

NITROGEN AND SULFUR MINERALIZATION
OF SEVERAL MANITOBA SOILS
AND N:S RATIOS IN
RAPE AND BARLEY

A Thesis
Submitted to
The Faculty of Graduate Studies and Research
University of Manitoba

In Partial Fulfillment
of the Requirements for the Degree
MASTER OF SCIENCE

by
J. Wallace Hamm
April, 1969



ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. R. J. Soper, Associate Professor, Department of Soil Science, University of Manitoba, for his supervision during the course of study as well as for his criticisms of the manuscript.

He also wishes to acknowledge the efforts of Dr. R. A. Hedlin, Professor and Head of the Soil Science Department, for his criticism of the manuscript; Dr. G. J. Racz, Assistant Professor in the same Department, and Dr. B. R. Stefansson, Associate Professor, Department of Plant Science, for serving on the examination committee.

Appreciation is also expressed to Mr. L. E. Emery, Technician, Department of Soil Science, for his laboratory assistance and to my wife for her patience during the study period and for typing the manuscript.

The financial assistance from the National Research Council in the form of a bursary is acknowledged as well.

ABSTRACT

A field experiment, conducted in the summer of 1967, disclosed that total N:S ratios of plants in the early stages of growth can be used to evaluate their sulfur status. The critical ratios above which rape and barley are sulfur deficient were suggested to be 12:1 and 16:1, respectively. The critical sulfur concentration in rape at the flowering stage was proposed to be 0.25% total sulfur. The water soluble SO_4 fraction of soils was further evaluated as an index of plant available sulfur. A critical level of 10 lb/Ac to the 24 inch depth at seeding was suggested for cereals. The corresponding value for rape was thought to be in the range of 20 to 25 lb/Ac.

The relative rates of nitrogen and sulfur mineralization in soils were studied under field and laboratory conditions. The mean ratio of $\text{NO}_3\text{-N}:\text{SO}_4\text{-S}$ release in soils cropped to rape and barley at two sites was found to be 4.3:1. This ratio was somewhat narrower than that observed in the laboratory experiment. The ratios of release in soils of the Chernozemic and Podzolic Orders after incubation for 12 weeks at 18°C and near field capacity moisture content were 11.9:1 and 28.4:1 respectively. Nitrogen was found to be released faster than sulfur. The amounts of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ released on incubation were correlated to the organic matter content of the soils.

Table of Contents

Chapter		Page
I	Introduction	1
II	Literature Review.	2
III	Field Experiment	12
	Introduction.	12
	Materials and Methods	12
	Results and Discussion.	16
IV	Incubation Experiment.	43
	Introduction.	43
	Materials and Methods	43
	Results	46
	Discussion.	58
V	Summary and Conclusions.	62
VI	Bibliography	65
VII	Appendix	71

List of Tables

Table		Page
I	Mean organic C:N:S ratios in soils of the world.	3
II	Suggested critical total sulfur levels and N:S ratios for some common field crops at the growth stages indicated.	10
III	Some chemical and physical characteristics of the soils selected as well as designation and past history.	13
IV	Yield of rape and barley as affected by different levels of applied nitrogen, phosphorous, and sulfur.	17
V	Water soluble NO_3^- nitrogen (ppm) in rape and barley with and without sulfur at different times during the growing season on two sites.	22
VI	Changes in accumulated NO_3^- -N and SO_4^{2-} -S during the intervals from spring (1967) to harvest, fall, and the following spring (1968); and from harvest to fall, as considered to different depths in the unfertilized soils cropped to rape or barley, or fallowed.	29
VII	Designation and chemical and physical characteristics of the soils incubated.	44
VIII	The amounts and ratios of NO_3^- -N and SO_4^{2-} -S released by some soils during incubation, as affected by temperature and moisture.	48
IX	Nitrogen and sulfur relationships in the soils as compared to the ratios of release on incubation.	55
X	Summary of carbon, nitrogen and sulfur relationships in the soils studied as related to N and S release.	56

List of Figures

Figure		Page
1	Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in rape during the growing season at the Kitching site.	19
2	Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in rape during the growing season at the Armstrong site.	19
3	Total nitrogen and sulfur (a) content and (b) ratios in rape during the growing season at the Surminsky site.	20
4	Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in barley during the growing season at the Kitching site.	20
5	Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in barley during the growing season at the Armstrong site.	21
6	Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in barley during the growing season at the Toews site.	21
7	Total water soluble (a) $\text{NO}_3\text{-N}$ and (b) $\text{SO}_4\text{-S}$ in the Surminsky soils during the sampling period.	31
8	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in fallow soils at Surminsky site: (a) spring (b) 18 days (c) 40 days (d) 60 days (e) 81 days after seeding.	32
9	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to barley at Surminsky site: (a) spring (b) 18 days (c) 40 days (d) 60 days (e) 81 days after seeding.	33
10	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to rape at Surminsky site: (a) spring (b) 18 days (c) 40 days (d) 60 days (e) 81 days after seeding.	34

List of Figures (Con't.)

Figure		Page
11	Total water soluble (a) $\text{NO}_3\text{-N}$ and (b) $\text{SO}_4\text{-S}$ in the Kitching soils during the sampling period.	35
12	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in fallow soils at the Kitching site: (a) spring (b) 18 days (c) 44 days (d) 65 days (e) 86 days (f) fall, 152 days after seeding.	36
13	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to barley at the Kitching site: (a) spring (b) 18 days (c) 44 days (d) 65 days (e) 86 days (f) fall, 152 days after seeding.	37
14	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to rape at the Kitching site: (a) spring (b) 18 days (c) 44 days (d) 65 days (e) 86 days (f) fall, 152 days after seeding.	38
15	Total water soluble (a) $\text{NO}_3\text{-N}$ and (b) $\text{SO}_4\text{-S}$ in the Armstrong soils during the sampling period.	39
16	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in fallow soils at the Armstrong site: (a) spring (b) 18 days (c) 43 days (d) 64 days (e) 87 days (f) fall, 151 days after seeding (g) spring of 1968.	40
17	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to barley at the Armstrong site: (a) spring (b) 18 days (c) 43 days (d) 64 days (e) 87 days (f) fall, 151 days after seeding (g) spring of 1968.	41
18	Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to rape at the Armstrong site: (a) spring (b) 18 days (c) 43 days (d) 64 days (e) 87 days (f) fall, 151 days after seeding (g) spring of 1968.	42

List of Figure (Con't.)

Figure		Page
19	NO ₃ -N and SO ₄ -S released upon incubation at: (a) 10°C, (b) 18°C and (c) 30°C.	49
20	Nitrogen and sulfur mineralized by a Poppleton C soil during incubation at 18°C and F.C. moisture.	50
21	Nitrogen and sulfur mineralized by soils with different internal drainage: (a) Erickson A, 0.80% CaCO ₃ eq. (b) Erickson B, 2.89% CaCO ₃ eq.	51
22	Nitrogen and sulfur mineralized by a Winkler soil during incubation at 18°C and F.C. moisture.	52
23	Nitrogen and sulfur mineralized by a Thalberg soil during incubation at 18°C and F.C. moisture.	52
24	Relative amounts of NO ₃ -N and SO ₄ -S released during incubation at 30°C (means of two moisture contents).	53
25	Relationship between organic matter content and sulfur mineralization in 15 soils.	54
26	Relationship between total sulfur content and sulfur mineralization in 14 soils.	54
27	Relationship between total sulfur and organic matter content in 14 of the soils examined.	57
28	Relationship between total nitrogen and sulfur content in 14 of the soils examined.	57

I INTRODUCTION

The role of sulfur in plant nutrition is fairly well defined at present. Recent research has indicated that sulfur and nitrogen are required in relatively constant ratios by plants. A limiting supply of one of these nutrients has been found to result in the accumulation of the other in soluble forms in the plant as well as in subsequent reduction of plant growth. Consequently, total N:S ratios are considered as a means of evaluating the sulfur status of plants, provided that nitrogen is not limiting growth.

Similarly, the sulfur supplying power of a soil can be described in terms of the relative rates of nitrogen and sulfur mineralization. If the ratios of available nitrogen to sulfur released in a soil are smaller than or correspond to the ratios of plant requirement, sulfur will not limit plant growth.

Research on sulfur as a macro-nutrient in Manitoba soils previous to that reported in this thesis concentrated on defining the regions which were possibly deficient in sulfur and on devising a chemical test for available soil sulfur supplies. The water soluble SO_4 fraction was found to be a practical and reliable index of these supplies. The adsorbed sulfur fraction, also readily available to plants, was not found to be important in Manitoba soils.

The objectives of research described in this thesis were to provide further information on the sulfur status and supplying power of Manitoba by:

- a) determining the critical total N:S ratios in two representative crops under field conditions;
- b) further evaluating the water soluble SO_4 fraction as an index of plant available sulfur;
- c) determining the rates of sulfur mineralization relative to that of nitrogen under field and laboratory conditions.

II LITERATURE REVIEW

Sulfur Status of Soils

The increasing awareness in recent years of the essential and sometimes limiting nature of sulfur to plant growth has prompted a corresponding interest in the status and transformation of soil sulfur. The chemical nature and forms of sulfur and the plant availability of these forms as well as their interconversion in the soil have been of particular interest. The apparent analogy between the sulfur and nitrogen cycles has resulted in investigations in sulfur parallel to those performed on nitrogen. Total organic carbon, nitrogen and sulfur relationships are well established, but information on their relative rates of transformation to inorganic forms is scant.

The total sulfur content in a surface soil will vary, depending on age, texture, and prevailing climate; values generally range from .006% to .120%. Evans and Rost (18) noted that 73% of the total sulfur in six Chernozemic surface soils of Minnesota was organic, while only 50% in 11 Podzolic soils was organic. Total and organic sulfur decrease sharply with depth in a soil profile. Lowe (31) noted a mean total sulfur content of 435 ppm in eight Alberta Chernozemic Ah horizons. Corresponding Bm horizons contained a mean of 273 ppm. Podzolic soils were found to contain a mean of 700 ppm for L-H layers and 80 ppm for Bt horizons. Since L-H horizons are destroyed on clearing it is evident that Podzolic soils are most likely to be sulfur deficient. The inorganic sulfur in a soil occurs largely as sulphates, some of which are soluble and move in drainage water, and to lesser extent as mineral sulfides.

Organic C:N:S ratios in soils reported in various agricultural areas of the world (Table I) are relatively similar even though methods of analysis differ. Ratios are consistently wider in Podzolic and acid surface soils than in Chernozemic and alkaline soils (18, 54). Limited data available on cultivated soils (25, 56) would indicate that they are characterized by wider ratios than undisturbed soils.

Variation among soils is greater than the mean values reported would suggest. C:S ratios in samples of undisturbed Scottish soils varied from 62 to 154, while N:S values ranged from 5.9 to 10.6. Evans and Rost (18) noted that the mean value for Chernozemic organic N:S ratios was 8.7; that for Podzolic soils was 17.4. Variation in these values was greatest among Podzolic soils. Considerable significance has been attached to C:S and N:S ratios in recent studies since it is felt that these may be used to identify sulfur deficient soils. Unfortunately most of the studies were done on virgin soils and are not truly indicative of relationships under cultivation. A project in Oregon indicated that the mean organic N:S ratio for a cross section of agricultural soils was 10:1.

Table I

Mean organic C:N:S ratios in soils of the world.

Area	Soil Description	C:N:S Ratio
N. Scotland (56) ³	¹ Non-calcareous	140:10:1.4
Minnesota (18)	Podzolic	135:10:1.3
	Chernozem + Bl. Prairie	116:10:1.5
N. Zealand (48)	Pasture	130:10:1.3
E. Australia (54)	² Acid	152:10:1.2
	Alkaline	140:10:1.5
N. Australia (53)	Podzolic, pasture	155:10:1.4
Oregon (25)	¹ Cross section	145:10:1.0
Miss. (36)	Cross section	126:10:1.1

¹ Cultivated agricultural soils.

² C:N non-sulphate ratio calculated.

³ Bibliography numbers.

The close intercorrelation between organic carbon, nitrogen, and sulfur (36, 48, 56) in soils has been one of the main reasons for considering sulfur transformations in a soil on a basis similar to carbon and nitrogen.

Sulfur Fractions

Extensive studies (18, 19, 31, 33) on the various organic and inorganic soil sulfur fractions have been reported, but considerably less information on their importance and availability for plant and microbial uptake is available. The amount of total sulfur in a surface soil is largely dependent on climatic conditions, with highest levels occurring under conditions favourable to the formation of Black soils. Soils occurring in areas of very high and very low rainfall, i.e. in the Podzolic and Brown soil zones respectively, contain the lowest amounts of total sulfur.

Research on organic sulfur has indicated that a considerable portion of this fraction exists in an inert and highly resistant form. Lowe (31) noted an inert fraction in four of his soils in amounts ranging from 2-44% of their total sulfur content. Evans and Rost (18), in an earlier study, concluded that their determination of "non-sulfate" sulfur consisted of an inert form of organic sulfur plus mineral sulfides. "Humus" sulfur, as denoted by the same workers, consists of the sulfur in organic matter extracted by dilute alkali solutions. This fraction was noted to be fairly constant (mean of 58 ppm) in the Black Prairie soils of Minnesota, and consistently higher than in Podzolic types (mean of 12 ppm). Humus sulfur was considered to be in the final stages of decomposition and hence of considerable importance in determining the sulfur supplying power of a soil.

Workers (19, 31, 32, 33, 55) now agree that a significant portion of the total sulfur in a soil exists as organically bound SO_4 groups. Lowe and DeLong (32, 33) obtained a release of easily soluble SO_4 on successive

extractions with dilute agents and considered this as well as other more direct determinations as evidence of organically bound SO_4 groups in their soils. Covalently bonded SO_4 groups in ester linkages were suggested responsible for this "carbon bonded" sulfur in soils. Similarly, Williams and Steinbergs (55) concluded that their "heat-soluble" SO_4 extraction consisted of easily soluble SO_4 plus groups split off from the organic fraction during heating. Anderson (2) found a good correlation ($r=.96^{**}$) between this determination and sulfur uptake by rape, confirming the theory that the organically bound SO_4 is indicative of soil sulfur reserves.

The inorganic fraction exists mainly as non-sulfate minerals characteristic of the parent material and to a lesser extent of sulfates occluded in calcite crystals or precipitated as insoluble salts of barium. Easily soluble sulfates, and in a few cases adsorbed sulfate are the smallest but most significant fractions of the inorganic soil sulfur, since they are available for plant and microbial use. Since adsorption processes are not operative in Manitoba soils suspected to be deficient in sulfur (2), it seems apparent that easily soluble and organically bound SO_4 would be indicative of the amount of available sulfur in Manitoba soils. Lowe (31) considered "HI-reducible" SO_4 , an estimate of organically bound plus inorganic SO_4 , to be the most important potential forms of sulfur for crop use. He also noted a clear dichotomy between Grey Wooded and Chernozemic soils on the basis of this fraction as well as easily soluble, adsorbed, and organically bound SO_4 , suggesting that these fractions are a criterion of sulfur supply.

Transformations in the Soil and Plant

A. Physical

The rates and mechanisms of physical SO_4 transformations in a soil are obscure at present. Thought to be at least similar to NO_3 movement, the mechanism is considered as a stepwise adsorption--desorption process

analogous to adsorption chromatography. Chao, Harward, and Fang (13) using S^{35} tagged sulfur in leaching columns, noted a SO_4 movement of 20 inches upon the addition of water equivalent to eight inches of rainfall. The amount of movement of the anion was proportional to the water added, and was increased by the addition of $CaCO_3$ and phosphate compounds.

B. Chemical

Although almost inseparable from biological transformations in a soil, there are several chemical reactions involving sulfur which are independent of microbial activity. Solution--precipitation reactions with calcium influenced by moisture, common ions, and ionic strength determine SO_4 behaviour in arid soils. Adsorption phenomena, dependent on pH, and clay mineral and sesquioxide content, are important in acid fine textured soils where they influence sulfate leaching rates and plant availability. Non-biological oxidation--reduction systems, such as that involving the oxidation of sulfides by the reduction of Mn^{4+} , are significant in acid soils as well.

C. Biological

Biological transformations of sulfur by both plant and micro-organisms dominate the soil sulfur system. The above ground portion of the "organic sulfur cycle" is relatively well understood (1). Sulfur, taken up by plants largely as SO_4 and SO_2 from the air in small amounts (46), is reduced to the sulfhydryl (SH-) form and incorporated in amino acids and other compounds characteristic of the species involved. Any SO_4 not required to satisfy the relatively constant protein N:S ratio (38, 40) accumulates in the cell sap. The intermediates which occur during the decomposition of plant residues are thought to follow the sequence: $R-SH \rightarrow RSO_2H \rightarrow RSO_3H \rightarrow SO_3H \rightarrow SO_3 \rightarrow SO_4$ (51). Because of structural

similarities between the amine (NH_2^-) and SH^- groups, many workers feel that the process of microbial stabilization of SH^- groups in a soil parallels that of the NH_2^- group.

Mineralization Patterns and Determining Factors

Original attempts to characterize sulfur mineralization in a soil concentrated on studies of SO_4 production from inorganic sources (23). Mineralization from organic sources, and the factors which affect the patterns and rates of SO_4 release, have only recently received significant attention (6, 19, 21). Incubation studies (3, 7, 36, 52) over periods ranging from two to four months indicate that four types of release occur: (i) a rapid initial rate of release followed by gradual decrease in rate with time, (ii) a gradual decrease in rate, (iii) a linear rate of release, (iv) an initial negative rate of release followed by gradual increase in rate with time. Several investigators (7, 50, 52) have noted that ratios of nitrogen:sulfur released are greater than total N:S ratios and that SO_4 is released from a soil at a slower rate than NO_3 . Williams (52) reported that ratios of N:S release increased with time, further supporting this theory. Many factors appear to affect the rates of release of nitrogen and sulfur since they are usually not closely related to total N:S ratios and show considerable variation among soils. Williams (52) recorded ratios of $\text{NO}_3\text{-N}:\text{SO}_4\text{-S}$ released after incubation for two weeks which ranged from 3.4 to 60.0 for a mean of 12.8. White (50) noted a range of 9.9 to 37.1 after four weeks of incubation.

A. Effect of Environment During Incubation

Sulfur and nitrogen mineralization appear to be affected by environment in a similar manner. Williams (52) recorded little sulfur mineralization at temperatures below 10°C . and reported increased mineralization with an increase in temperature to a maximum of 35°C . Optimum moisture conditions

for mineralization occurred at or slightly below field capacity. Addition of CaCO_3 stimulated SO_4 and NO_3 release, possibly due to increased pH which is believed more favourable for growth of the bacteria concerned. High soil pH's are also thought to enhance release of SO_4 by increasing chemical hydrolysis of organic residues as well as by releasing adsorbed SO_4 . Alternate wetting and drying of soils during incubation have also been noted to increase SO_4 as well as NO_3 release.

Root growth is thought to stimulate sulfur release by some workers and to depress it by others. Freney and Spencer (21) observed net immobilization of added sulfur in soils incubated without plants and net mineralization in the presence of plants. Sulfur would differ from nitrogen in this respect since the increased microbial population in the rhizosphere generally is thought to immobilize any mineral nitrogen released until death of the plant (24, 57). Evidence for any real effect of root growth on sulfur mineralization is small at present.

B. C:S Ratios in Plant Residues and Sulfur Mineralization

Recent investigations (3, 4, 6, 20) have implied that residual C:S ratios influence sulfur mineralization in a manner analogous to the relationship between residual C:N ratios and nitrogen mineralization. It is now apparent that the C:S ratio in freshly added organic residues determines the rates and patterns of inorganic sulfur release from them (7). The existence of SO_4 immobilization phenomena have been suggested and supported by several workers (15, 45).

Barrow (4, 6) reported that a soil with a C:S ratio of less than 200 would accumulate SO_4 on incubation. Soils with values in the range of 200-400 either immobilized or mineralized small amount of SO_4 , while those with values greater than 400 tied up SO_4 in organic matter. He felt that an interaction between freshly added plant residues and soil organic residues could occur, resulting in enhanced decomposition of the latter. Nitrogen supply during incubation had little effect on sulfate release.

Plant Sulfur Requirements Relative to Nitrogen

The sulfur requirement of a crop has been defined as "the minimum uptake of this nutrient associated with maximum yield of dry matter" (41). The sulfur requirements of some common representative field crops based on Manitoba field trials and a review of the literature are as follows:

- (i) rape yielding 2,200 pounds of seed/A requires 35 pounds of sulfur/A.
- (ii) alfalfa yielding 6,000 lb/A requires 18 pounds of sulfur/A.
- (iii) wheat yielding 2,400 pounds of seed requires 9 to 12 pounds of sulfur/A.

Diagnostic Criteria

Determination of sulfur deficiency by plant analysis is based on a knowledge of the "critical level" of this element in the plant. Above this level there is "luxury consumption" and below it there is "poverty adjustment" until the completely limiting concentration is reached (17). Total sulfur has long been used as a criterion of plant sulfur status; typical levels at different stages of sufficiency are given in Table II.

Recent research (38, 40, 47) has indicated that the N:S ratio in the protein of common field crops is relatively constant throughout the growing season. Stewart and Whitfield (44) varied the levels of nitrogen and sulfur available to wheat and noted a mean protein N:S ratio of 15.1:1. Pumphrey and Moore (38) and Diukshoorn (16) made similar observations, concluding that any excess nitrogen and sulfur taken up accumulates in the plant as NO_3 and SO_4 , or other non-protein forms. If one of these nutrients is limiting growth, the other accumulates in the plant. The protein N:S ratio of 15:1 has been observed in other field crops as well and appears to be an acceptable constant.

The knowledge of the constancy of the protein N:S ratio has led first to the consideration of SO_4 content, and more recently, total N:S ratios as criteria for plant sulfur status. Anderson (2) noted an accumulation of SO_4 in rape when the crop ceased to respond to additional increments of applied sulfur. Several workers (34, 38, 44) have observed that the total N:S ratios in a plant are constant at a given growth stage and

Table II

Suggested critical total sulfur levels and N:S ratios for some common field crops at the growth stages indicated.

