have shown sulfate adsorption to be strongly pH dependent. Little sulfate is adsorbed at pH greater than 6.0. Most of the soils of this study are less acid than 6.0. Those that are more acid evidently do not contain constituents capable of retaining sulfate ions.

The data for Section B, in which the soil-sulfate solution suspensions were shaken for 2 hours, allowed to stand for 48 hours and then shaken for an additional two hours, are presented in Table XVII. A comparison of the per cent recovery values in Section A, and Section B reveals that or similar soils per cent recovery values are less after the longer shaking periods. It appears as if there may be a slight amount of exchange of sulfate ions in the soil with the sulfate ions in solution. It is possible that the sulfate ions held on the organic matter (30) could exchange with the sulfate in solution. Harward et al.(21) report that the bulk of sulfate adsorption and exchange was complete after 10 minutes of shaking. These soils do not have a marked ability to adsorb

TABLE 16

RECOVERY OF ADDED SULFATE FROM SOIL:SULFATE SOLUTION
SUSPENSIONS AFTER A 2 HOUR SHAKING PERIOD.

Soil	Counts/Minute	Standard Count	% Recovery
Waitville Ae	799.4	837.5	95.4
Waitville Bt	810.6	837.5	96.7
Waitville C	761.6	837.5	90.9
Newdale Ah	792.9	837.5	94.6
Newdale Bm	825.6	837.5	98.5
Newdale C	806.7	837.5	96.2
Sandilands Ae	838.4	837.5	100.5
Sandilands Bfj	839.6	837.5	100.6
Sandilands C	824.7	837.5	98.4
Vassar Ae	820.5	837.5	97.5
Vassar Bt	785.2	837.5	93.7
Stockton Ap	802.0	837.5	95.7
Stockton Bm	774.7	837.5	92.4
Stockton C	819.3	837.5	95.1
Stockton IV	763.2	837.5	91.0
Seven Sisters Ae	855.6	837.5	102.1

TABLE 17

RECOVERY OF ADDED SULFATE FROM SOIL:SULFATE SOLUTION SUSPENSIONS
AFTER SHAKING FOR 2 HOURS, STANDING FOR 48 HOURS,
AND SHAKING FOR AN ADDITIONAL TWO HOURS

Soil	Counts/Minute	Standard	% Recovery
Stockton IV	770.0	869.5	88.6
Stockton V	740.2	869.5	85.1
Almasippi I	809.6	869.5	93.1
Firdale VIII	793.6	869.5	91.2
Wellwood IX	793.6	869.5	91.2
Stockton Ap	766.8	869.5	88.2
Stockton Bm	731.1	869.5	84.1
Stockton C	766.3	869.5	88.1
Waitville Ae	781.5	869.5	89.9
Waitville Bt	727.5	869.5	83.0

sulfate, and it is difficult to assess the mechanisms of sulfate reten-
tion in these soils. It is possible that a slow exchange of sulfate for
sulfate ions of the soil constituents may account for the lower per cent
recovery values associated with the longer shaking periods. Some of the
added sulfate may have been utilized by the soil mocro-organisms, thereby
rendering it non-recoverable. Generally, sulfate adsorption does not
appear to be an important process on these soils.

F. GENERAL CONCLUSIONS AND SUMMARY

Experiments A, B and C indicate that sulfate adsorption is not
a significant process in most Manitoba soils. Some of the more acid soils,
such as the Sandilands, Vassar and Stockton were able to retain small
amounts of sulfate. However, this sulfate is not tightly held, and de-
sorbs readily with water extraction. The more neutral and alkaline soils
had no capacity to adsorb sulfate. These date indicate that water sol-
uble sulfate should be a good measure of the more readily available sul-
fate in our soils.

VIII   FIELD EXPERIMENT

A field experiment involving sulfur fertilizers on Stockton
soil was conducted in 1965. Some of the factors influencing the decision
to place such a trial on the Stockton soils were: the water soluble sul-
fate and soil sulfur contents of the Stockton soil association are much
lower than in most Manitoba soils, significant yield responses were ob-
tained with sulfur fertilizer on the Stockton soils in the greenhouse,
and farmers have reported responses resulting from additions of sulfur
fertilizer to these soils.

A. MATERIALS AND METHODS

The trial was situated on a wheat stubble field in the south-
west corner of the southeast quarter of section 32, township 10, range
12 west of the Principal Meridian. The trial consisted of 19 treatments
comparing various rates of nitrogen, phosphorus, potassium, boron and
sulfur fertilizers, and two varieties of rape. Only those treatments in-
volving varying rates of sulfur fertilizer, and different sulfur fert-
ilizer carriers are reported in this discussion. The statistical analysis
considered all 19 treatments.