Crop Plant Part, Stage & Reference	Total S (%)			N:S Ratio	
	S Deficient	Critical Level	S Sufficient	S Deficient	S Sufficient
Alfalfa					
Tops, 1/3 bloom (25)	.10-.15	.22	.30-.40	-	-
Tops (9)	-	.20	-	-	-
Tops, bloom (38)	-	-	-	15-25	11.0
Tops, bloom (40)	-	-	-	-	10.6
Clover					
Whole (28)	-	-	-	24	14
Cotton					
Whole (44)	-	.13	-	-	15.0
Whole, early bud (35)	-	.15	-	-	-
Peanuts	-	-	-	-	13-15
Sugar Beets					
Leaves (41)	-	.12-.13	-	-	-
Wheat					
Whole (44)	-	-	-	-	17.0

concluded that this ratio is more indicative of the sulfur status of a plant than sulfur content alone. Table II includes total N:S ratios for some common crops. These ratios differ from the protein N:S ratio noted earlier because of varying non-protein nitrogen and sulfur requirements.

Diagnostic criteria in the soil include a host of extractants too numerous to mention--all have been used in an attempt to estimate the readily available sulfur in a soil. A few unique determinations such as "heat soluble SO_4 " (55), have been devised in order to extract the "labile" organic SO_4 not normally removed by other agents. Water and dilute phosphate solutions

show the most promise as standard soil test procedures. Phosphate solutions are favoured by many (3) because of their ability to extract adsorbed SO_4 , as well as their favourable effect on filtration procedures.

Since adsorption processes were found to be negligible in coarse textured, well drained soil in Manitoba, i.e. soils most apt to be sulfur deficient, Anderson (2) suggested that the water soluble $\text{SO}_4\text{-S}$ content of these soils would be an adequate sulfur criterion. He suggested that 10 lb of water soluble $\text{SO}_4\text{-S}$ in the upper 24 inches of soil are adequate for most crops. Similarly, Walker¹ working on Grey Wooded soils in Alberta has had considerable success in using the water soluble SO_4 content of soils as a criterion of plant available sulfur. He proposed that the S content of the surface 12 inches only need be considered. He has suggested that 10 lbs. of water soluble $\text{SO}_4\text{-S}$ to this depth are adequate for legumes.

¹ Background research on sulfur analysis. 1967 Report of the Western Section of the National Soil Fertility Committee Meeting; and personal communication.

III FIELD EXPERIMENT

Introduction

The purposes of a field experiment carried out at four sites during the summer of 1967 were threefold. The experiment was primarily designed to investigate total N:S ratios in rape and barley as affected by varied soil and fertilizer nitrogen and sulfur supplies, and to provide further information on the water soluble SO_4 test as a criterion of available soil sulfur. In addition, an attempt was made to characterize nitrogen and sulfur mineralization processes in the profiles of fallow and non-fertilized cropped soils by measuring water soluble $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ during the growing season.

Materials and Methods

A. Soils

The soils for the plot sites were selected on the basis of drainage, texture, and water soluble SO_4 content, with emphasis on the soils which Anderson (2) designated as possibly deficient in available sulfur. Two of the soils chosen belonged to the Almasippi association (Armstrong and Kitching sites) with levels of water soluble $\text{SO}_4\text{-S}$ at and above the critical level (10 lb /Ac to 2 feet) suggested by Anderson (2). Both these sites were moderately well drained, although the Kitching soil had an impeding clay layer at the 36-48 inch depth, accounting for the higher SO_4 content. The other two sites belonged to the Stockton association.

A summary of chemical characteristics for all the sites is given in Table III. A more detailed description of the Almasippi profiles is given in Table 1A (appendix). The latter provided an interesting comparison since the only measured difference between them appeared to be the water soluble $\text{SO}_4\text{-S}$ content.

Table III

Some chemical and physical characteristics of the soils selected as well as designation and past history.

Characteristics	Plot Designation			
	Armstrong	Kitching	Toews	Surminsky
Association	Almasippi VFS	Almasippi VFS	Stockton SL	Stockton LS
Subgroup	Rego Black	Rego Black	Orthic Black	Orthic Black
Legal Description	NE-33-7-5W	SE-18-7-4	SE-21-13-15	SW-15-10-12
Past History	Fallow	Crop (Barley)	Crop (Oats)	Crop (Oats)
Seeding Date (1967)	May 22'nd	May 22'nd	May 17'th	May 20'th
pH (0-6")	7.5	7.5	6.1	6.5
NO ₃ -N Content (lb/Ac to 2')	14.4	13.1	15.1	1.6
SO ₄ -S Content (lb/Ac to 2')	11.3	28.8	6.7	13.2
NaHCO ₃ Extractable Phosphorous (lb/Ac) 0-6"	25.9	12.7	20.3	28.1
6-12"	15.6	4.2	-	-
Exchangeable K ⁺ (lb/Ac) 0-6"	238	198	588	393
6-12"	162	174	284	293

B. Experimental Design

The trials consisted of five treatments, including one fallow, arranged in a randomized complete block design with six replicates. Nitrogen, phosphorous, and sulfur were applied to rape, Brassica napus (Target), and barley, Hordeum vulgare (Conquest) in the amounts and combinations listed in Table IV. Nitrogen and sulfur were broadcast by hand, phosphorous was applied with the seed. The carriers were NH_4NO_3 (33.5-0-0), $\text{NH}_4\text{H}_2\text{PO}_4$ (11-55-0), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and a urea plus $(\text{NH}_4)_2\text{SO}_4$ blend (34.0-0-0). Sulfur was applied as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in treatment 3 and as $(\text{NH}_4)_2\text{SO}_4$ in treatment 4. All experimental units consisted of plots 3.5 feet by 30 feet. The 95N + 20P and 95N + 20P + 30S treatments (#2 and #3) were applied to adjacent units to enable sampling of plant material during the growing season. A six row 'V-belt' seeder was used to apply seed and drilled fertilizers. The fallow plots were tilled periodically and kept free of weed growth. Recommended rates of T.C.A. were applied with a hand sprayer to control wild millet in rape.

C. Sampling Technique

Soil samples were taken to a depth of four feet at time of seeding and at three week intervals during the growing season from the fallow and non-fertilized rape and barley treatments on all sites except Toews. Samples were taken with a $1\frac{1}{2}$ inch screw auger, air dried and ground to pass through a 2 mm sieve prior to analysis. Composites of corresponding depths for each treatment and time of sampling were made and subsampled for water soluble NO_3 and SO_4 determination. The samples taken in spring were analyzed on a replicate basis to determine the variability within the plots. Regular sampling procedures were terminated at harvest; fall samples at the Kitching and Armstrong locations, and a spring sampling at the latter site were taken and prepared in the same manner.

Plant samples of both crops with and without added sulfur (#2 and #3)

were taken at three week intervals beginning six weeks after seeding and extending till harvest. All samples, including the final harvest, were taken as 10 foot cuts of the center two rows of each experimental unit. Samples taken prior to final harvest were air dried, weighed, and ground to pass through a 2 mm mesh sieve. Composites of the six replicates for each treatment at each sampling date were made in a manner analogous to that used on soils. These composites were then subsampled for total Kjeldahl nitrogen, total sulfur, and NO_3 nitrogen determinations. Samples obtained at the final harvest were threshed and prepared in a similar manner, with the exception of the rapeseed which was not ground in order to prevent oil losses and to facilitate laboratory procedures.

D. Analytical Procedures

The NO_3 -N content of the soils was determined colorimetrically using the phenoldisulfonic acid method (11). A water extract with a soil to water ratio of 1:4 (w/w) was used. The color intensities were measured on a Coleman Junior 6A colorimeter at a wavelength of 415 m μ . The readings obtained were compared to a standard curve ranging from 1 to 100 ppm.

The SO_4 sulfur content of the soils was determined by a modification of the turbidimetric method described by Chesnin and Yien (14). Fifty gm of soil in 100 ml of distilled water were shaken for 30 minutes on a reciprocating shaker; 1.8 to 2.0 gm of NaCl and $\frac{1}{2}$ teaspoon of washed charcoal were added, and the shaking continued for an additional 30 seconds. A 25 ml aliquot of the filtered extract was placed in a 150 ml beaker. Three ml of a 100 ppm SO_4 in 6N HCl solution were added to provide precipitation centers. Exactly 0.2 gm of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals (20-30 mesh) were then added to the extract and the solution stirred for 1 minute. The optical density of samples and standards were read against distilled water five minutes after the barium chloride was added. A Coleman 6A colorimeter set at a wavelength of 420 m μ was used. Adjustments to all readings were made by subtracting the optical density of a chemical blank run with each set of samples.

Soil pH was measured in a soil--0.01M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ suspension using the glass indicating and calomel reference electrodes in conjunction with a Canlab pH Meter 22, type PHM22p. The electrical conductivity of soil-paste extract was measured with a Canlab Model RC16B2 Conductivity Bridge. The CaCO_3 content of the soils was determined by gravimetric measurement of CO_2 liberated on digestion with HCl as described by Black (11).

The total nitrogen content of plant material was determined by the macro-Kjeldahl method as detailed by Black (11). Total sulfur analysis of plant material consisted of acid digestion and oxidation of sulfur to SO_4 followed by turbidmetric determination of the latter as outlined by Blancher, Rehm, and Caldwell¹. Water soluble NO_3 nitrogen was measured by adapting the method used for NO_3 determination in soils; 0.5 gm of plant material in 50 ml of extraction solution were allowed to soak overnight to ensure lysis of the plant cells. The suspension was then treated exactly as described above for soils.

Results and Discussion

A. Nitrogen-Sulfur Relationships in Rape and Barley

Drought conditions severely reduced the growth of both barley and rape on the Stockton soils. Rape did not germinate at the Toews site; yields of barley and rape on the Surminsky location were very poor. Sampling procedures on the latter were performed, but yield data were not recorded. Observations at the Toews site were limited to periodic plant samples and the final harvest. The Almasippi soils had adequate moisture and good growing conditions throughout; all phases of the study were carried out at these locations.

¹ Contained in a publication of the Dept. of Soil Science, University of Minn., U.S.A.

The final seed yields of rape and barley as affected by nutrient application are given in Table IV. Total dry matter yields, measured at intervals during the growing season, are included in Tables 2A and 3A (appendix). Substantial yield increases due to applied nitrogen and phosphorous were realized and anticipated at all sites in view of the available supplies of these nutrients in the soil.

Increases in rapeseed yields due to added sulfur were noted on both Almasippi sites. A 40% increase in yield due to sulfur (significant at 1% level) added as $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$ occurred at Armstrong's and a 15% increase in yield was noted at Kitching's (not significant). Barley yields were not affected by addition of sulfur, although a visual response was noted at the Armstrong site. Barley plants treated with sulfur at this location appeared darker in color and more succulent than untreated plants in the early part of the growing season. These observations, however, were not substantiated by differences in dry weight of plant material collected.

Table IV

Yield of rape and barley as affected by different levels of applied nitrogen, phosphorous, and sulfur.

Treatment No.	Nutrients Applied (lb/Ac)			Seed Yields				
	N	P	S	Rape (lb/Ac)		Barley (bus/Ac)		
				Armstrong	Kitching	Armstrong	Kitching	Toews
1	0	0	0	955	642	32.3	27.9	16.1
2	95	20	0	1572	1523	67.0	57.3	32.1
3	95	20	30	2197	1794	66.0	53.7	33.5
4	95	20	30	2115	1720	66.0	57.1	33.9
		L.S.D.						
			.05	400	381		-N.S.- ¹	
			.01	593	565			

¹ Effect due to added sulfur.

The total amounts and ratios of nitrogen and sulfur utilized by the rape and barley at various times during the growing season were determined for the plant material grown with and without added sulfur. The values obtained for rape (Table 2A, appendix) indicate that nitrogen utilization by this crop was not affected by applied sulfur (Figure 1a and 2a). The total N:S ratios of rape grown without added sulfur were widest on the Armstrong site, particularly in the early part of the growing season (Figure 1c, 2c and 3b). The ratio after 40 days growth at the Armstrong site was 20.3:1.0 as compared to 7.1:1.0 for rape grown at the Kitching location.

Nitrogen content in rape decreased sharply with time on all sites, as did sulfur content on the slightly responsive (Kitching) site (Figure 1b, 2b and 3a). Total sulfur content in rape grown with added sulfur increased with time on the highly responsive (Armstrong) site (Figure 2b). The relationships existing between nitrogen and sulfur contents and ratios in rape grown at the Surminsky site (Figure 3a and 3b) were similar to those noted at the Armstrong location, suggesting that this soil was also low in available sulfur.

The total nitrogen and sulfur contents of barley grown with and without added sulfur (Table 3A, appendix) also indicate that nitrogen utilization is not affected by applied sulfur. Patterns of nitrogen and sulfur absorption by barley were similar to those noted for rape (Figures 4a, 5a and 6a).

The N:S ratios of the plants grown on the non-sulfur treatment (#2) of the Armstrong site were appreciably wider than corresponding values observed for the other plots (Figure 5c). This would indicate that a response to sulfur may have occurred early in the growing season.

NO₃ nitrogen accumulations (Table V) in rape and barley were greatest in the non-sulfur treatment (#2) of the Armstrong site at the first date sampled. Concentrations of 1,862 and 1,016 ppm were detected for rape and barley respectively. Sulfur deficiencies were visually apparent in rape on this treatment and resembled the symptoms described and photographed by Anderson (2). Characteristic cupping and purple discoloration of the leaves were evident.

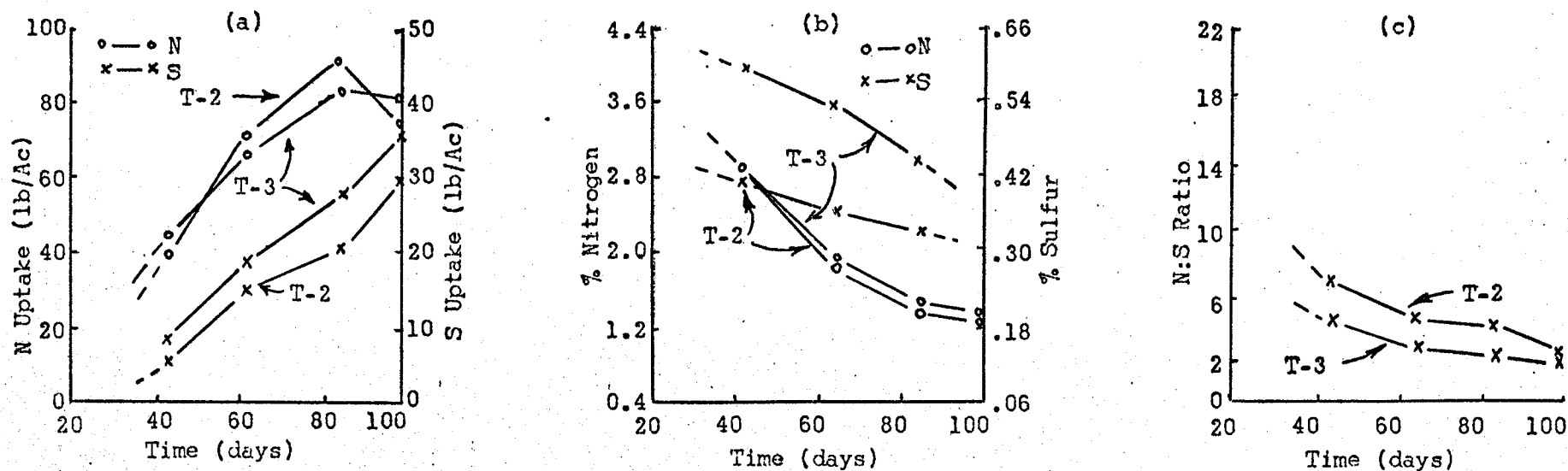


Figure 1. Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in rape during the growing season at the Kitching site.

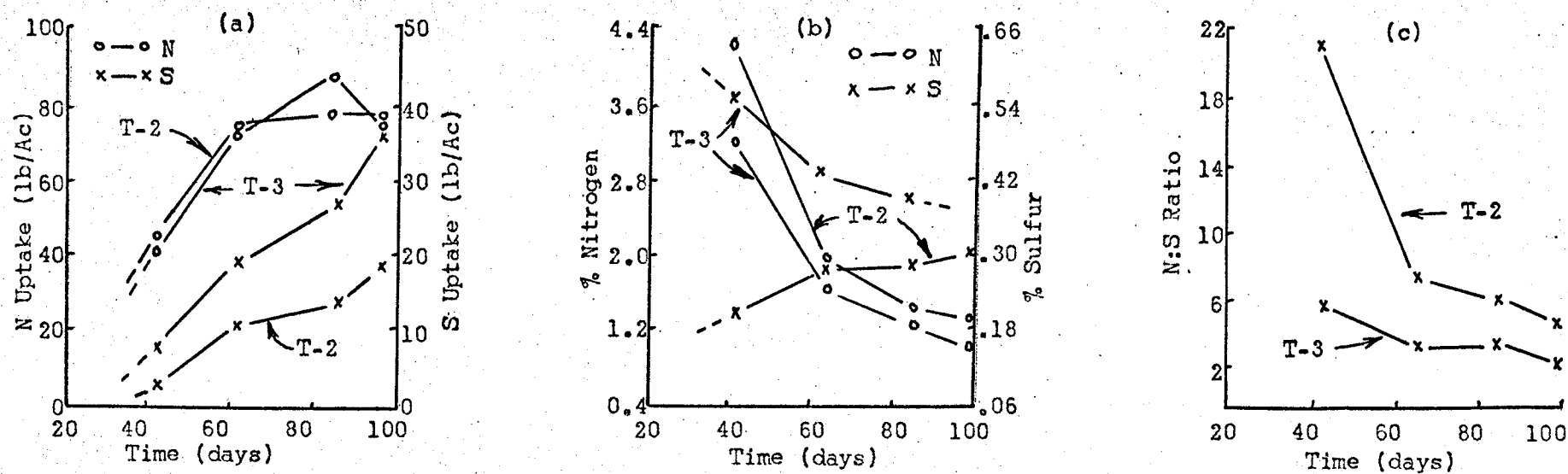


Figure 2. Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in rape during the growing season at the Armstrong site.

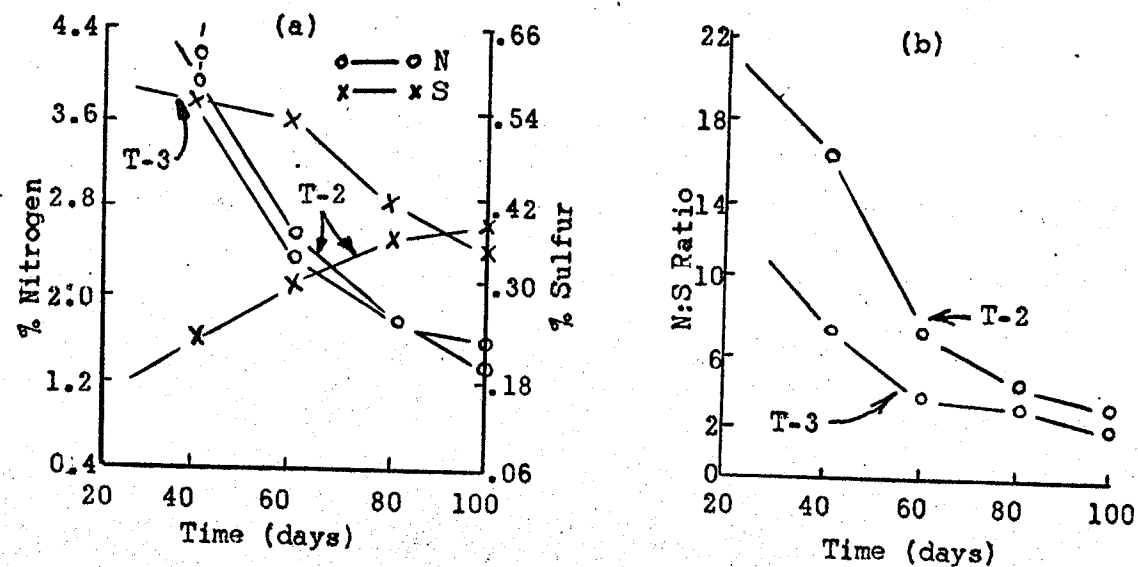


Figure 3. Total nitrogen and sulfur (a) content and (b) ratios in rape during the growing season at the Surminsky site.

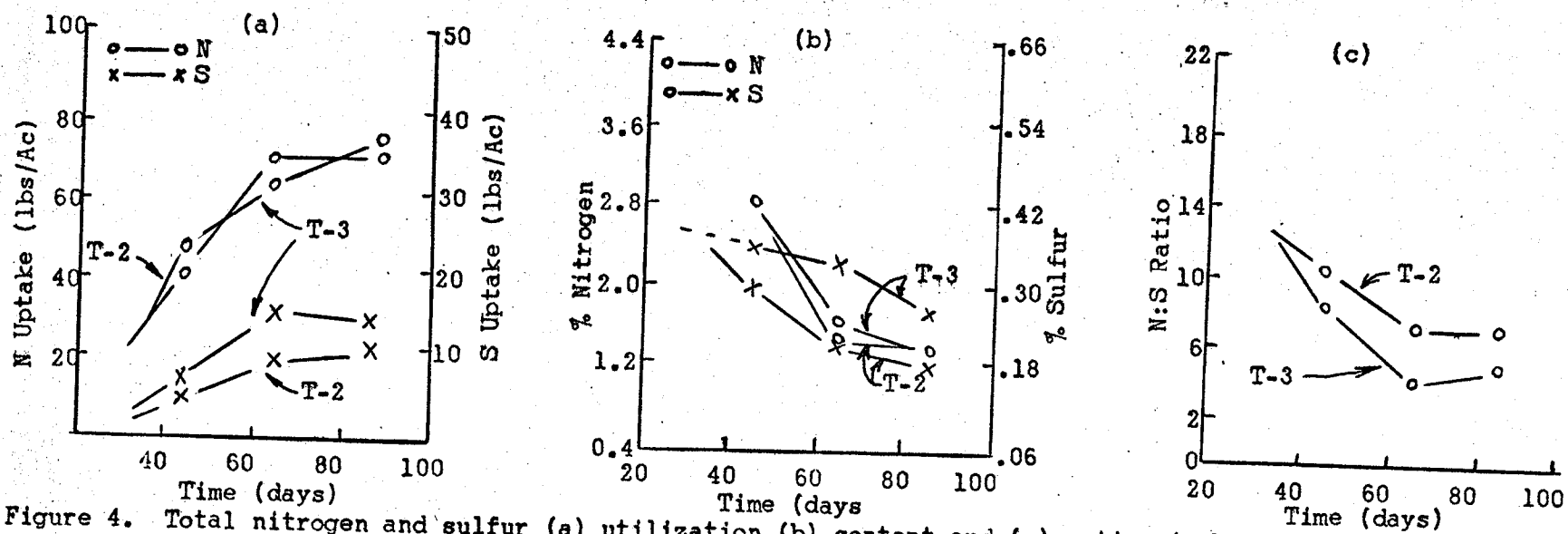


Figure 4. Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in barley during the growing season at the Kitching site.

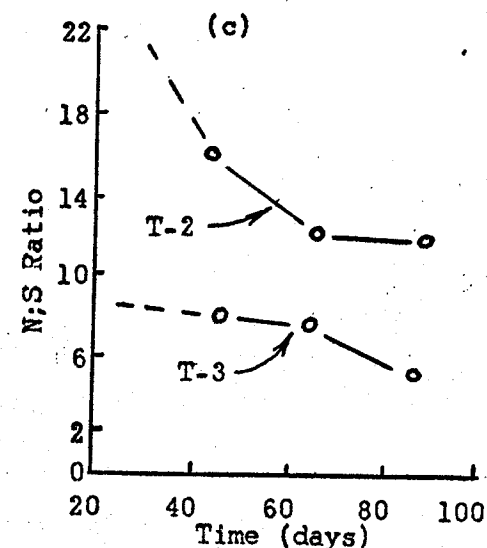
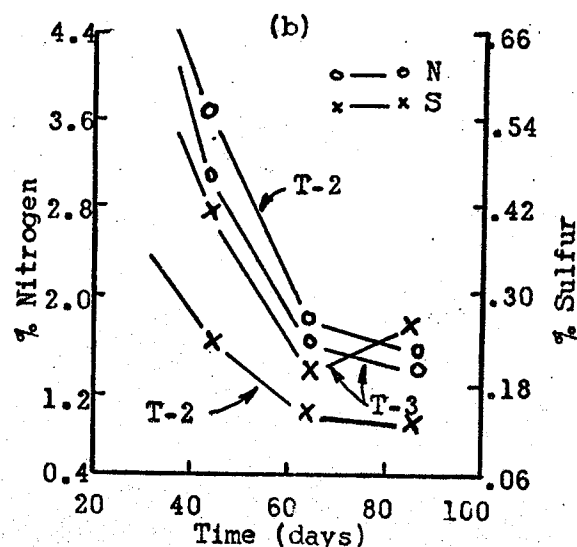
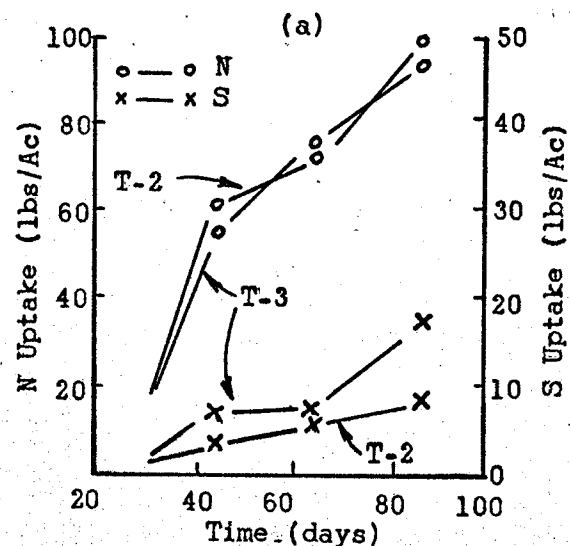


Figure 5. Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in barley during the growing season at the Armstrong site.

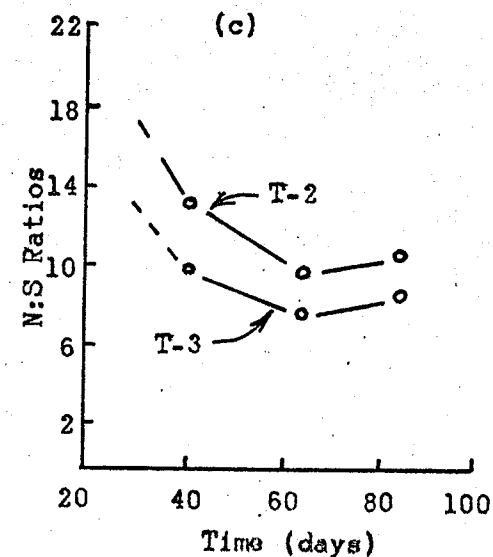
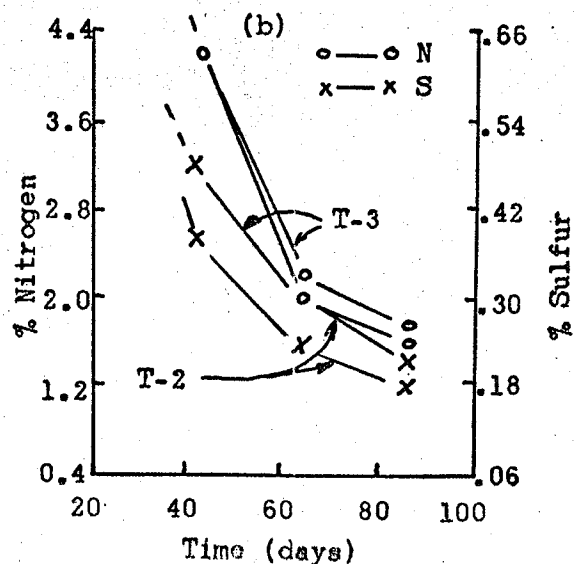
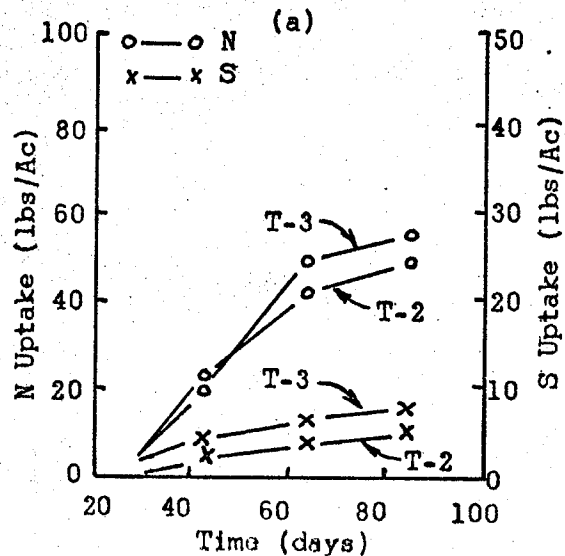


Figure 6. Total nitrogen and sulfur (a) utilization (b) content and (c) ratios in barley during the growing season at the Toews site.

Table V

Water soluble NO_3 nitrogen (ppm) in rape and barley with and without sulfur at different times during the growing season on two sites.

		Time After	Rape		Barley	
Site	Date	Sowing (days)	N+P	N+P+S	N+P	N+P+S
Kitching						
	July 4	44	207	170	83	167
	July 26	65	60	66	39	119
	Aug. 16	86	71	60	40 ¹	30
	Aug. 29	99	27	30	-	-
Armstrong						
	July 5	43	1,863	336	1,016	558
	July 25	64	221	119	125	81
	Aug. 16	87	142	51	44 ¹	41
	Aug. 29	99	37	27	-	-

¹ Final harvest sample.

Since water soluble SO_4 sulfur content was the only measured chemical difference noted between the Kitching and Armstrong sites, these locations provide a comparative study of sulfur responsive and non-responsive soils, respectively. The available sulfur content of the soil at the Kitching site was adequate for cereals and almost so for rape. At the Armstrong site, available soil sulfur supplies were just sufficient for cereals, but definitely insufficient for rape.

Further support for the consideration of the water soluble SO_4 -S content in Manitoba soils at seeding time as a criterion for plant available sulfur, particularly in coarse textured soils, is lent by the following observations: (i) SO_4 adsorption processes are insignificant in Manitoba soils (2), hence it is apparent that water soluble SO_4 and SO_4 released from organic sites or mineralized are the only immediate and potential plant available forms, (ii) deficient soils, particularly coarse textured ones, are usually quite

low in organic matter and have little potential for release of sulfur during the growing season as indicated by the results of an incubation experiment described in Chapter IV, (iii) the amounts of SO_4 which are mineralized in these soils are small relative to SO_4 movements in drainage water. Therefore, a measure of the amount of water soluble SO_4 in a soil at seeding time is probably the best indication of sulfur supply in coarse textured soils.

Several factors, as evident from this experiment and work done elsewhere, should be considered in determining the depth to which a soil profile should be sampled to estimate the amount of water soluble SO_4 sulfur available to a plant. SO_4 ions are readily leached from surface soil horizons, as indicated by the low SO_4 contents in samples obtained in the fall (Table VII) for the incubation experiment. The changes in SO_4 distribution noted in the mineralization aspect of the field study also suggest that water soluble SO_4 ions are readily leached from surface layers. Also, SO_4 changes due to mineralization and capillary movement were noted to be greatest in the second and third feet of the soils examined in this study. Plant roots are known to absorb SO_4 sulfur from depths of two feet and greater (37). In addition, a good relationship has been noted to exist between uptake of sulfur by rape and the amount of water soluble SO_4 sulfur in the upper 24 inches of several Manitoba soils (Table 8A). All of these factors suggest that soil profiles should be sampled to a depth greater than the plow layer.

If the upper 24 inches of a soil profile is considered as an adequate sample depth, the results of this experiment and the observations of others (2) suggest that 10 lb of water soluble SO_4 sulfur to this depth at seeding time is adequate for cereal crop production. The sulfur requirements of rape are somewhat higher than that of cereals perhaps in the range of 20 to 25 lb of SO_4 sulfur. If a profile is sampled to less than 24 inches, the suggested critical levels would decrease proportionally. SO_4 sulfur supplies at depths greater than 24 inches are considered to be of decreasing importance to crop production on the basis of this study.

Generally, the well-drained coarse textured sands and Grey Wooded soils of Manitoba can be suspected of having SO_4 sulfur levels in the ranges noted above. The actual soil types have been discussed previously (2).

The observations made on nitrogen and sulfur relationships in rape and barley in this experiment are similar to those reported by others for common field crops (40, 44). Nitrogen absorption was not affected by sulfur supply in this study. It is suggested that any excess nitrogen over that required to satisfy the protein N:S ratio of these crops, accumulates in the plant in soluble forms, predominantly NO_3 and amino compounds. Rape has a high sulfur requirement relative to that of cereals such as barley, and is considerably more sensitive to available sulfur supplies. The glucoside and mustard oils in rapeseed are high in sulfur and account for this relative difference. The (total) N:S ratio of this crop is relatively narrow as a result.

The fact that the protein N:S ratios of the different plant species are fairly constant at specified growth stages (16) proposes that total N:S ratios are a better criterion of plant sulfur status than either total sulfur or SO_4 sulfur content. The additional analysis required to calculate this ratio ensures that nitrogen has not been a limiting growth factor. Total N:S ratios clearly identify the sulfur deficient rape treatments in this experiment and appear to be a good criterion for evaluating the sulfur status of plants.

From the observations on total N:S ratios made in this study, it is suggested that a ratio of less than 12:1 at the four week stage in rape is sufficient for normal growth. A corresponding critical ratio of 16:1 is suggested for barley. If total sulfur content is considered as an index of sulfur supply, the analyses of rape grown on sulfur deficient sites in Manitoba (Table 8A, appendix) suggest that a content of less than 0.25% at flowering is indicative of a sulfur deficiency in this crop. This value is meaningful only when other nutrients are not limiting growth.

B. Field Mineralization Study

The soils of the non-fertilized rape and barley treatments and the fallow plots of the Surminsky, Kitching and Armstrong sites were sampled periodically during the growing season in an effort to characterize water soluble NO_3 and SO_4 relationships in a soil profile under field conditions. Of particular interest were the times and relative amounts of these nutrients mineralized.

Considerable variation in the amounts of NO_3 and SO_4 accumulated in the cropped and fallowed soils was noted (Figures 7, 11 and 15). However, the maximums or minimums in accumulated NO_3 and SO_4 in the soils of any given treatment occurred simultaneously in many instances. The $\text{NO}_3\text{-N}$ content of all the fallowed plots reached a maximum and then declined sharply by the middle of August (harvest date), with the exception of the fallow plots at the Armstrong site. A net deficit over the entire sampling period was noted at this site when $\text{NO}_3\text{-N}$ content to the fourth foot was considered. The pattern described above for the other plots was, however, evident at this site when $\text{NO}_3\text{-N}$ to 12 or 24 inches was considered. The soil $\text{NO}_3\text{-N}$ levels of the fallow and non-fertilized crop treatments were essentially the same at harvest time.

Maximum accumulations of $\text{NO}_3\text{-N}$ in the unfertilized soils cropped to barley at the Kitching and Armstrong trials were greater than those noted in fallow soils. The maximums also occurred earlier in the season in soils cropped to barley. $\text{NO}_3\text{-N}$ measurements in the unfertilized soils cropped to rape were not made during the interval when the maximums described above were noted. However, the apparent similarities during the remainder of the sampling period would suggest that early maximums in accumulated NO_3 had occurred in soils cropped to rape as well.

The $\text{SO}_4\text{-S}$ content of the unfertilized-cropped soil profiles appeared related to the $\text{NO}_3\text{-N}$ contents at the Surminsky and Kitching locations (Figures 7 and 11). Little resemblance was noted between accumulated $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils of the remaining fallow or cropped treatments sampled.

An accumulation of SO_4 occurred early in the growing season in the Surminsky fallow plots. Little or no accumulation of SO_4 was observed in the fallow plots of the Kitching and Armstrong sites. The occurrence of maximums in accumulated $\text{SO}_4\text{-S}$ in unfertilized soils cropped to barley paralleled those observed for $\text{NO}_3\text{-N}$. Slight accumulations of $\text{SO}_4\text{-S}$ in unfertilized soils cropped to rape were noted at the six week sampling date.

The quantitative changes¹ in $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ content to different depths in unfertilized soils cropped to rape and barley show net gains of both nutrients in the top two feet during the interval from spring to fall (Table VI). Net losses of $\text{SO}_4\text{-S}$ in unfertilized-cropped soils were noted when changes to 36 and 48 inches over this same interval were considered. Generally, both $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ contents of fallowed soils decreased by harvest time with the exception of the Surminsky site where little change in $\text{NO}_3\text{-N}$ content and an accumulation of 19.6 lb/Ac of $\text{SO}_4\text{-S}$ to four feet were noted. The losses of $\text{NO}_3\text{-N}$ during the growing season were greatest in soils of the Armstrong site. The increases in $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ content of cropped soils after harvest (part (B) Table VI) were considerably greater after barley than after rape.

The changes in $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ during the growing season as discussed above are illustrated more fully by the distribution of these ions in the soil profile (Figures 9 to 10, 12 to 14, and 16 to 18). The $\text{NO}_3\text{-N}$ accumulations in fallowed soils occurred in the upper 12 inches of the profile. The decrease in $\text{NO}_3\text{-N}$ content of fallowed soils by harvest time appears to have occurred in sub-surface horizons. The maximums in accumulated NO_3 in unfertilized soils cropped to barley corresponded to increases in the upper 24 inches (Figure 9, 13, and 17).

¹ Net changes in unfertilized cropped soils were calculated as follows:

$$\Delta \text{NO}_3\text{-N} = \text{Total N}_c - (\text{NO}_3\text{-N}_s - \text{NO}_3\text{-N}_h)$$

Where: c = crop; s = spring; h = harvest.

The distribution of $\text{SO}_4\text{-S}$ in the soil profiles was found to be more variable than $\text{NO}_3\text{-N}$ and did not appear to be related to it. Some similarities between the distribution of these ions during the growing season were evident in cropped soils (Figures 13, 14 and 17). The accumulation of $\text{SO}_4\text{-S}$ in the Surminsky fallow plots occurred in the second and third foot of the profile. The maximums in accumulated $\text{SO}_4\text{-S}$ in cropped soils at the Armstrong site also occurred at this depth (Figures 17 and 18).

The decreases in $\text{NO}_3\text{-N}$ content of the Almasippi fallow soils were probably due to leaching processes. These losses were greater for the Almasippi soils than for the Stockton soil. Approximately 27 lb of $\text{NO}_3\text{-N}$ originally in the soil was lost from the 0-48" depth in one year at the Armstrong site. An additional 27¹ lb of $\text{NO}_3\text{-N}$ mineralized during the summer months were also probably leached out of the profile. Approximately 8.3 inches of precipitation, distributed as designated in Table 7A was received on the Almasippi trials from seeding to harvest time. Precipitation at the Stockton site was insufficient for crop growth.

The effects of this precipitation were evident in the redistribution of NO_3 and SO_4 in the soils at the Armstrong site (Figures 16, 17 and 18). A marked downward displacement of SO_4 during the interval of the second and third sampling dates was evident in the soil at this site. Approximately 4.2 inches of rainfall was recorded in this interval. This site had been fallowed during the previous year resulting in a marked accumulation of NO_3 in the lower horizons of the profile (Figure 16a). This accumulation of $\text{NO}_3\text{-N}$, as well as the amount mineralized, had been leached from the sampling zone by the end of the second year of fallow (Figure 16g). Cropping of this soil resulted in a greater accumulation of

¹ This value represents the mean increase in $\text{NO}_3\text{-N}$ noted in unfertilized cropped soils. It is assumed that mineralization of nitrogen under crop and fallow are the same.

both $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ than fallowing.

Little evidence of NO_3 or SO_4 redistribution in the Stockton soil (Surminsky) was noted, although some upward movement of SO_4 was apparent. As a result, the data collected from this location represent changes in situ.

In view of the NO_3 and SO_4 redistribution by water movement in the fallowed Almasippi soils, the changes during the year were not considered in terms of mineralization processes. Leaching activities in cropped soils, however, were not as great as suggested by the accumulations of NO_3 and SO_4 noted early in the growing season. Therefore, mineralization activities in these soils are best described by the changes in $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ detected in the unfertilized-cropped soils.

The general lack of resemblance between NO_3 and SO_4 distributions in the soil profiles is in disagreement with the conclusions of some workers such as Harward and Reisenauer (26). Their lysimeter studies led them to believe that soluble inorganic nitrogen and sulfur have similar profile distributions. Although evidence of such a similarity was noted at the Armstrong site where leaching effects were greatest (Figures 16a and 16g, 17d, 17f and 17g) most of the NO_3 and SO_4 distributions showed little resemblance to one another.

There are several possible reasons why the distribution of NO_3 and SO_4 in the soil profiles were not similar: (i) differential crop uptake, mineralization and movement of the two ions involved; (ii) the sources of these ions and the systems in which they are in equilibrium with are not the same; NO_3 ions are essentially in equilibrium with an organic system whereas SO_4 ions are in equilibrium with both an organic and an inorganic system; in the latter, the factors which affect the solubility of sulfates, such as CaSO_4 and MgSO_4 as well as sulfates co-precipitated with CaCO_3 , will have a bearing on the amount of water soluble SO_4 in a soil under a given condition; (iii) adsorption processes are also considerably more important in the sulfur system than they are in that of the nitrogen system.

If the net changes in the amounts of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ to the 24 inch depth in the Almasippi soils cropped without added fertilizer (Table VI)

Table VI.

Changes in accumulated $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ during the intervals from spring (1967) to harvest, fall, and the following spring (1968); and from harvest to fall, as considered to different depths in the unfertilized soils cropped to rape or barley, or fallowed.

Treatment and Locations	(A) Changes in NO ₃ -N and SO ₄ -S (lb/A) from initial spring sampling to periods designated								(B) Changes in NO ₃ -N and SO ₄ -S (lb/A) harvest to fall		
	to 24"		to 36"		to 48"		Spr.	to 24"	to 36"	to 48"	
	Har.	Fall	Har.	Fall	Har.	Fall					
<u>Fallow</u>											
Surminsky (Stockton)	NO ₃ -	3.9	-	-0.1	-	-3.3	-	-	-	-	-
	SO ₄ =	4.4	-	12.0	-	19.6	-	-	-	-	-
Kitching (Almasippi)	NO ₃ -	-8.4	0.0	-10.3	-0.3	-12.5	-1.4	-	8.4	10.0	11.1
	SO ₄ =	-7.7	-3.0	-43.0	3.2	-23.3	-23.5	-	4.7	46.2	-0.2
Armstrong (Almasippi)	NO ₃ -	-12.9	1.6	-23.2	-5.1	-34.9	-15.9	-27.4	14.5	18.1	19.0
	SO ₄ =	-1.6	-8.7	0.6	-4.6	3.7	-1.3	0.9	-7.1	-5.2	-5.0
<u>Barley Check Plot</u>											
Kitching (Almasippi)	NO ₃ -	-19.4	26.3	17.5	24.8	16.4	26.0	-	6.9	7.3	9.6
	SO ₄ =	0.4	0.8	-15.6	-9.8	-67.9	-45.6	-	0.4	5.8	22.3
Armstrong (Almasippi)	NO ₃ -	22.6	38.4	12.3	30.9	-3.2	19.7	28.8	15.8	18.6	22.9
	SO ₄ =	4.4	12.1	8.9	14.3	12.0	17.4	10.9	7.7	5.4	5.4
<u>Rape Check Plot</u>											
Kitching (Almasippi)	NO ₃ -	22.1	25.6	27.6	26.0	25.7	24.9	-	-3.5	-1.6	-0.8
	SO ₄ =	5.2	9.7	-8.9	-9.8	-56.1	-62.3	-	4.5	0.9	-6.2
Armstrong (Almasippi)	NO ₃ -	18.8	33.3	8.0	24.0	-6.8	11.4	7.7	14.5	16.0	18.2
	SO ₄ =	13.6	7.4	11.3	8.8	19.8	11.9	16.6	-6.2	-2.5	-7.9

are considered as representative of mineralization--immobilization relationships in these soils, then 32 lb of $\text{NO}_3\text{-N}$ and 7 lb of sulfur were mineralized in soils cropped to barley. Soils cropped to rape released 30 lb of $\text{NO}_3\text{-N}$ and 9 lb of $\text{SO}_4\text{-S}$. Since plant uptake of nitrogen and sulfur during the growing season was not measured on the unfertilized crop treatments, no comment as to when this mineralization occurred or how important it was to plant growth can be made. However, the NO_3 accumulations under fallow at the Surminsky site suggest that nitrogen mineralization activities are greatest in the latter periods of the growing season and do not contribute to the available sulfur supply to the extent as previously has been thought.