The trial was sown in early May. A six row self-propelled
seeder was used to drill in the seed, and any fertilizer added with the
seed. The seeder was of a V-belt design. The seed and fertilizer were
distributed evenly along the V-belt. As the seeder moved forward the seed
and fertilizer was distributed evenly along a twenty foot row. Each in-
dividual plot was 6 rows in width (42 inches) and twenty feet in length.
There were four replicates in a randomized block design. The sulfur treat-
ments are listed in Table 18. All those treatments in which rates of

sulfur and sulfur carriers varies, received 90 pounds of N, 20 pounds of P_2O_5, and 100 pounds of K_2O per acre. The phosphorus ($NH_4H_2PO_4$) was drilled in with the seed. The nitrogen (NH_4NO_3) and potassium (K Cl) were broadcast by hand over the area of each plot. Treatment 5 received 40 pounds of S, and treatment 15 received 20 pounds of S, broadcast as $CaSO_4 \cdot 2H_2O$. Ten pounds of S, as $CaSO_4 \cdot 2H_2O$, was drilled in with the seed in treatment 16. Treatment 17 received 40 pounds of S, broadcast as $(NH_4)_2SO_4$. Treatment 14 received no sulfur fertilizer.

Plants were removed from treatments 5, 14 and 17 when the rape was in flower. These plants were dried, and total sulfur and water soluble sulfate were measured.

A ten foot portion from each of the two central rows was harvested in each plot. The plants were cut off a few inches above the ground, placed in bags, and dried. The plant material from each plot was threshed, and the seed weighed.

The soil involved was a Stockton, Fine Sandy Loam type. The 0 - 6 inch depth had the following characteristics: very fine sandy loam texture, pH of 6.85, organic matter content 2.7%, $NaHCO_3$ extractable phosphorus 19.8 p.p.m., NH_4Ac exchangeable potassium 181 p.p.m., very low in nitrate nitrogen, and, $CaCO_3$ equivalent 0.91%. The water soluble sulfate, and soil sulfur content to 48 inches were:

Depth in Inches	Water Soluble Sulfate - p.p.m.	Soil Sulfur p.p.m.
0 - 6	1.7	96.3
6 - 12	1.8	-
12 - 24	2.4	54.1
24 - 36	0.8	-
36 - 48	1.6	51.4

B. RESULTS AND DISCUSSION

The results of the trial are listed in Table 18. A comparison of the yields of treatments 14 and 17 indicates that forty pounds of S, broadcast as $(NH_4)_2 SO_4$ resulted in a significant (.05 level) increase in yield of rape seed on this soil. Substantial, but not statistically significant increases in yield were obtained by broadcasting twenty or forty pounds of S as gypsum as in treatments 15 and 5. Although differences in yield were statistically significant only where 40 pounds of S as $(NH_4)_2SO_4$ was broadcast, the consistent increases with 20 or 40 pounds of S broadcast as gypsum indicate that sulfur probably is in short supply in this soil. Twenty or forty pounds of S, as gypsum or ammonium sulfate, resulted in yield increases of 212 to 272 pounds of rape seed per acre. This soil contained 25.2 pounds of water soluble sulfate in the top 48 inches. Many of the Stockton soils studied (Chapter III, Part B) contained much less water soluble sulfate than this. On those soils of lower water soluble sulfate content, responses to sulfur fertilizer are probable. There is insufficient experimental evidence for establishing a water soluble sulfate level that would identify deficient soils. Consistent, although not always statistically significant increases in yield due to sulfur fertilization were obtained on the soil of this trial. If we consider this soil to be nearly deficient in sulfur, arbitrary values of 16 pounds of water soluble sulfate per acre in the upper 48 inches, and 10 pounds per acre in the 0 - 24 inch depth may serve as approximate levels below which soils may be considered deficient. These values are approximate and arbitrary, and a great deal more investigation is required.

The yield result for treatment 16 is interesting. Ten pounds of sulfur, as gypsum, was drilled in with the seed in this treatment.

TABLE 18

THE YIELD OF RAPE SEED, AND THE SULFATE SULFUR AND TOTAL
SULFUR CONTENT AT FLOWERING, UNDER DIFFERENT
LEVELS OF SULFUR SUPPLY ON A STOCKTON SOIL.

Treatment	Pounds S Supplied Per Acre	Carrier	Method of Application	Yield of Rape Seed Lbs./Acre	% Total Sulfur in Plants At Flowering	P.P.M. Water Soluble Sulfate Sulfur in Plants at Flowering
5	40	$CaSO_4 \cdot 2H_2O$	broadcast	1494	1.12	3540
14	0			1282	0.29	815
15	20	$CaSO_4 \cdot 2H_2O$	broadcast	1523		
16	10	$CaSO_4 \cdot 2H_2O$	drilled in with seed	1230		
17	40	$(NH_4)_2 SO_4$	broadcast	1554	1.05	2985

$L.S.D._{01} \neq 344$ pounds/acre

$L.S.D._{05} \neq 259$ pounds/acre

Although differences are not statistically significant, the yield of this
treatment was less than the yield of the 0 pounds S treatment, and consid-
erably less than the 20 pound S treatment. There are two possible explana-
tions. The first explanation is that insufficient sulfur was supplied,
and consequently the yield of this treatment is similar to the 0 pounds S
treatment. A more probable explanation is that the low yield is a result
of seedling injury, caused by the placing of fairly large amounts of two
acid fertilizer carriers with the seed. There was approximately 38 pounds of
ammonium phosphate and 50 pounds of gypsum drilled in with the seed. It
is possible that such a concentration of acid material resulted in injury
to the seedlings, and subsequent reduced yields.

A comparison of the water soluble sulfate and total sulfur cont-
ents of the plant material from treatments 5, 14 and 17, indicates an in-
crease in total sulfur and water soluble sulfate sulfur with added sulfur
fertilizer. Several investigators have reported increases in sulfur con-
tent resulting from sulfur fertilizers, without yield increases (24,25).

The water soluble sulfate content of the check treatment is well
above the value for the critical level (approximately 200 p.p.m.) as sug-
gested in Chapter V. The total sulfur content of the check treatment,
0.29%, is higher than the value determined as the critical level (.10%)
in Chapter V. Although the water soluble sulfate and total sulfur analyses
of the plants indicate adequate supplies of sulfur, sulfur may have been
in inadequate supply in later stages of growth (i.e. seed-set). The values
for the critical levels as determined on the basis of yield of forage in
the greenhouse may not be valid when extended to consider yield of seed
under field conditions. It is possible that a concentration of sulfate

sulfur in the plant at the flowering stage is necessary in order to ensure adequate supplies of sulfur during seed production.

When sulfur is available, plants take up more sulfur than they require. This luxury consumption of sulfur results in high sulfate concentration in the plants. This is indicated by the high sulfate sulfur contents of the plants from the sulfur treatments.

In summary it is noted that consistent increases in yield of rape seed were obtained by broadcasting 20 to 40 pounds of S on this soil. It appears as if ammonium sulfate and gypsum are equivalent suppliers of sulfur. These soils of the Stockton association, or similar associations, that contain less than 10 pounds of water soluble sulfate in the 0 - 24 inch depth may be sulfur deficient. If these soils are not adequately supplied with nitrogen, and nitrogen fertilizers are to be broadcast, the use of ammonium sulfate should be encouraged. However, this must be regarded only as a suggestion, and further investigations are a requisite, before more refined fertilizer recommendations can be made.

SUMMARY AND CONCLUSIONS

The measurement of water soluble sulfate contents of several Manitoba soils indicated adequate supplies of sulfur in most soils. Substantial amounts of sulfur were measured in all but the soils of the Stockton association. More detailed investigation, involving 9 sampling sites within the Stockton association illustrated that these soils vary in water soluble sulfate and soil sulfur content and that the Stockton soils generally contain much less water soluble sulfate and soil sulfate than most other Manitoba soils.

A greenhouse experiment involving 11 soils of varying sulfur content illustrated that the surface horizons of some Manitoba soils contain insufficient plant available sulfur. Significant yield increases were obtained on 7 of the 11 soils. Those soils which responded to additions of sulfur contained less than 2 p.p.m. water soluble sulfate. Values for linear correlation between sulfur uptake by rape plants and water soluble sulfate ($r = 0.75$), heat soluble sulfate sulfur ($r = 0.96$), and sulfate present after incubation ($r = 0.89$) were significant. Correlations between sulfur uptake and soil sulfur, HCl soluble sulfate sulfur, and organic matter content were poor.

The results of a second greenhouse experiment indicated that rape plants with less than 0.1% total sulfur, and less than 200 p.p.m. water soluble sulfate are sulfur deficient. Sulfur deficient plants are: stunted, chlorotic, the leaves have a leathery feel, and are thickened and cupped upwards, and, the stems and lower surfaces of the leaves contain a purple to red pigment.

The sulfate adsorption characteristics of several Manitoba soils

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APPENDIX

A COMPARISON OF THE SOIL SULFUR[1] AND TOTAL SULFUR[2] CONTENTS
OF THE SURFACE HORIZONS OF 11 MANITOBA SOILS

Soil		Soil Sulfur p.p.m.	Total Sulfur p.p.m.
Almasippi	I	142	100
Almasippi	II	254	270
Almasippi	III	172	175
Stockton	I	112	116
Stockton	II	119	85
Wellwood	I	209	255
Stockton	III	82	60
Firdale	I	289	290
Sandilands	I	20	27
Lundar	I	926	810
Plum Ridge	I	586	450

1. Soil Sulfur by the method outlined by Bardsley and Lancaster (2).

2. Total Sulfur using a Leco Model 522 Induction Furnace and Model 517-000 Titrimetric Sulfur Determinator, as described by Lowe (28).