The ratios of $\text{NO}_3\text{-N}:\text{SO}_4\text{-S}$ released in cropped soils were 5.0:1.0 and 3.5:1.0 for barley and rape, respectively. These ratios are somewhat narrower than the mean of 11.6:1.0 noted for the same soils when incubated at 18°C and near field capacity moisture (Chapter IV). The ratios of release in these soils are adequate for crop growth.

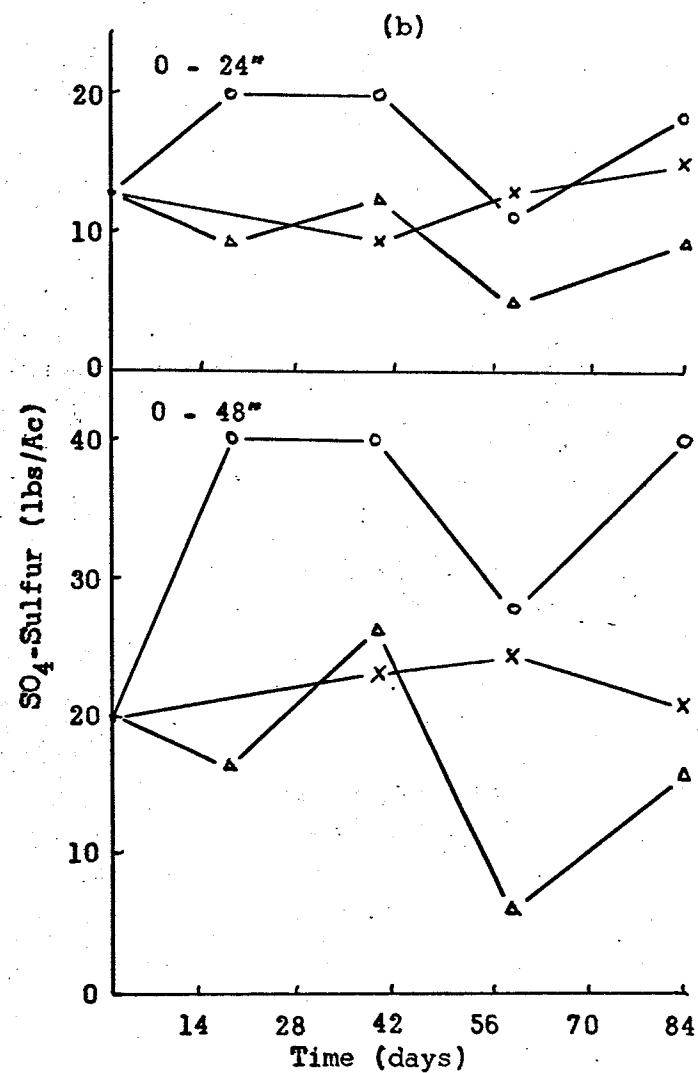
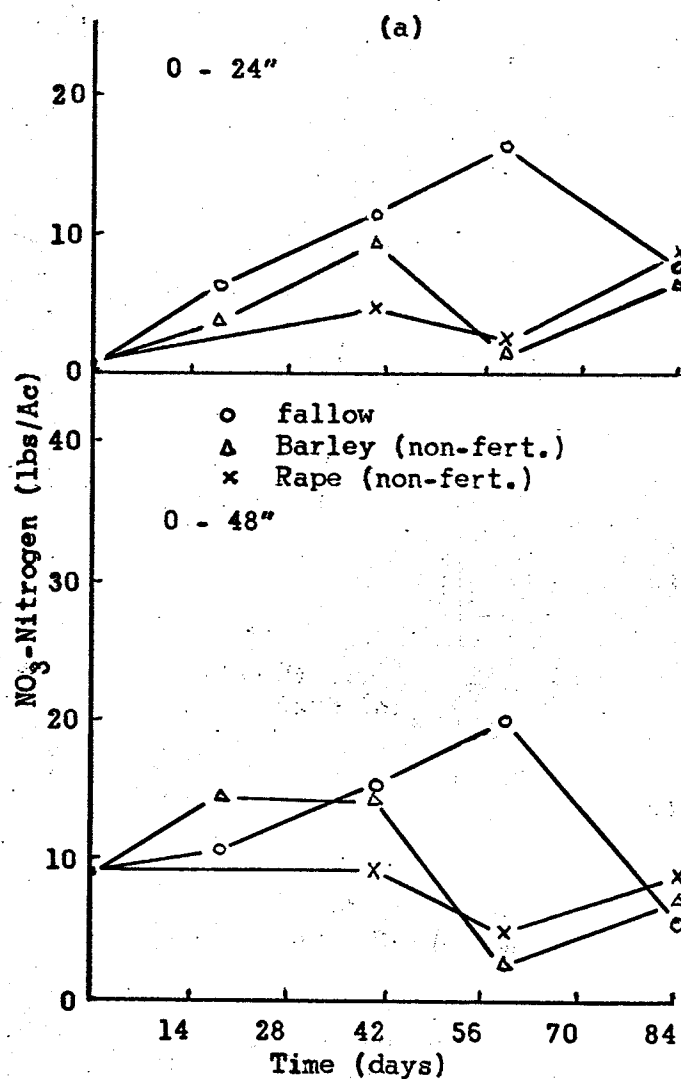


Figure 7. Total water soluble (a) NO₃-N and (b) SO₄-S in the Surminsky soils during the sampling period.

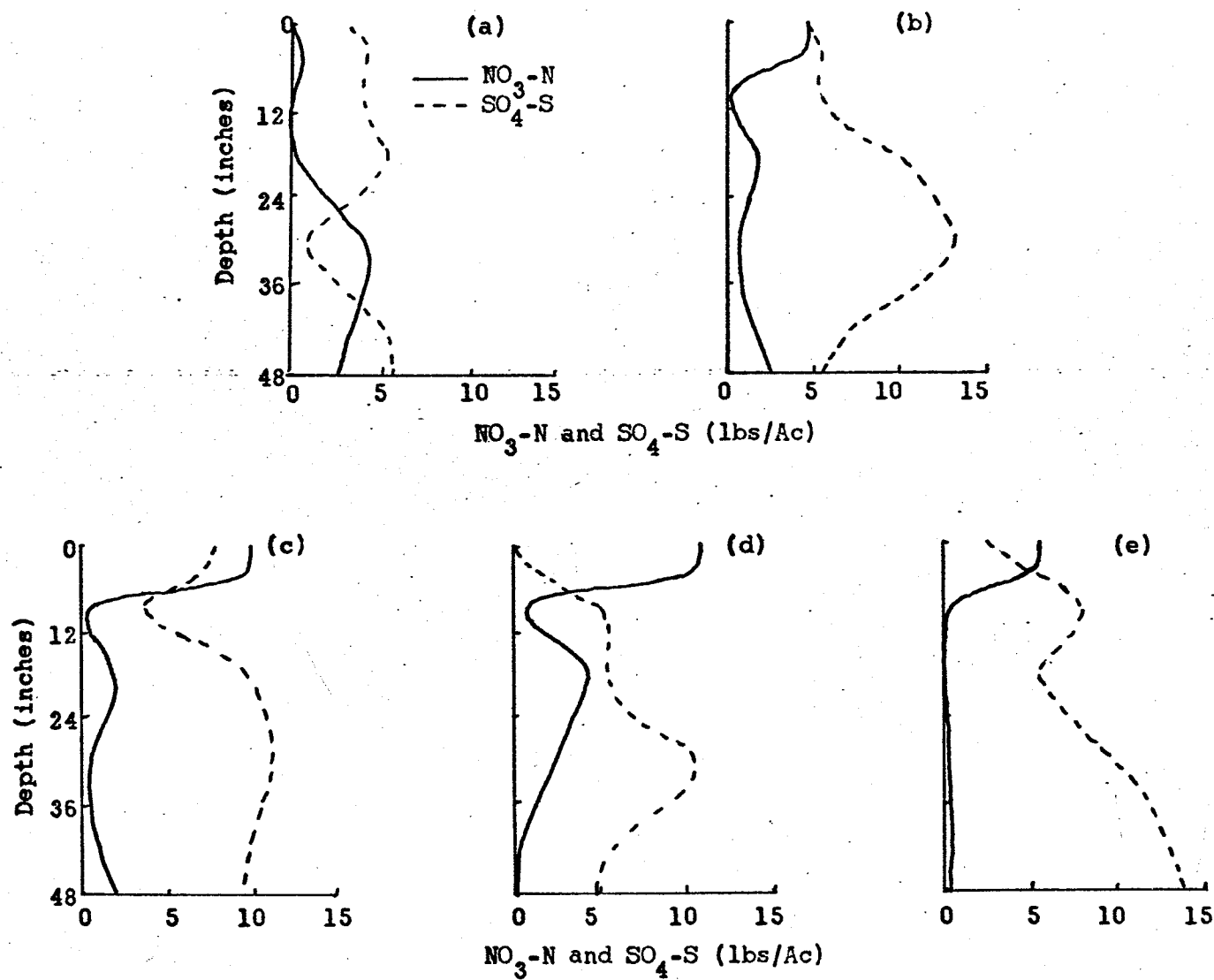


Figure 8. Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in fallow soils at the Surminsky site: (a) spring (b) 18 days (c) 40 days (d) 60 days (e) 81 days after seeding.

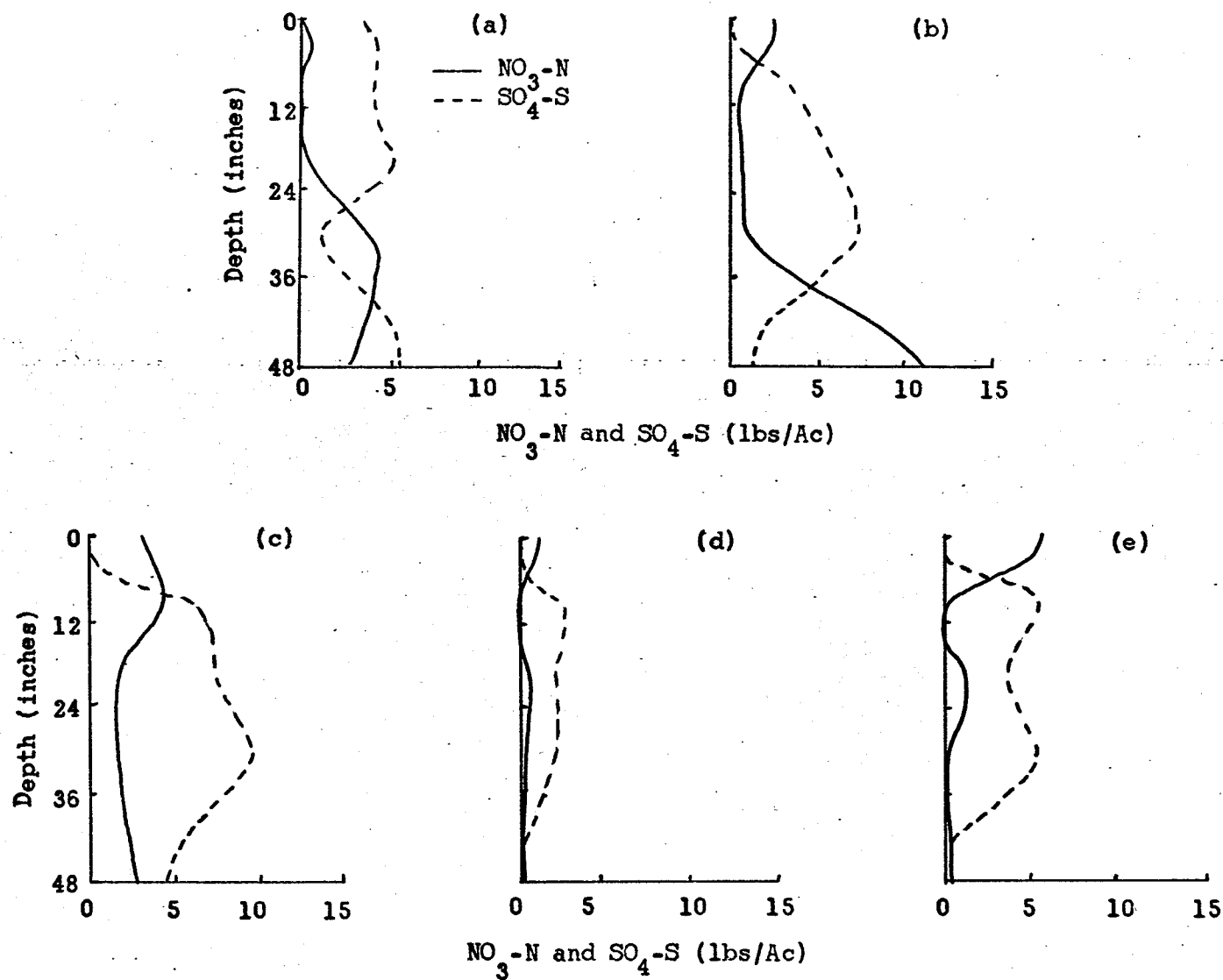


Figure 9. Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to barley at the Surminsky site: (a) spring (b) 18 days (c) 40 days (d) 60 days (e) 81 days after seeding.

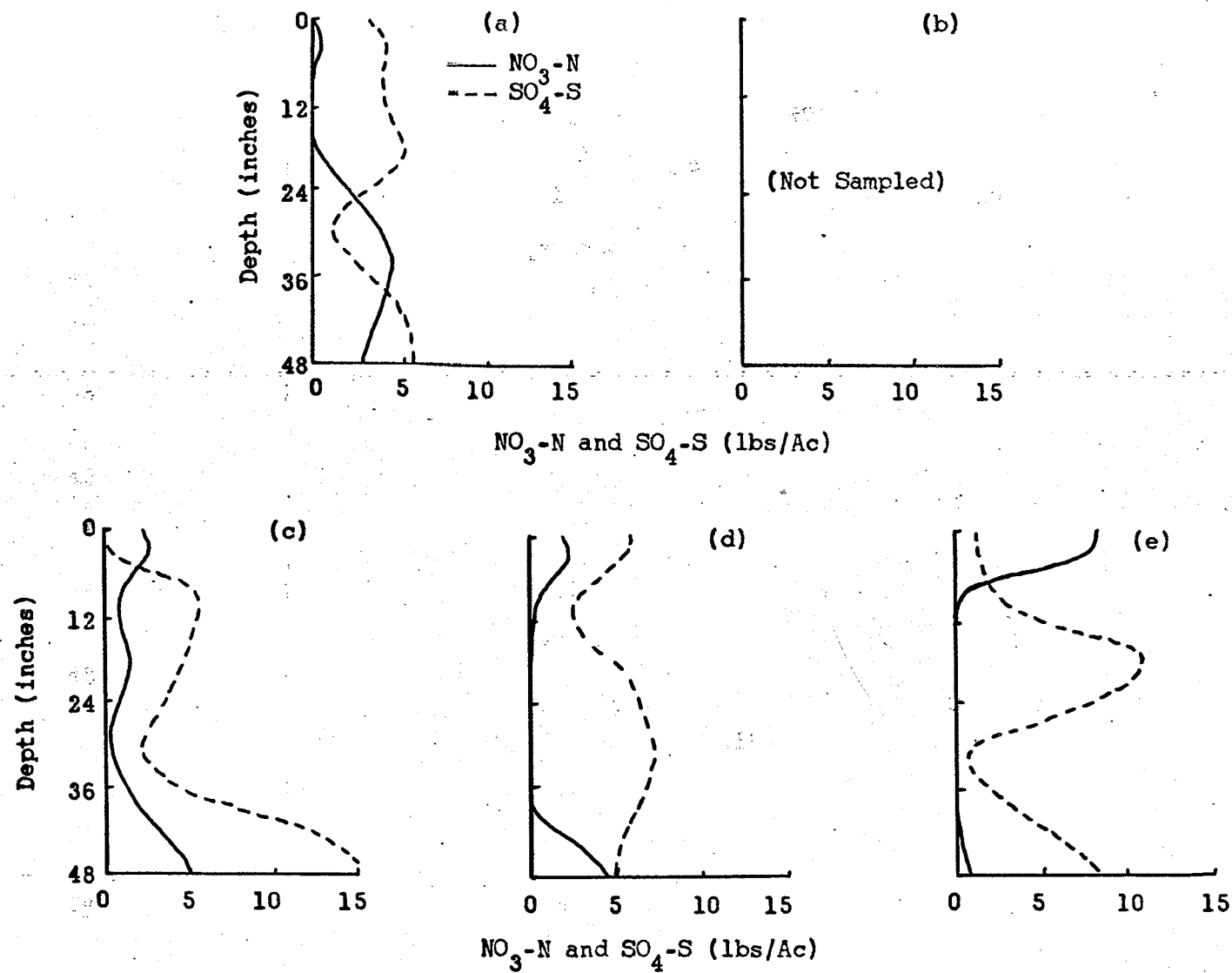


Figure 10. Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to rape at the Surminsky site: (a) spring (b) 18 days (c) 40 days (d) 60 days (e) 81 days after seeding.

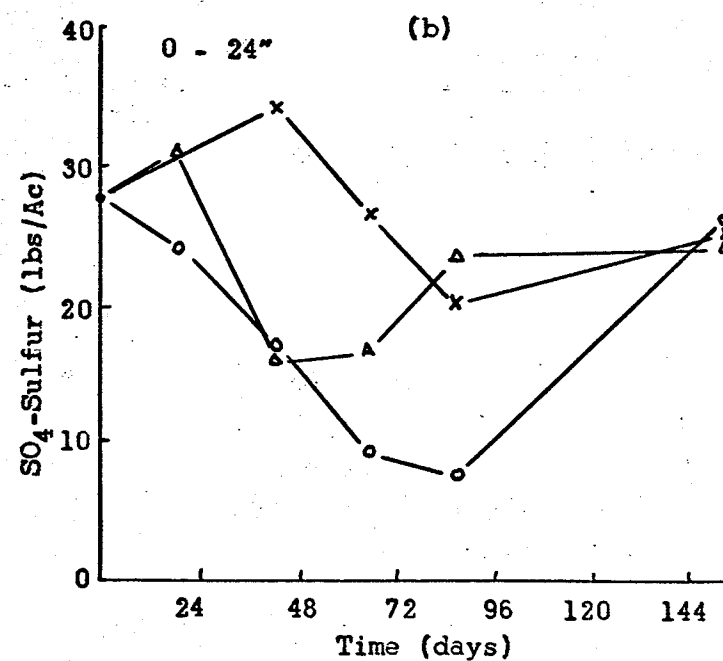
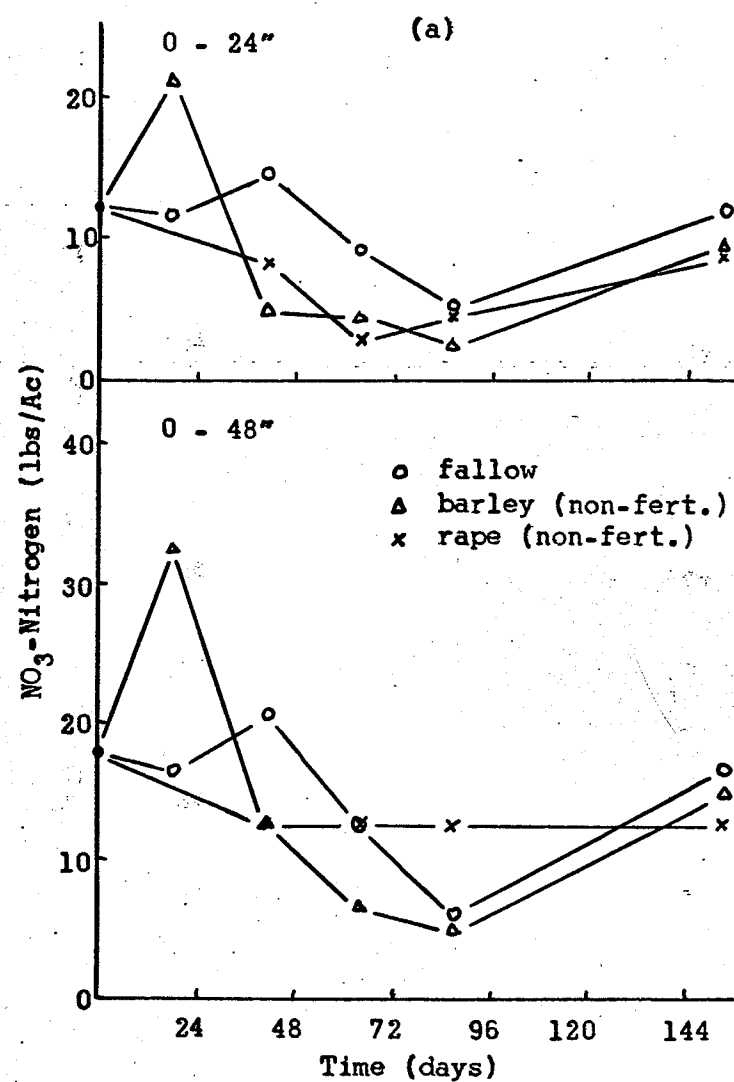


Figure 11. Total water soluble (a) NO₃-N and (b) SO₄-S in the Kitching soils during the sampling period.

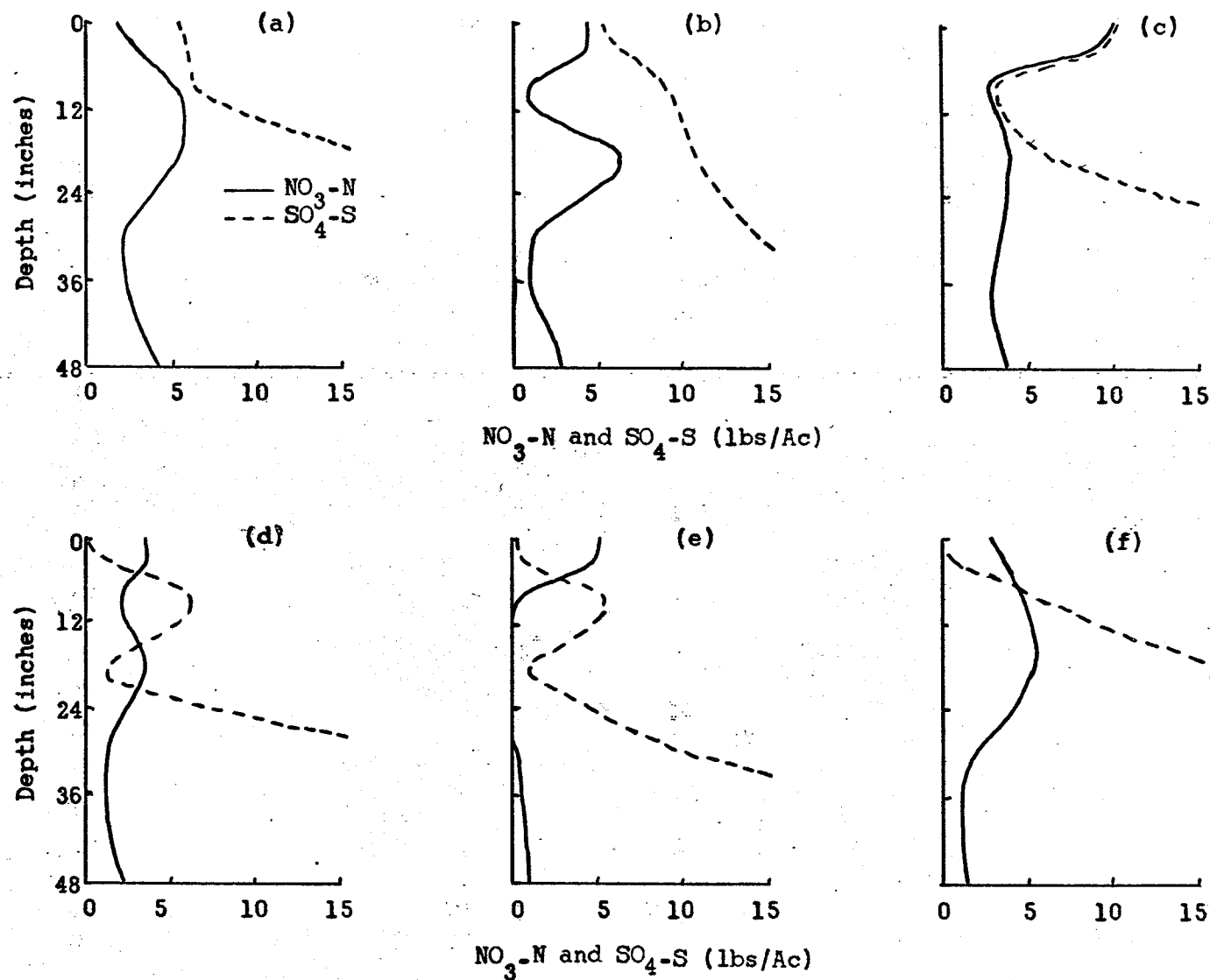


Figure 12. Distribution of NO₃-N and SO₄-S in fallow soils at the Kitching site: (a) spring (b) 18 days (c) 44 days (d) 65 days (e) 86 days (f) fall, 152 days after seeding.

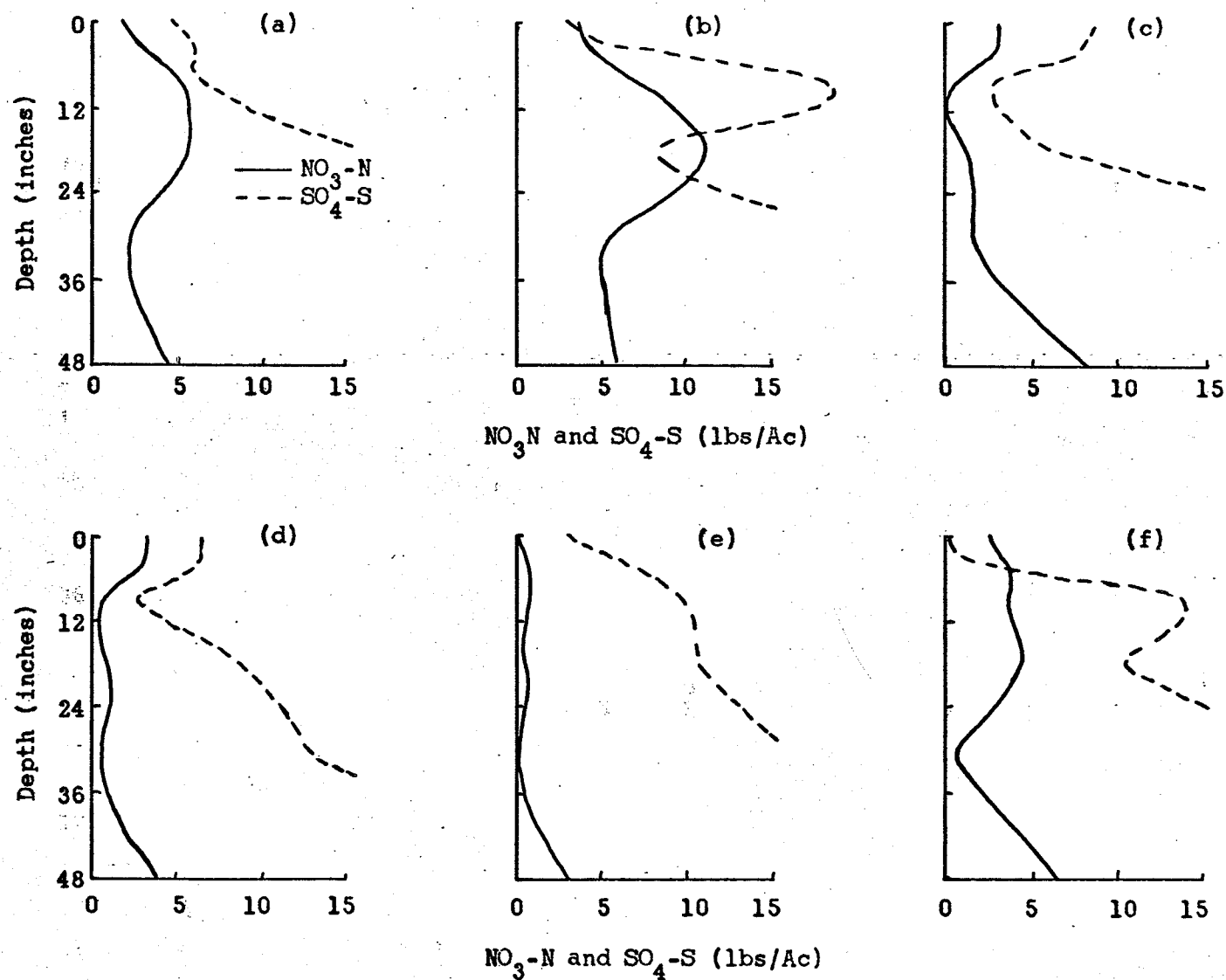


Figure 13. Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to barley at the Kitching site: (a) spring (b) 18 days (c) 44 days (d) 65 days (e) 86 days (f) fall, 152 days after seeding.

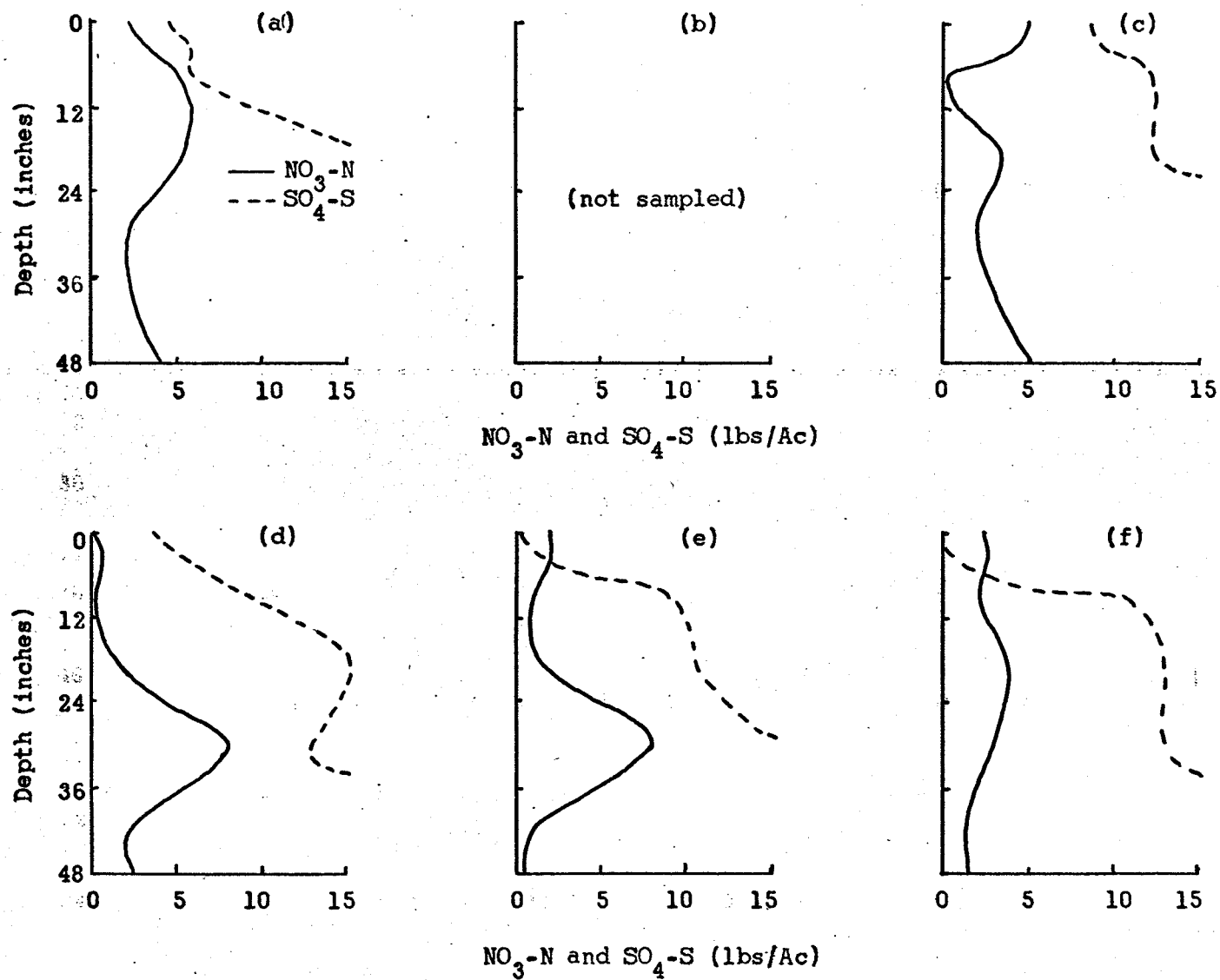


Figure 14. Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to rape at the Kitching site: (a) spring (b) 18 days (c) 44 days (d) 65 days (e) 86 days (f) fall, 152 days after seeding.

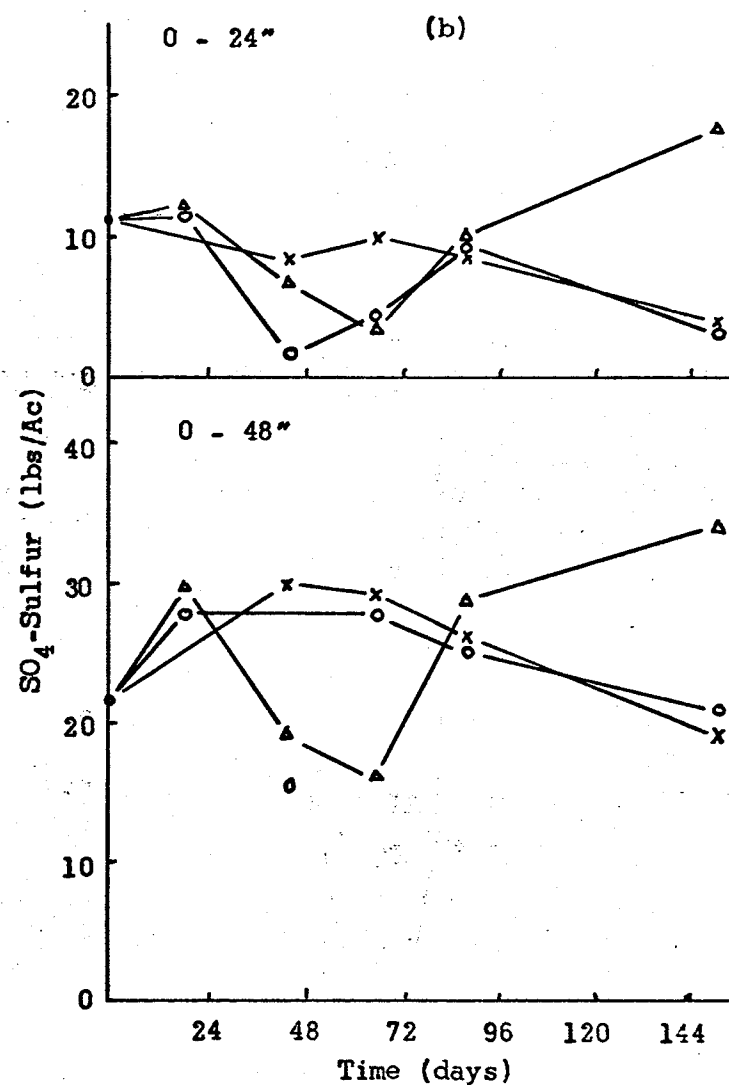
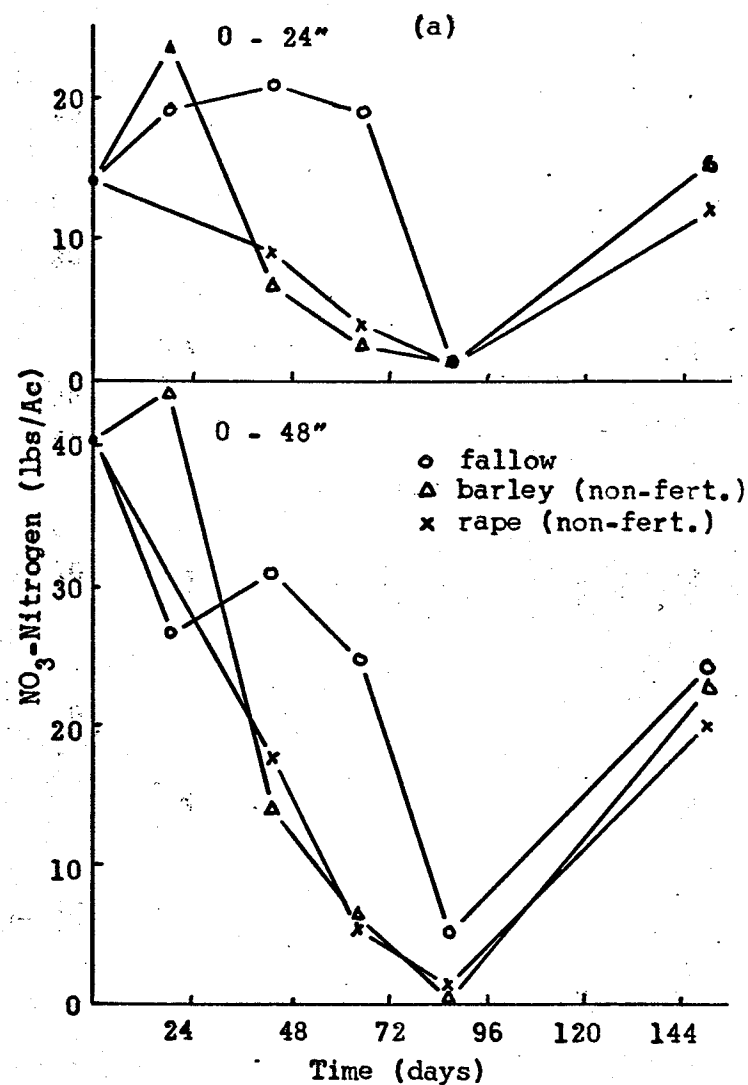


Figure 15. Total water soluble (a) NO₃-N and (b) SO₄-S in the Armstrong soils during the sampling period.

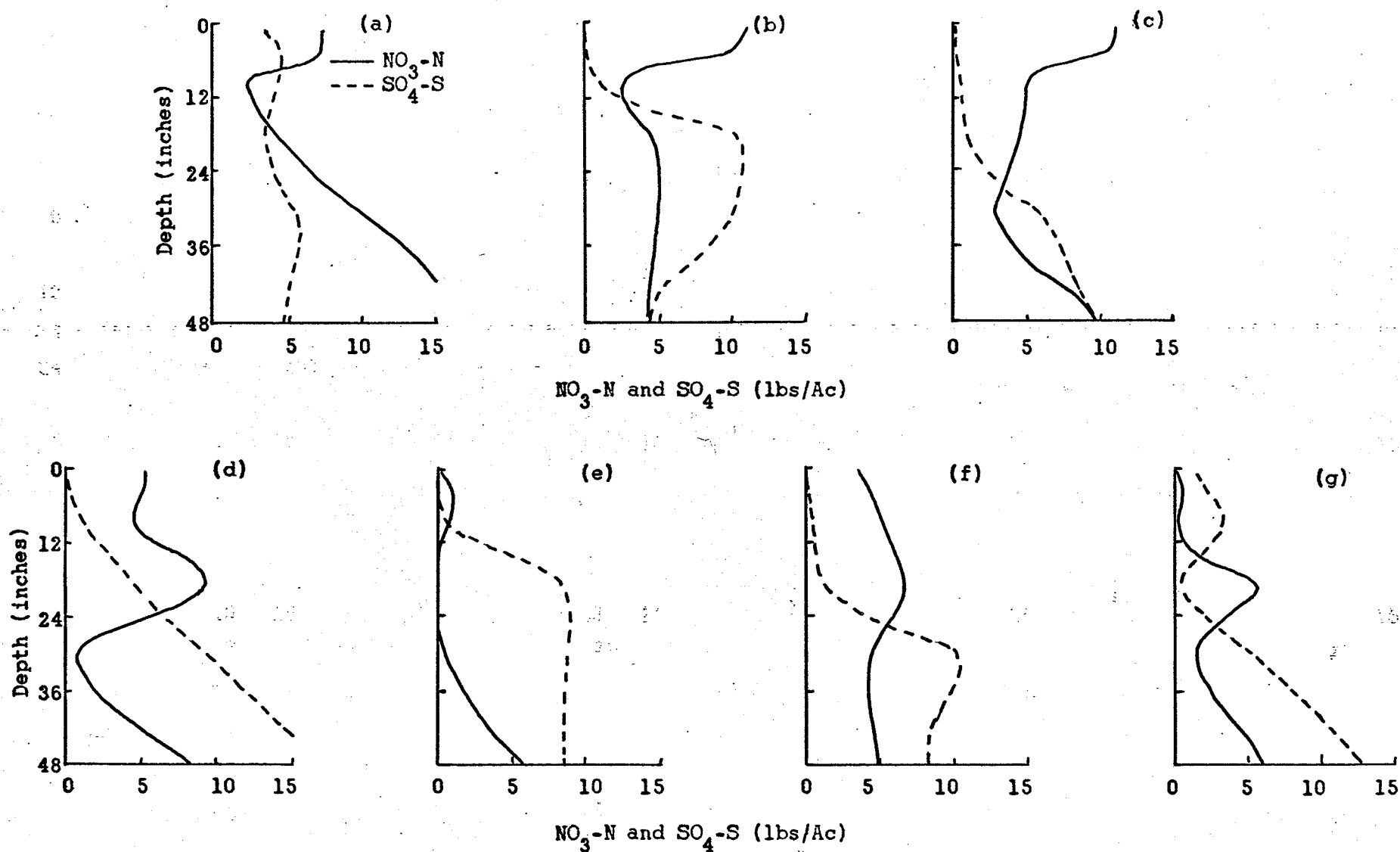


Figure 16. Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in fallow soils at the Armstrong site: (a) spring (b) 18 days (c) 43 days (d) 64 days (e) 87 days (f) fall, 151 days after seeding (g) spring of 1968.

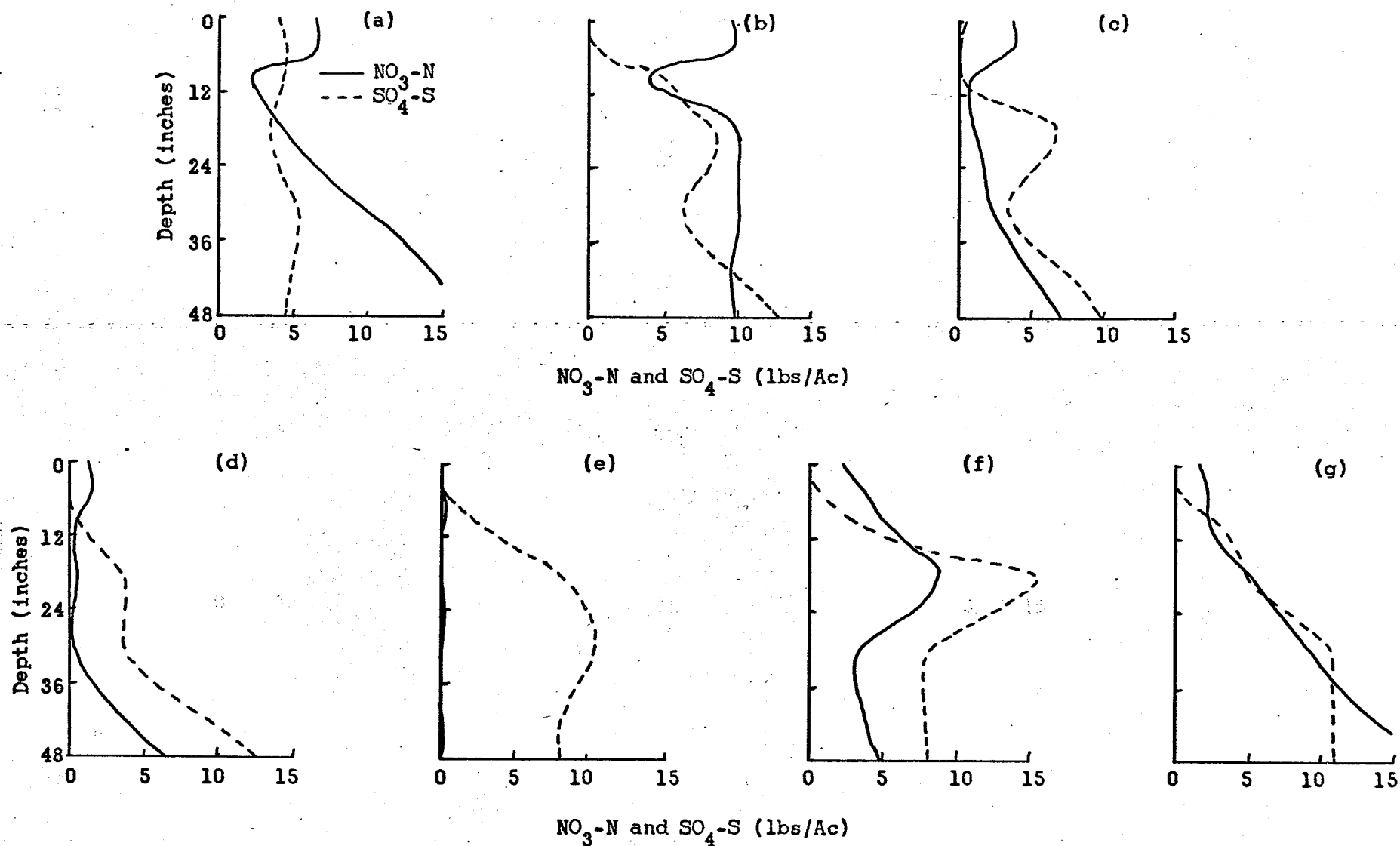


Figure 17. Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to barley at the Armstrong site: (a) spring (b) 18 days (c) 43 days (d) 64 days (e) 87 days (f) fall, 151 days after seeding (g) spring of 1968.

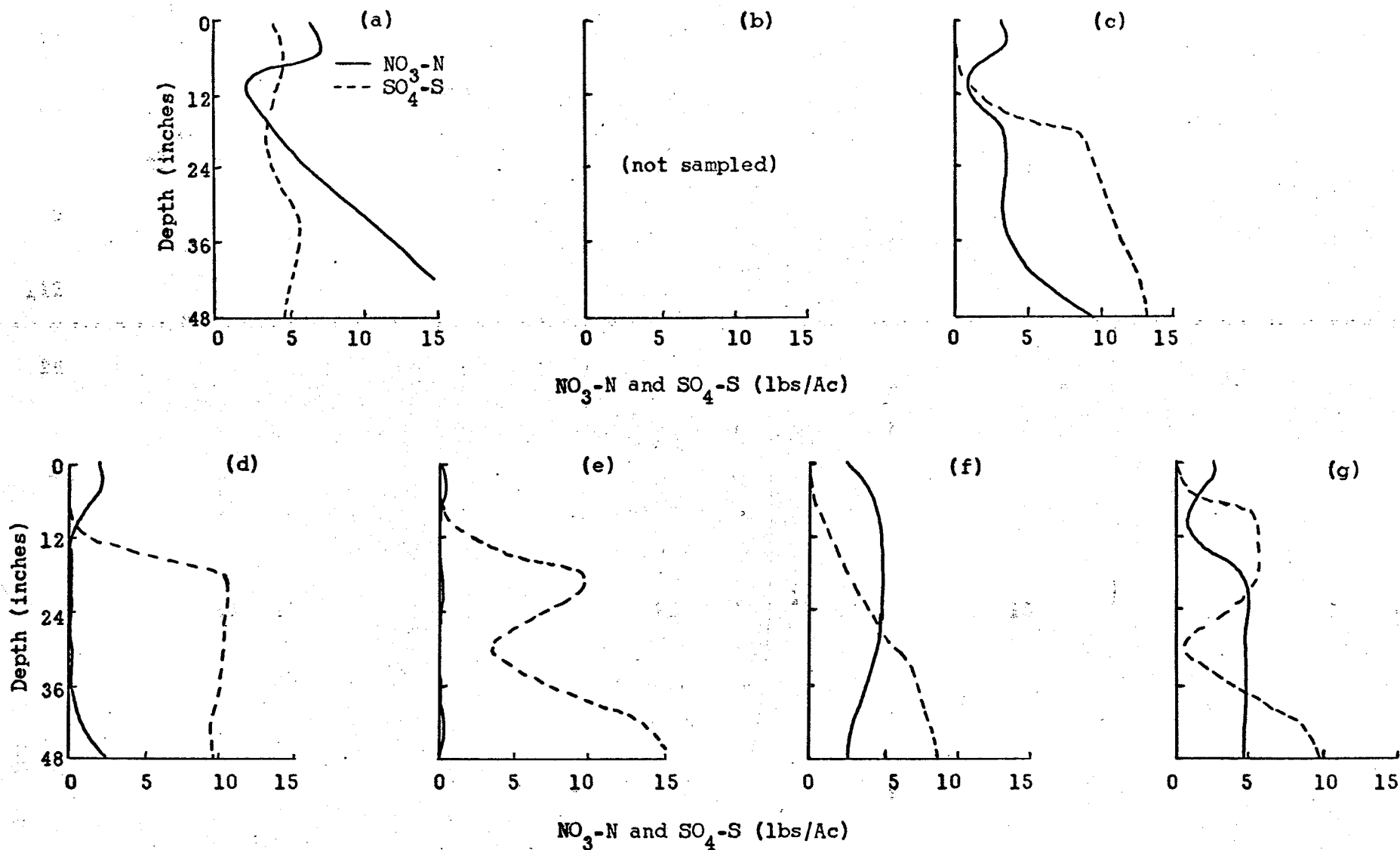


Figure 18. Distribution of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ in soils cropped to rape at the Armstrong site: (a) spring (b) 18 days (c) 43 days (d) 64 days (e) 87 days (f) fall, 151 days after seeding (g) spring of 1968.

IV INCUBATION EXPERIMENT

Introduction

The rates and mechanisms of nitrogen mineralization in a soil during incubation, as well as the factors which affect this process, are fairly well understood at present. Considerably less is known about sulfur mineralization, although a close analogy to nitrogen mineralization is postulated by many. A great deal of attention (32, 31, 18) has been devoted to characterizing surface soils in terms of total sulfur content and various organic and inorganic sulfur fractions. However, relatively little information is available on the contribution and influence of these fractions on the rates and amounts of sulfur mineralized in a soil. Although organic nitrogen and sulfur are known to exist in relatively constant ratios in a soil, little is known about their relative rates of conversion to inorganic plant available forms, particularly on the Canadian prairies.

Considerations such as these prompted a laboratory study of the relative rates of nitrogen and sulfur mineralization in cultivated surface soils of Manitoba. The effects of temperature and moisture control during incubation and chemical factors of the soil were also considered.

Materials and Methods

Surface samples of 21 cultivated Manitoba soils with physical and chemical characteristics as described in Table VII were collected for this experiment. Although four soil orders are represented, the soils selected are not a true cross-section of Manitoba. Considerable emphasis was placed on soils in the Chernozemic and Podzolic orders which were suspected of having sulfur supplies in the range limiting to crop growth. These were mainly the soils of the humid South Eastern, Central, and North Western areas of Manitoba. Soils of the more arid South Western

Table VII

Designation and chemical and physical characteristics of the soils incubated.

Order and Subgroup	Association or Series	Text- ure	pH (0.01M CaCl ₂)	CaCO ₃ Equiv. (%)	Organic C (%)	Total N (%)	Total S (%)	Total C:N:S: Ratio	Non-SO ₄ S (ppm)	1.0 NHC1 Sol. SO ₄ (ppm)
Chernozemic										
Orthic Black	Winkler	C	6.31	0.32	4.16	0.33	0.026	126:10:0.8	250	10
	Wellwood	CL	5.90	0.30	3.67	0.29	0.014	127:10:0.5	138	2
Rego Black	Almasippi A	VFS	6.85	0.34	1.06	0.08	0.021	133:10:2.6	208	2
	Almasippi B	VFS	6.95	0.39	1.18	0.10	0.021	118:10:2.1	204	6
Gleyed Rego Black	Red River	C	7.09	0.30	4.20	0.34	0.024	123:10:0.7	230	10
	Newdale	CL	7.46	2.27	3.87	0.30	0.013	129:10:0.4	120	10
Orthic Dark Gray	Poppleton A	FS	6.85	0.75	1.22	0.09	0.013	136:10:1.4	122	8
	Libau	C	6.78	0.39	3.64	0.28	0.018	130:10:0.6	172	8
Gleyed D. Gray	Poppleton B	FS	7.55	0.59	3.95	0.29	0.027	136:10:0.9	238	32
	Poppleton C	FS	7.40	0.68	1.26	0.10	0.010	126:10:1.0	90	10
	Poppleton D	VFS	7.45	0.68	1.03	0.08	0.011	129:10:1.4	102	8
Gleyed Salontzic D. Gray	Thalberg	SiC	6.44	0.39	2.97	0.29	0.009	102:10:0.3	76	14
Podzolic										
Orthic D.G. Wooded	Erickson A	CL	7.14	0.80	4.03	0.32	0.025	126:10:0.8	240	10
Gleyed D.G. Wooded	Erickson B	CL	7.40	2.89	3.46	0.30	0.012	115:10:0.4	112	8
Orthic G. Wooded	Granville	L	6.05	0.41	4.68	0.39	0.017	120:10:0.4	168	2
Sol. G. Wooded	Lettonia	VFS	6.36	0.23	1.86	0.16	0.011	116:10:0.7	105	5
Gleyed G. Wooded	Caliento	FS	7.25	0.18	0.80	0.07	0.012	114:10:1.7	115	5
	Clarkesville A	CL	6.15	0.45	4.56	0.35	0.006	130:10:0.2	50	10
	Clarkesville B	L	6.30	0.16	2.26	0.18	0.007	125:10:0.4	60	10
Regosolic										
Cutanic Podzo Regosol	Sandilands	S	5.88	0.30	0.59	0.04	0.006	148:10:1.5	58	2
Gleysolic										
Carbonated Rego										
Humic Gleysol	Osborne	SiCL	7.60	4.41	4.16	0.43	0.031	97:10:0.7	181	129

region of the province are not represented in this study. Soils were selected which represented a considerable range in texture, organic matter content, and internal drainage.

A. Incubation Technique

Soil samples were collected late in the fall (October) of 1967 and stored at or below 0°C. without drying or alteration until February (1968) when the experiment was started. Samples (at field moisture content) were thoroughly mixed and stored in sealed plastic bags after sieving to remove extraneous materials and undecomposed residues. Two moisture levels were employed, one just below field capacity (F.C.) and the other just above the wilting point (W.P.). To obtain these levels, the soils were divided into three textural groups and brought to the moistures listed in Table 9A. This grouping procedure was warranted by considerations in the literature (52) which indicated that small differences in moisture have insignificant effects on mineralization in soils.

The procedures used in adjusting the moisture contents of the soils were slightly different for the two levels. Samples held just below field capacity were adjusted by additions of distilled water in a fine spray as the soil was being stirred. The amounts to be added were calculated on the basis of an air-dried subsample of each soil. Samples held at the moisture level just above wilting point were air-dried prior to adjustment, but otherwise were treated identically to the other soils.

After preparation in the manner described above, the soils were placed in 100 ml beakers, enclosed in a plastic bag, and placed in an incubator. The bags were opened periodically to permit aeration. One of the five replicates of each soil at all combinations of conditions was taken out at one, three, and six week intervals, air dried and $\text{NO}_3^- \text{N}$ and $\text{SO}_4^{2-} \text{S}$ determined. The analysis at 12 weeks were performed on a subsample of two combined replicates.

Since the major objective of this experiment centered on the relative rates of nitrogen and sulfur mineralization in a soil, the observations on temperature and moisture effects were limited to seven of the 21 soils selected. These were incubated at the two moisture contents referred to above and at 10°, 18°, and 30°C in all possible combinations. In addition, the remaining soils were incubated at the 18°C and near field capacity condition. Emphasis during discussion will be placed on the results realized from this combination.

B. Analytical Procedures

The water soluble NO_3^- -N and SO_4^{2-} -S contents and chemical characteristics of the soils were determined as outlined in Chapter III. Total nitrogen was determined by the regular macro-Kjeldahl method adapted to include NO_3^- -N, using a boric acid plus indicator solution (11). Total sulfur was determined by the combustion method; employing a Leco Model 532 Automatic Sulfur Titrator. One gm of soil was ignited at 1,500°C in a pure oxygen atmosphere and the sulfur reduced to SO_2 which was then collected in a solution of iodine and starch and determined by titration with KIO_3 in dilute HCl. The method used to determine the SO_4^{2-} -S in the 0.1 N HCl soil extract was similar to that used for the water extract except that iron and aluminum were removed by precipitation with NaOH and filtration (2). The sulfur fraction described as "non-sulfate sulfur" in this thesis was obtained by subtracting the 0.1 N HCl soluble SO_4^{2-} -S from total sulfur content, assuming that a dilute acid will extract essentially all of the SO_4 in a soil. Mechanical analysis was performed by a modification of the pipette method outlined by Kilmer and Alexander (29).

Results

Considerable variation was noted in the amounts of NO_3 nitrogen and SO_4 sulfur released by the soils during incubation (Table 11A and 12A). The time course of mineralization was followed for all of the soils

incubated, indicating a considerable variation in time and manner of mineralization as well (Figures 19 to 23). Generally, it was apparent that sulfur is mineralized differently than nitrogen. Sulfur mineralization was characterized by an initial rapid rate of release followed by a decrease in rate in later periods of incubation (Figure 19). Nitrogen however appears to be released linearly with time, an observation made by numerous previous workers. These differences were most apparent at 18°C and 30°C. Moisture content appeared to affect the mineralization of these elements in a similar way. The amounts of NO_3 and SO_4 released after 12 weeks at field capacity were approximately double those released at wilting point.

Typically, the sands released the smallest amounts of NO_3 and SO_4 . The Poppleton soils are representative of this textural group (Figure 20). The loam and clay loam textured soils, most of which were obtained in North Western Manitoba, mineralized intermediate amounts of nitrogen and sulfur. One soil in this group belonging to the Erickson association was obtained from upper and lower slope positions. The amounts of nitrogen and sulfur released by these soils appeared to be differentially influenced by their previous moisture regime and perhaps CaCO_3 content (Figure 21).

Three types of changes were noted in the SO_4 -S content of clay textured soils: (i) no release - Osborne, (ii) substantial release - Winkler (Figure 22) and Red River, and (iii) net decrease - Thalberg (Figure 23). NO_3 -N content increased in all of the soils of this group.

The ratios of NO_3 -N: SO_4 -S released on incubation, as summarized in Table VIII, were not constant but tended to increase with time, i.e. nitrogen was mineralized faster than sulfur (Figure 24). The ratios of release also tended to increase with increase in degradation of the original soil. Ratios of release in Podzolic soils were almost three times as wide as those in Chernozemic (Black) soils incubated at the same moisture content and temperature (Tables IX and X).

A study of the relationships existing between the amounts of nitrogen and sulfur mineralized and various soil fractions indicated that the amount of NO_3 mineralized was best correlated with the organic matter content of

Table VIII

The amounts and ratios of $\text{NO}_3^- \text{N}$ and $\text{SO}_4^- \text{S}$ released by some soils during incubation, as affected by temperature and moisture.¹

Incubation Time (weeks)	Temperature and Moisture ¹					
	10°C		18°C		30°C	
	W.P.	F.C.	W.P.	F.C.	W.P.	F.C.
$\text{NO}_3^- \text{N}$ (ppm)						
1	-	0.0	2.9	5.9	9.8	16.0
3	3.8	4.8	5.0	11.8	18.6	32.2
6	4.0	8.5	9.2	18.3	39.8	53.6
12	6.3	18.6	18.1	31.9	62.9	122.7
$\text{SO}_4^- \text{S}$ (ppm)						
1	0.0	0.0	0.6	1.0	1.5	1.7
3	0.5	0.5	1.0	1.3	2.4	2.5
6	0.5	1.2	1.6	2.0	2.3	4.5
12	0.8	0.6	2.0	2.3	3.1	5.5
Ratios of Release						
1	-	-	5.2	6.5	6.4	9.3
3	7.1	9.4	5.1	9.4	7.7	13.1
6	7.5	7.1	5.8	9.0	17.5	12.0
12	7.5	29.0	8.9	13.9	20.0	22.5

¹ Where F.C. = moisture content just below field capacity and
W.P. = moisture content just above wilting point.

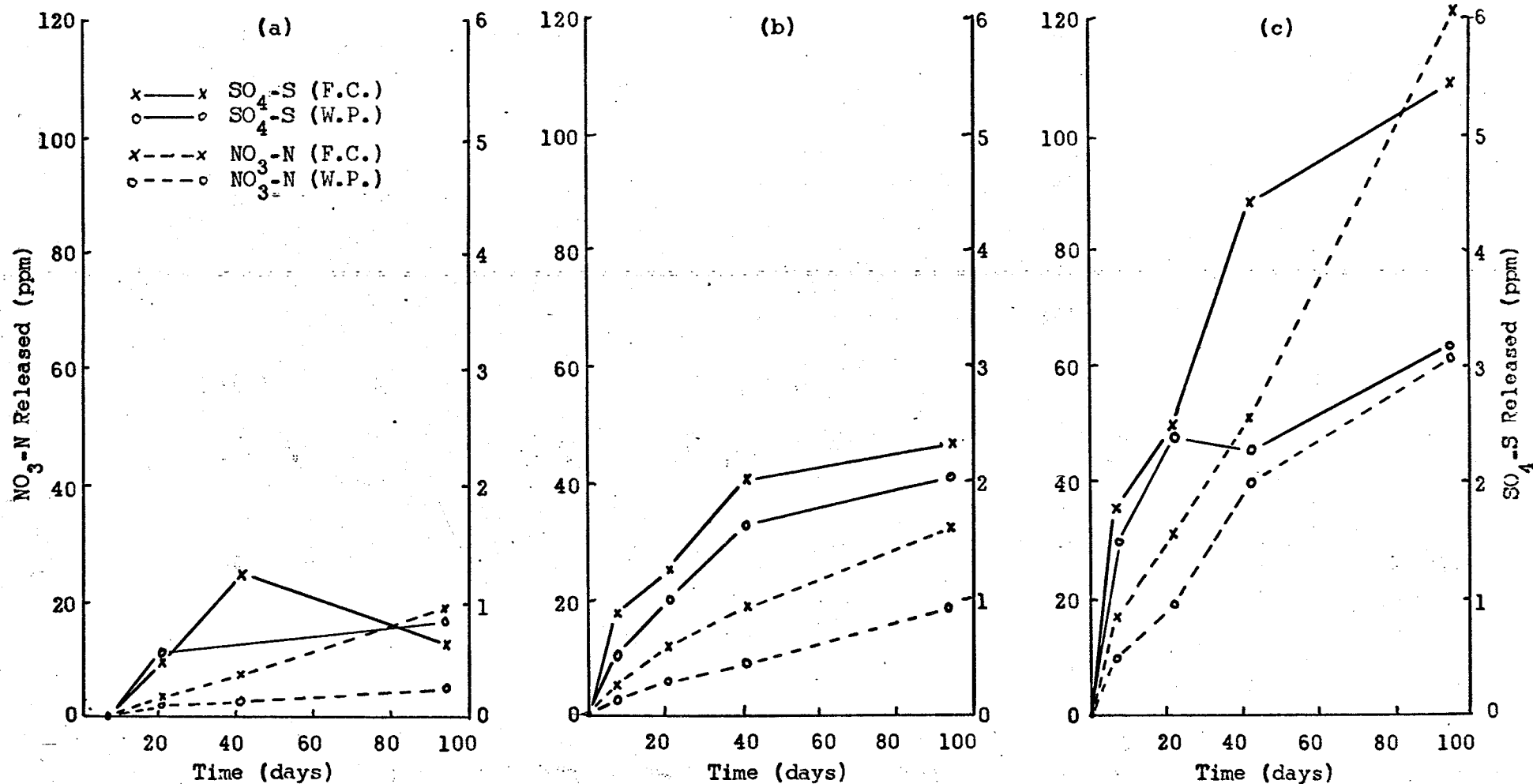


Figure 19. $\text{NO}_3\text{-Nitrogen}$ and $\text{SO}_4\text{-Sulfur}$ released by soils upon incubation at: (a) 10°C (b) 18°C (c) 30°C.

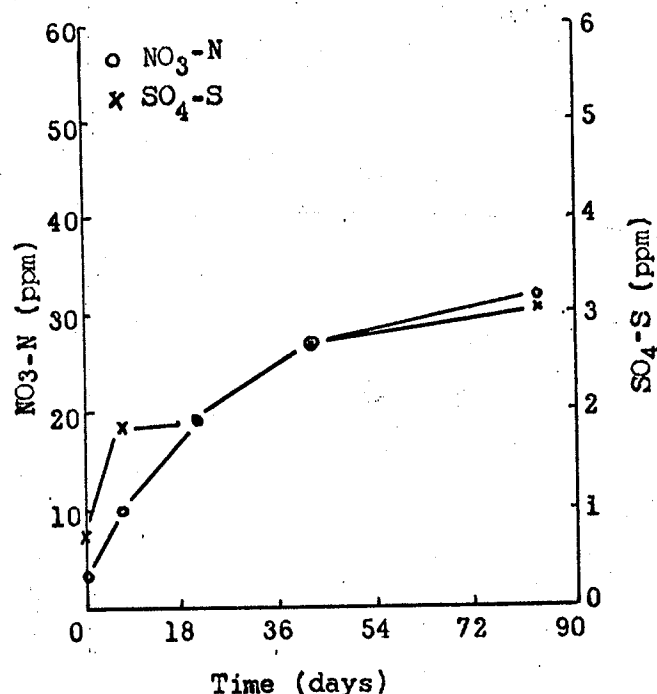


Figure 20. Nitrogen and sulfur mineralized by a Poppleton C during incubation at 18°C and field capacity moisture.

the soils, particularly under the most favourable incubation conditions. The correlation coefficient after three weeks incubation at 30°C and near field capacity moisture was $r=.82^*$. The amounts of NO_3 mineralized were not related to total nitrogen contents to the same degree.

The mineralization of sulfur was also correlated with the organic matter content of the soils incubated. The coefficient after 12 weeks at 18°C and near field capacity moisture was $r=.85^{**}$ (Figure 25). Total sulfur and 1.0 NHCl soluble SO_4 sulfur were found somewhat related to the amount of sulfur mineralized by the soils. The coefficient for total sulfur vs. sulfur mineralized after 12 weeks at 18°C and near field capacity moisture was $r=.68^{**}$ (Figure 26). The "non-sulfate sulfur" fraction, which is considered as an estimate of organic sulfur, was not correlated to sulfur mineralization.

The ratios of $\text{NO}_3\text{-N}:\text{SO}_4\text{-S}$ released were not related to total soil N:S ratios. The mean ratios of release (Table X) were essentially the same as total N:S ratios in Chernozemic soils and considerably greater than total N:S ratios in Podzolic soils. The ratios of release tended to increase with increase in degradation of the original soils.

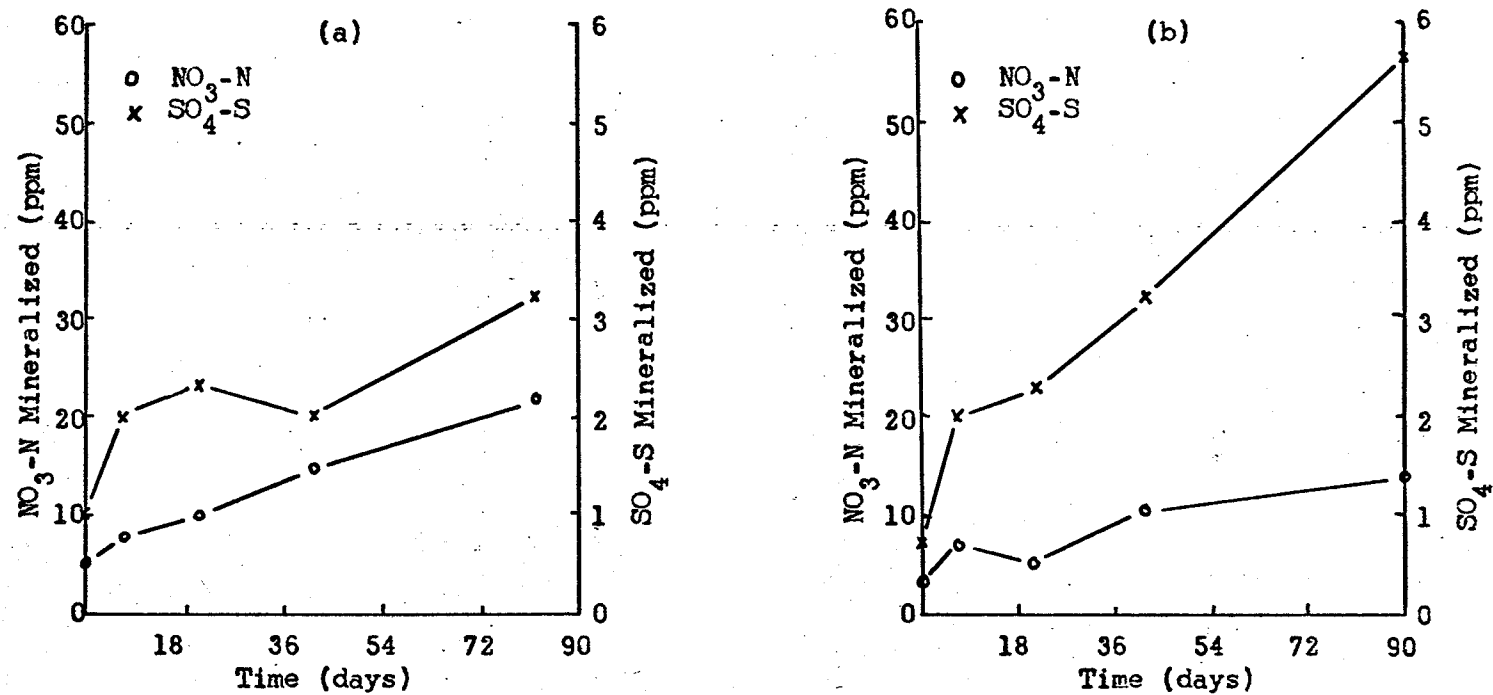


Figure 21. Nitrogen and sulfur mineralized by soils with different internal drainage:
 (a) Erickson A, 0.80% CaCO₃ eq., (b) Erickson B, 2.89% CaCO₃ eq.

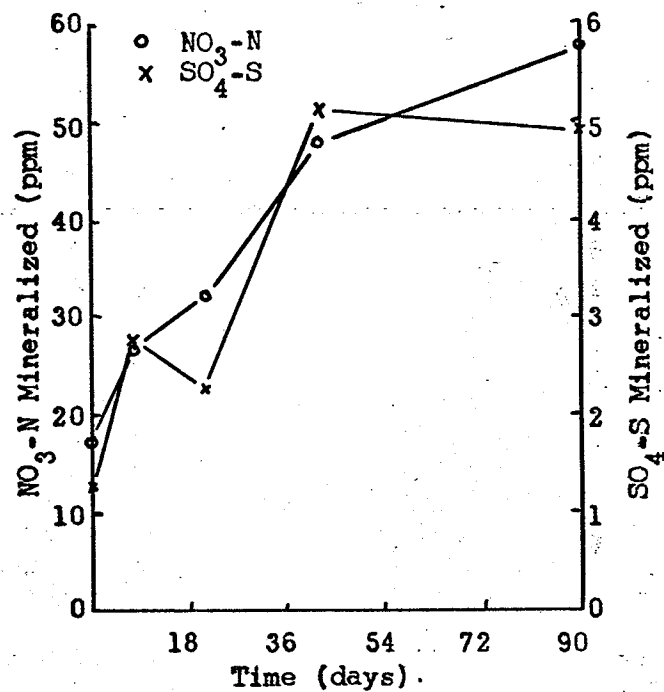


Figure 22. Nitrogen and sulfur mineralized by a Winkler soil during incubation at 18°C and F.C. moisture.

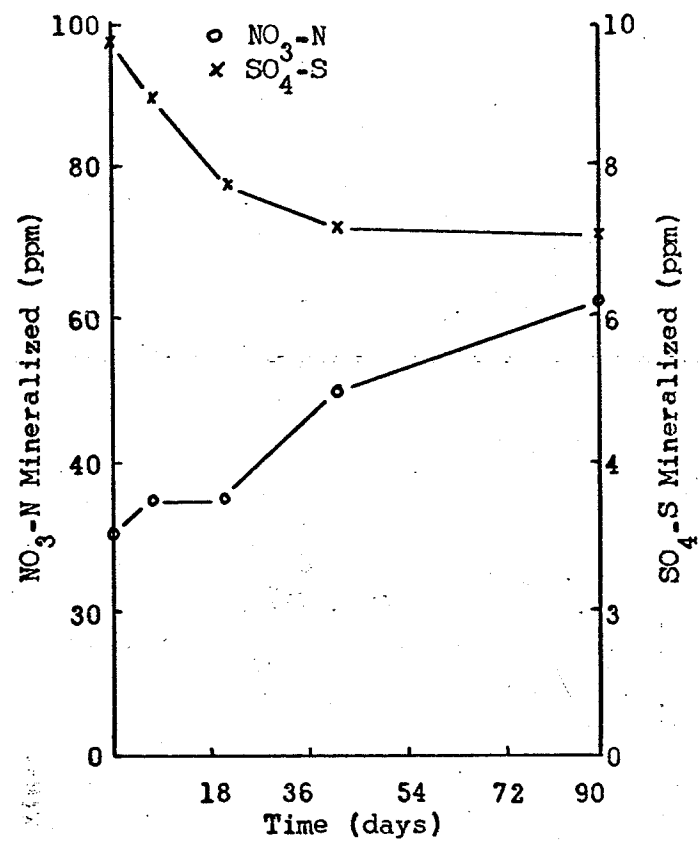


Figure 23. Nitrogen and sulfur mineralized by a Thalberg soil during incubation at 18°C and F.C. moisture.

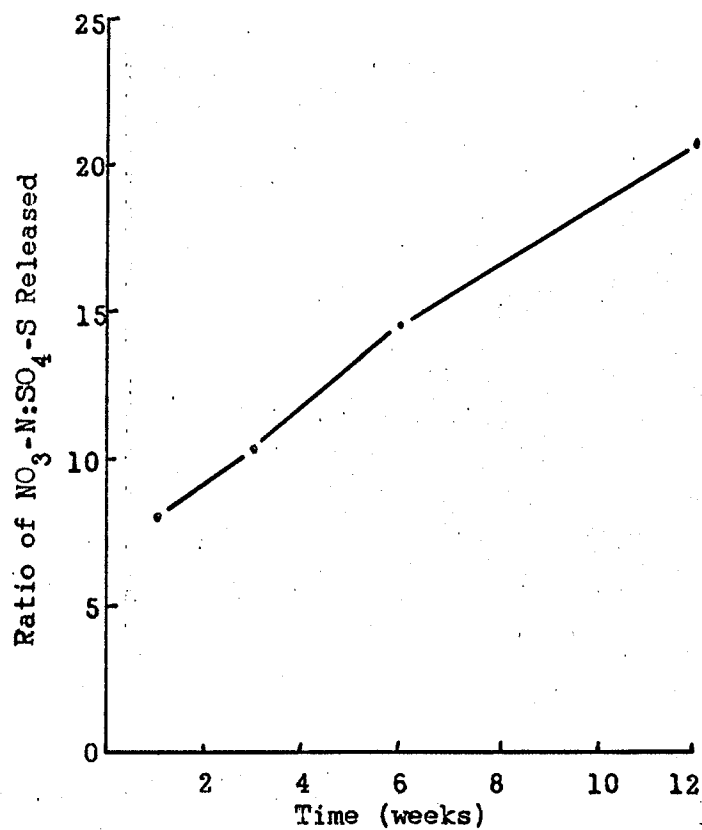


Figure 24. Relative amounts of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ released during incubation at 30°C (means of two moisture contents).

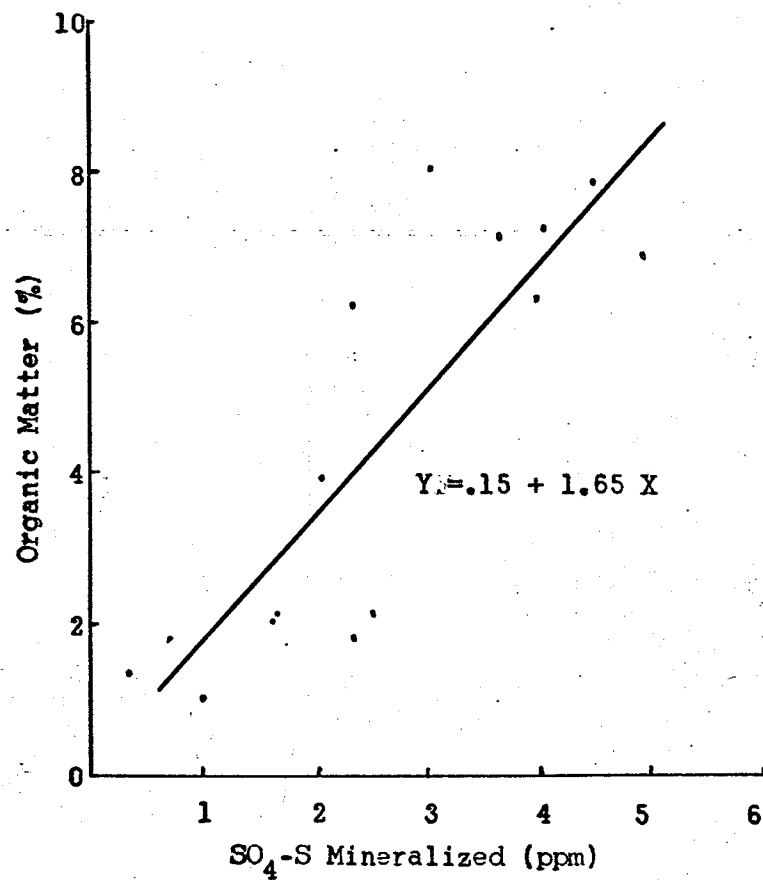


Figure 25. Relationship between organic matter content and sulfur mineralization in 15 soils.

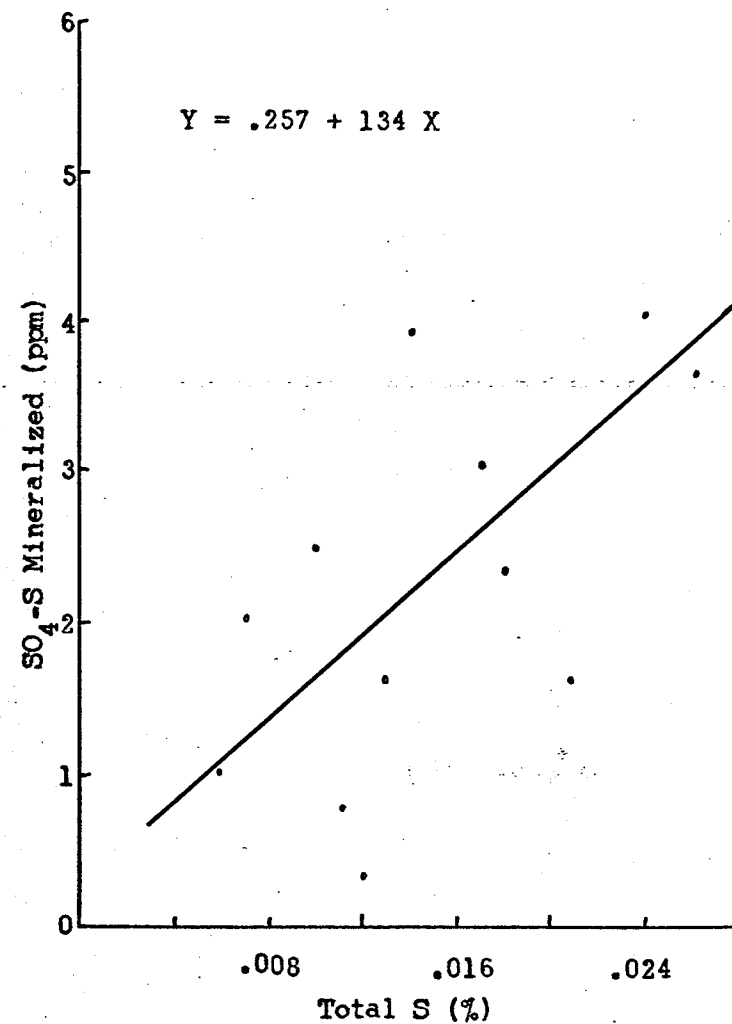


Figure 26. Relationship between total sulfur content and sulfur mineralization in 14 soils.

Table IX

Nitrogen and sulfur relationships in the soils as compared to the ratios of release on incubation.

Order and Association or Series	Total N:S Ratio	Initial H ₂ O Sol.		Initial NO ₃ -N:SO ₄ -S Ratio	Ratio of Release NO ₃ -N:SO ₄ -S
		NO ₃ -N (ppm)	SO ₄ -S (ppm)		
Chernozemic					
Winkler	12.69	17.3	1.3	12.87	9.80
Wellwood	20.71	2.0	0.0	-	3.07
Almasippi A	3.81	1.1	0.0	-	12.74
Almasippi B	4.76	1.0	0.0	-	10.42
Red River	14.17	5.7	2.3	2.52	3.76
Newdale	23.08	2.1	3.9	0.50	-
Poppleton A	6.92	2.2	0.8	2.97	19.48
Libau	15.56	12.3	5.2	2.37	11.31
Poppleton B	10.74	9.9	27.1	0.36	11.09
Poppleton C	10.00	3.1	0.7	4.68	12.00
Poppleton D	7.27	0.5	1.2	0.39	25.60
Thalberg	32.22	28.4	9.9	2.89	-
Podzolic					
Erickson A	12.80	5.2	1.0	5.22	-
Erickson B	25.00	3.4	0.7	5.04	-
Granville	22.94	5.5	0.6	9.53	9.48
Lettonia	14.55	5.2	0.6	8.70	-
Caliento	5.83	4.4	1.8	3.76	60.26
Clarkesville A	58.33	11.7	0.4	28.60	18.54
Clarkesville B	25.71	4.4	0.3	12.90	25.50
Regosolic					
Sandilands	6.67	1.1	0.3	3.26	27.26
Gleysolic					
Osborne	13.87	9.4	37.2	0.25	-

Table X

Summary of carbon, nitrogen and sulfur relationships in the soils studied as related to N and S release.

Grouping	Total Content(%)			NO ₃ -N:SO ₄ -S Ratio of Release	C:S Ratio	N:S Ratio	Initial NO ₃ -N:SO ₄ -S Ratio
	C	N	S				
All Soils	2.83	.23	.016	16.6	177	14.4	6.5
Chernozemic	2.68	.21	.017	11.9	158	12.4	3.3
Black	3.02	.24	.020	8.0	151	12.0	5.3
D. Gray	2.35	.19	.015	15.9	157	12.6	2.3
Podzolic	3.09	.25	.013	28.4	238	19.2	10.5

A very good correlation ($r=.98^{**}$) was found between organic matter and total nitrogen content in the soils examined. The correlations between organic matter and total sulfur content were not as good. A coefficient of $r=.72^{**}$ was noted when soils from the North Western region of Manitoba were omitted from calculations (Figure 27). Organic matter and "non-sulfate sulfur" were not found to be significantly related. Total nitrogen and sulfur contents were found to be significantly related ($r=.70^{**}$) only when the soils of the North Western region were excluded (Figure 28).

Consideration of the carbon, nitrogen and sulfur fractions and ratios in the soils selected, as listed in Table VII and summarized in Table X, suggests that the Chernozemic and Podzolic soils differ considerably with respect to those constituents. Carbon and nitrogen contents were highest in the Podzolic soils while sulfur content was highest in the Chernozems. The mean C:N:S ratio for the soils of these orders was found to be 123:10:0.7 which is comparable to values cited in the literature for cultivated soils (Table I). Total C:S, N:S and initial NO₃-N:SO₄-S ratios were highest in Podzolic soils.

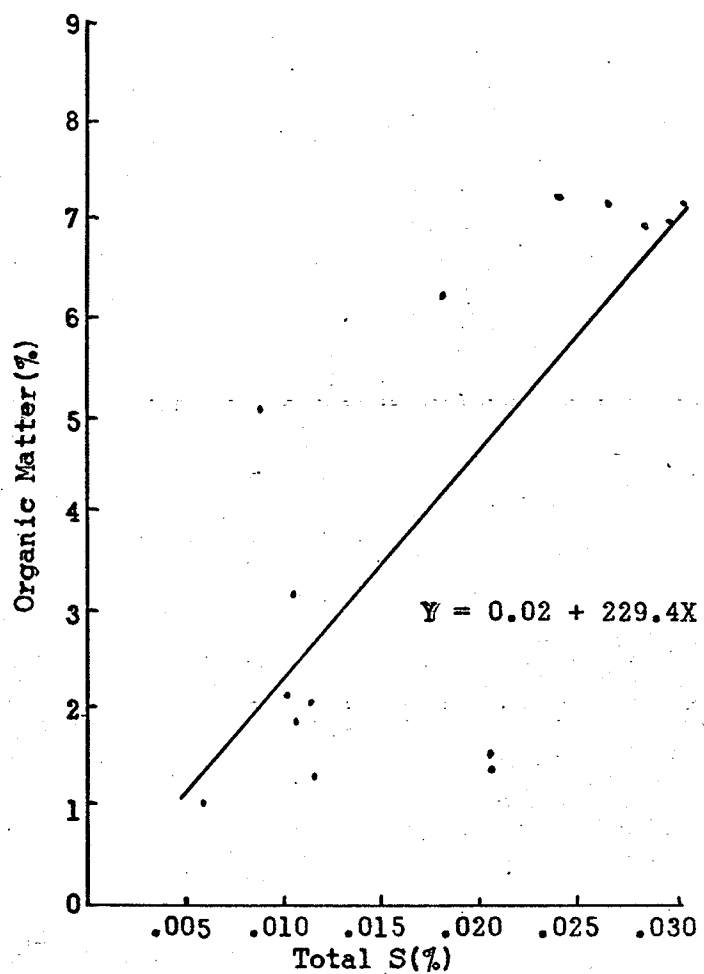


Figure 27. Relationship between total sulfur and organic matter content in 14 of the soils examined.

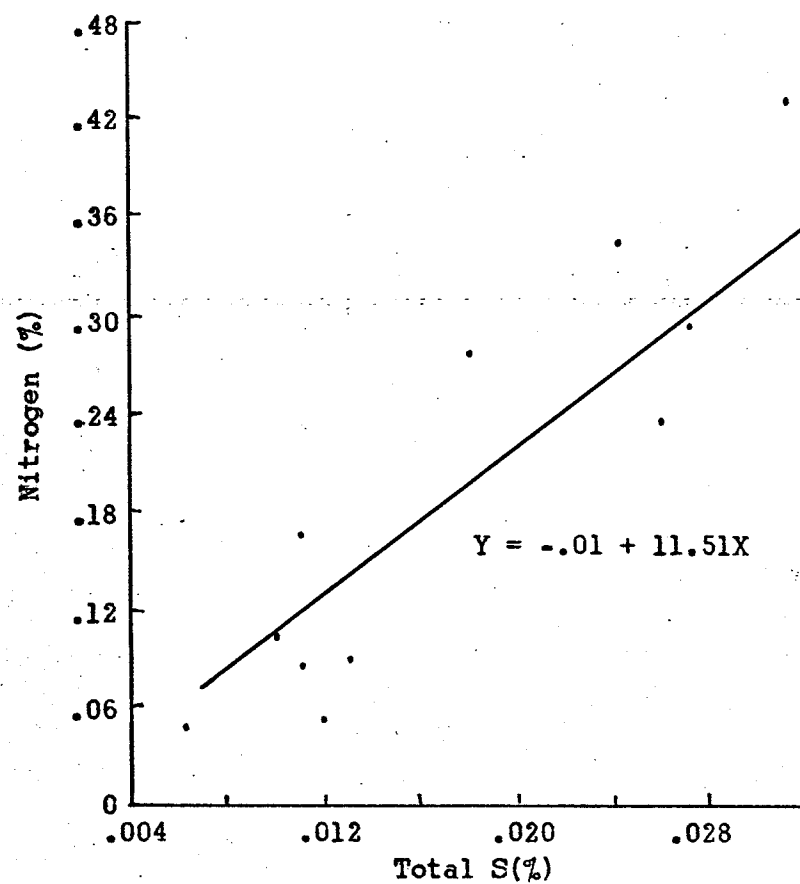


Figure 28. Relationship between total nitrogen and sulfur content in 14 of the soils examined.

Discussion

The results of this experiment indicate that nitrogen and sulfur are not mineralized at a constant ratio in soils. Nitrogen was mineralized faster than sulfur, an observation which previous workers have made as well (7, 52). The ratios of release varied considerably and were not related to total N:S ratios in the soil. The fact that mean ratios of release were considerably wider than total ratios in Dark Gray and Podzolic soils suggests that the sulfur supplying power of these soils is smaller than that of Black soils. The quantitative amounts of $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ mineralized under laboratory conditions indicate potential supplying power only. The relative rates of release in the laboratory may, however, be representative of rates of release in the field. The discrepancy noted between field ratios of release (Chapter III) and laboratory ratios for the Almasippi soils places some doubt on this assumption. Incubation ratios are quite possibly wider than actual field ratios of release.

If the ratios of release observed after 12 weeks of incubation at 18°C and near field capacity moisture are indicative of release under field conditions, it is apparent that NO_3 and SO_4 in Chernozemic soils are released in a ratio sufficient to satisfy the ratios of requirement in common field crops (Table II). A similar conclusion could not be made for soils of the Podzolic order as the ratios of release were considerably wider than ratios of plant requirement. The results suggest that sulfur rather than nitrogen is most apt to be limiting crop growth in Podzolic soils dependent on mineralization for these nutrients.

Very little significance can be attached to the observations made on the time course of NO_3 and SO_4 release, since past history, incubation technique and the nature of recently added organic residues influence mineralization--immobilization relationships for both these elements. Changes in soluble $\text{SO}_4\text{-S}$ content during incubation were small and best reflected these influences. Williams (52) showed that sampling and incubation technique have a decided influence on the manner and amounts of $\text{SO}_4\text{-S}$ mineralized in a soil. Drying and rewetting of soils led to enhanced mineralization of sulfur; soils collected in spring mineralized greater amounts of SO_4 than the same soils collected in fall.

Since the most recently added organic residues undergo most rapid decomposition in a soil, it is evident that the C:S ratios of these residues will influence sulfur release during incubation, particularly in the initial stages (4, 6). Similarly, the N:S ratios of recently added crop residues and roots influence the relative rates of NO_3 and SO_4 release in a soil. This influence partially explains the lack of correlation between total N:S ratios and ratios of release noted in this and similar incubation experiments.

The observation of Barrow (4, 6) on the influence of C:S ratios on sulfur mineralization and immobilization in a soil, namely that soils with C:S ratios in the range of 200 to 400 either immobilize or mineralize small amounts of sulfur on incubation, explains the decrease in soluble SO_4 noted in the Thalberg soil. This soil had a C:S ratio of 330:1, widest of all the Chernozemic soils sampled. Decreases in soluble SO_4 on incubation have been noted in other experiments as well (3). Nelson (3) attributed a reduction in soluble SO_4 in a soil on incubation to high N:S and C:S ratios. Freney and Spencer (21) observed net immobilization of added sulfur in one experiment, and a decrease of 3.9 ppm water soluble SO_4 over an eight week period in one of five soils incubated in another experiment. They attributed these losses to microbial conversion of SO_4 to organically bound forms.

Adsorption processes may also be involved in clay soils such as the Thalberg. Studies on adsorption processes in Manitoba soils (2) indicated that soils in the South Eastern area of the province, where the Thalberg soil is located, have abilities to absorb small amounts of SO_4 from solution. The pH (6.44) of this soil is in the range where SO_4 adsorption processes can occur. Similar arguments may apply to the lack of change noted in the Osborne soil, although a more logical reason is the relatively large initial SO_4 content of this soil which may have masked any changes.

The difference in SO_4 mineralized by the upper and lower slope samples of the Erickson soil may be attributed to the relatively high CaCO_3 content of the latter. Williams (52) noted increased sulfur mineralization upon the addition of CaCO_3 to soils. Other chemical factors, such as the degree

of aeration of the two soils prior to sampling and organic matter content may also have influenced sulfur mineralization processes.

The fact that both NO_3 and SO_4 release were best correlated with the organic matter contents of the soils examined, suggests that the mechanism of release and sources were similar. Total nitrogen and sulfur contents of the soils were not indicative of the amounts of these respective elements mineralized on incubation. The existence of a constant labile organically bound SO_4 fraction in the organic matter of soils, as postulated by many workers (32,33,55) explains the good correlation between organic matter and SO_4 release. Chemical release of these "carbon-bonded SO_4 groups as well as biological oxidation of SH^- groups and other sulfur compounds associated with organic carbon in a soil were considered responsible for the increases in $\text{SO}_4\text{-S}$ detected. It is considered doubtful that mineralization from primary minerals in weathered surface soils contribute significantly to these releases.

The correlation between organic matter and total sulfur content in the soils of this experiment was considerably lower than values reported in the literature (36). The reasons suggested for this anomolous correlation, and the improvement noted when soils from the North Western region were excluded, include the fact that inorganic sulfides and sulfates may have been present in varying amounts. Subtraction of dilute acid soluble SO_4 from total sulfur values, resulting in the fraction termed "non-sulfate" sulfur, did not, however, improve the correlation with organic matter content. The most logical explanation is the difference in mean total sulfur contents observed between the Podzolic and Chernozemic soils of this study. The mean of the Chernozemic group of soils is located at .017% total sulfur while that of the Podzolic group is located at .013% sulfur. The soils of the North Western region were predominantly Podzolic and included degraded soils with C:S ratios considerably higher than those of the Black Great Group. In view of this, a linear correlation between organic matter and total sulfur could not be expected.

Mean total sulfur contents, total C:S ratios, total N:S ratios, initial $\text{NO}_3\text{-N}:\text{SO}_4\text{-S}$ ratios and ratios of release all indicate a distinct dichotomy in

the Chernozemic and Podzolic soils investigated. The relatively wide mean total N:S ratios observed in soils of the Podzolic Order were reflected in wide mean initial $\text{NO}_3^- \text{N} : \text{SO}_4^{2-} \text{S}$ ratios and ratios of release. Although carbon and nitrogen contents of both major orders sampled were similar, sulfur contents were considerably lower in the Podzolic Order, accounting for their wide mean C:S ratio.

V Summary and Conclusions

A field experiment was initiated in the summer of 1967 with the objectives of investigating the total N:S ratios in rape and barley and obtaining more information on the water soluble SO_4 test as a criterion of soil sulfur supply. An effort was also made to observe the relative rates of nitrogen and sulfur mineralization in a soil under field conditions. A subsequent laboratory experiment, conducted in the winter of 1967 to 1968, was designed to further characterize the relative rates of mineralization under controlled conditions.

The field experiment disclosed that the total N:S ratios of rape and barley at the four to six week stage are indicative of the sulfur status of these species. Total N:S ratios were suggested as a means of diagnosing the sulfur status of all crops at a research level. A critical ratio above which rape is deficient in sulfur was suggested as 12:1. A corresponding value for barley was 16:1. A sulfur content of less than 0.25% at the flowering stage of rape was described as inadequate for maximum production of this crop when other nutrients are not limiting.

Results from the field study also gave further support to the consideration of water soluble SO_4 as an index of soil sulfur supply in coarse textured soils. A critical level of 10 lb/Ac of water soluble SO_4 -S to the 24 inch depth at seeding is suggested for cereals. A corresponding critical value for rape is not suggested on the basis of this study. However, the value is thought to be in the range of 20 to 25 lb of SO_4 -S/Ac. It is suggested that dilute phosphate solutions be used in fine textured soils in order to extract any adsorbed SO_4 ions as well as to facilitate filtering procedures.

The observations on nitrogen and sulfur mineralization rates under field conditions have limited application due to the interferences encountered and the duration of the study. However, the measurements made in soils cropped without added fertilizer were considered as indicative of water soluble NO_3 and SO_4 relationships in a soil. NO_3 -N and SO_4 -S were

found to be released in a ratio of 4.3:1.0 during the interval of crop growth. This ratio was somewhat narrower than that observed in a subsequent laboratory study. The discrepancy between the two values was attributed in part to movement of SO_4 ions in the field experiment. The general lack of similarity between NO_3 and SO_4 distribution in the cropped soil profiles was thought due to differential rates of release, leaching and crop uptake. The source and chemical equilibria of the two ions are also vastly different. The quantitative increase in SO_4 -S in cropped soils was found to be 5.9 lb/Ac to 24 inches in the Almasippi soils. An additional increase of 1.6 lb/Ac was noted from harvest to fall for a total release of 7.5 lb/Ac during the interval from May 22 to October 21, 1967.

The laboratory study, involving the incubation of 21 Manitoba soils at three temperatures and two moistures, indicated that water soluble NO_3 and SO_4 are not released from soil organic matter in a constant ratio. Ratios of release were found to increase with time and temperature of incubation, suggesting that nitrogen is mineralized faster than sulfur. The ratios for soils from the Chernozemic and Podzolic Orders after 12 weeks incubation at 18°C and near field capacity moisture were 11.9:1 and 28.4:1 respectively. The values were considered to be wider than those expected under field conditions.

The relative amounts of NO_3 and SO_4 released in Chernozemic soils were concluded to be adequate for crops dependent on mineralization as a source of these nutrients. A similar conclusion for Podzolic soils was not warranted on the basis of this study. The application of nitrogen fertilizers would undoubtedly widen the ratio of $\text{NO}_3\text{-N}:\text{SO}_4\text{-S}$ available to plants. On Podzolic soils such as those sampled, it is evident that 'nitrogen induced' sulfur deficiencies could result.

The time courses of mineralization for the two ions were not the same. Generally, sulfur mineralization was rapid in initial stages with a decrease in rate as time progresses. Nitrogen appeared to be released linearly with time. The amounts of NO_3 and especially SO_4 released were found closely related to the organic matter content of the soils. Biological

oxidation of organic sulfur compounds as well as chemical and biological release of organically bound SO_4 groups were considered responsible for SO_4 releases. No relationship was found to exist between total N:S ratios and ratios of release. The Chernozemic and Podzolic soils selected for this study could be separated on the basis of mean total sulfur contents as well as C:S, N:S, initial NO_3^- :N: SO_4 -S ratios, and ratios of release.

The research reported in this thesis indicated that total N:S ratios can be used to accurately evaluate the sulfur status of plants, perhaps more so than total sulfur content. The critical N:S ratios in the common field crops need to be established in future studies. Field experiments supported a previous suggestion, namely that the SO_4 -S content in a water extract of Manitoba soils can be used to determine their sulfur status. Additional field trials are required to corroborate this theory. Mineralization experiments conducted in the laboratory suggest that sulfur may be a limiting factor in the production of crops on Podzolic soils, particularly if fertilizer nitrogen is added. These results should be verified in the field.

VI BIBLIOGRAPHY

1. Allaway, W.H. and Thompson, J.F. 1966. Sulfur in the nutrition of plants and animals. *Soil Sci.* 101:240-247.
2. Anderson, D. W. 1966. Available sulfur in some Manitoba soils as estimated by plant growth and chemical analysis. M. Sc. thesis, Univ. of Manitoba, Chapt. 5:27-42.
3. Barrow, N.J. 1966. Studies on extraction and on availability to plants of adsorbed plus soluble sulfate. *Soil Sci.* 104:242-249.
4. Barrow, N.J. 1959. The effects of varying the nitrogen, sulphur, and phosphorus content of organic matter on its decomposition. *Aust. J. Agric. Res.* 11:317-330.
5. Barrow, N.J. 1959. Stimulated decomposition of soil organic matter during the decomposition of added organic materials. *Aust. J. Agric. Res.* 11:331-338.
6. Barrow, N.J. 1960. A comparison of the mineralization of nitrogen and of sulphur from decomposing organic materials. *Aust. J. Agric. Res.* 11:960-969.
7. Barrow, N.J. 1961. Studies on the mineralization of sulfur from soil organic matter. *Aust. J. Agric. Res.* 12:306-319.
8. Bates, T.E. and Tisdale, S.L. 1957. The movement of nitrate nitrogen through columns of coarse textured soil materials. *Soil Sci. Soc. Amer. Proc.* 21:525-528.
9. Bear, F.E. and Wallace, A. 1950. "Alfalfa - Its Mineral Requirements and Chemical Composition." *New Jersey Agr. Expt. Sta. Bull.* 748.

10. Beaton, J.D. 1966. Sulfur requirements of cereals, tree fruits, vegetables, and other crops. *Soil Sci.* 101:267-282.
11. Black, C.A., Editor 1965. *Methods of Soil Analysis, Part 2.* Monograph 9. American Society of Agronomy Inc., Madison, Wisconsin, U.S.A.
12. Cairns, R.R. and Richer, A.C. 1960. A comparative study of a sulfur responsive and a non-responsive Grey Wooded soil. *Can. J. Soil Sci.* 40:246-254.
13. Chao, T.T., Harvard, M.E. and Fang, S.C. 1962. Movement of S^{35} tagged sulfate through soil columns. *Soil Sci. Soc. Amer. Proc.* 26:27-37.
14. Chesnin, L. and Yien, C.H. 1950. Turbinmetric determination of available sulfates. *Soil Sci. Soc. Amer. Proc.* 15:149-151.
15. Conrad, J.P. 1950. Sulfur fertilization in California and some related factors. *Soil Sci.* 70:43-54.
16. Dijkshoorn, W., Lampe, J.E.M. and Van Burg, D.F.J. 1960. A method of diagnosing the sulphur nutrition status of herbage. *Plant and Soil* 13:227-241.
17. Ensminger, L.E. and Freney, J.R. 1966. Diagnostic techniques for determining sulfur deficiencies in crops and soils. *Soil Sci.* 101:283-290.
18. Evans, C.A. and Rost, C.O. 1945. Total organic sulfur and humus sulfur of Minnesota soils. *Soil Sci.* 59:125-137.

19. Freney, J.R. 1961. Some observations on nature of organic sulfur compounds in soil. Aust. J. Agric. Res. 12:424-432.
20. Freney, J.R., Barrow, N.J. and Spencer, K. 1962. A review of certain aspects of sulphur as a soil constituent and plant nutrient. Plant and Soil 17:295-308.
21. Freney, J.R. and Spencer, K. 1959. Soil sulphate changes in the presence and absence of growing plants. Aust. J. Agric. Res. 11:339-345.
22. Freney, J.R. and Stevenson, F.J. 1965. Organic sulfur transformations in soils. Soil Sci. 101:307-316.
23. Halverson, W.V. and Bollen, W.B. 1923. Studies on sulphur oxidation in Oregon soils. Soil Sci. 16:479-490.
24. Harmsen, G.W. and Kohlenbrander, G.J. 1965. Soil Inorganic Nitrogen. Soil Nitrogen, Monograph 10. Editors, W.V. Bartholomew and F.E. Clark. American Society of Agronomy Inc., Madison, Wisconsin, U.S.A.
25. Harward, M.E., Chao, T.T. and Fang, S.C. 1962. The sulfur status and sulfur supplying power of Oregon soils. Agron. Jour. 54:101-106.
26. Harward, M.E. and Reisenauer, H.M. 1965. Reactions and movement of inorganic soil sulfur. Soil Sci. 101:326-335.
27. Jackson, M.L. 1964. Soil Chemical Analysis. Prentice Hall Inc. Englewood Cliffs, N.J.
28. Jordan, H.V. 1958. The role of sulfur in soil fertility. Adv. in Agron. 10:407-434.
29. Kilmer, V.J. and Alexander, L.T. 1949. Methods of making mechanical analysis of soils. Soil Sci. 68:15-24.

30. Lobb, W.R. and Reynolds, D.G. 1956. Further investigation into use of sulphur in North Otago. *New Zealand J. Agric.* 92:17-25.
31. Lowe, L.E. 1965. Sulphur fractions of selected Alberta soil profiles of the Chernozemic and Podzolic orders. *Can. J. Soil Sci.* 45:297-303.
32. Lowe, L.E. and DeLong, W.A. 1960. Aspects of sulphur status of three Quebec soils. *Can. J. Soil Sci.* 41:141-146.
33. Lowe, L.E. and DeLong, W.A. 1962. Carbon bonded sulphur in selected Quebec soils. *Can. J. Soil Sci.* 43:151-155.
34. Martin, W.E. and Walker, T.W. 1966. Sulfur requirements and fertilization of pasture and forage crops. *Soil Sci.* 101:248-257.
35. Nearpass, D.C., Fried, M. and Kilmer, V.J. 1961. Greenhouse measurement of available sulfur using radioactive sulfur. *Soil Sci. Soc. Amer. Proc.* 25:287-289.
36. Nelson, L.E. 1963. Status and transformation of sulfur in Mississippi soils. *Soil Sci.* 97:300-306.
37. Pawluk, S. and Bentley, C.F. 1963. The uptake of S^{35} by crops from variable depths in the soil. *Can. J. Soil Sci.* 44:261-263.
38. Pumphrey, F.V. and Moore, D.P. 1965. Diagnosing sulfur deficiency of alfalfa from plant analysis. *Agron. Jour.* 57:364-366.
39. Racz, G.J., Webber, M.D., Soper, R.J., and Hedlin, R.A. 1965. Phosphorous and nitrogen utilization by rape, flax, and wheat. *Agron. Jour.* 57:335-337.

40. Sorensen, R.C., Penos, E.J. and Alexander, U.U. 1967. Sulfur content and yield of alfalfa in relation to plant nitrogen and sulfur fertilization. *Agron. Jour.* 60:20-23.
41. Stanford, G. and Jordan, H.V. 1966. Sulfur requirements of sugar, fiber, and oil crops. *Soil Sci.* 101:258-266.
42. Starkey, R.L. 1965. Oxidation and reduction of sulfur compounds in soils. *Soil Sci.* 101:297-306.
43. Stevenson, F.J. 1956. Effect of some long-time rotations on the amino acid composition of the soil. *Soil Sci. Soc. Amer. Proc.* 20:204.
44. Stewart, B.A. and Whitfield, C.J. 1965. Effect of crop residue, soil temperature and sulfur on the growth of winter wheat. *Soil Sci. Soc. Amer. Proc.* 29:752-755.
45. Stewart, B.A., Porter, L.K. and Viets, F.G. Jr. 1966. Effect of sulfur content of straws on rates of decomposition and plant growth. *Soil Sci. Soc. Amer. Proc.* 30:355-358.
46. Ulrich, A. 1967. Sulfur content of the alfalfa in relation to growth in filtered and unfiltered air. *Plant and Soil* 26:235-252.
47. Walker, D.R. and Bentley, C.F. 1960. Sulfur fractions of legumes as indicators of sulfur deficiency. *Can. J. Soil Sci.* 41:164-168.
48. Walker, T.W. and Adams, A.F.R. 1957. Studies on soil organic matter. *Soil Sci.* 85:307-318.
49. Walker, T.W., Adams, A.F.R. and Orehiston, H.D. 1954. Some effects of sulphur and phosphorous on the yield and composition of rape. *New Zealand J. Sci. & Tech.* 36:103-110.

50. White, J.G. 1959. Mineralization of nitrogen and sulfur in sulfur-deficient soils. *N. Zealand J. Agric. Res.* 2:255-258.
51. Whitehead, D.C. 1964. Soil and plant nutrition aspects of the sulphur cycle. *Soils and Ferts.* 27:1-8.
52. Williams, C.H. 1967. Some factors affecting the mineralization of organic sulfur in soils. *Plant and Soil* 26:205-223.
53. Williams, C.H. and Donald, C.M. 1957. Changes in organic matter and pH in a Podzolic soil as influenced by subterranean clover and superphosphate. *Aust. J. Agric. Res.* 8:179-189.
54. Williams, C.H. and Steinbergs, A. 1958. Sulphur and phosphorous in some Eastern Australian soils. *Aust. J. Agric. Res.* 9:483-491.
55. Williams, C.H. and Steinbergs, A. 1958. Soil sulfur fractions as chemical indices of available sulfur in some Australian soils. *Aust. J. Agric. Res.* 10:340-352.
56. Williams, C.H., Williams, E.G. and Scott, N.M. 1960. Carbon, nitrogen, sulphur and phosphorous in some Scottish soils. *J. Soil Sci.* 11:334-346.
57. Woldendorp, J.W. 1963. The quantitative influence of the rhizosphere on denitrification. *Plant and Soil* 17:267-270.

VII APPENDIX

Table 1A

Profile characteristics of the Almasippi and Stockton plot sites sampled in the field mineralization study.¹

Depth "	Texture	pH	Cond'y mmhos	CaCO ₃ Equiv. (%)	Organic Matter (%)	NO ₃ -N (lbs/A)	H ₂ O Sol. SO ₄ -S (lbs/A)
<u>Armstrong - Almasippi (Rego Black)</u>							
0-6	FS	7.5	0.53	0.00	2.05	7.0	4.1
6-12	FS	7.6	0.34	0.68	1.14	2.4	4.0
12-24	FS	7.7	0.39	6.48	0.74	5.0 (14.4)	3.2 (11.3) ²
24-36	FS	7.9	0.39	8.41	0.55	10.8	5.9
36-48	FS	8.0	0.52	9.62	0.50	15.3	5.0
<u>Kitching - Almasippi (Rego Black)</u>							
0-6	LS	7.5	0.52	0.61	2.16	2.5	5.8
6-12	LS	7.6	0.46	3.18	1.45	5.2	6.8
12-24	LS	7.8	0.35	4.91	1.56	5.4 (13.1)	16.2 (28.8) ²
24-36	FSCL	7.8	0.48	8.60	1.12	2.3	32.4
36-48	CL	7.7	0.72	9.35	0.68	3.0	111.3
<u>Surminsky - Stockton (Orthic Black)</u>							
0-6	LS	6.5	0.41	0.23	4.00	1.0	4.0
6-12	LS	6.6	0.30	0.82	2.64	0.9	4.0
12-24	LS	7.1	0.45	0.73	1.41	0.4 (2.3)	5.2 (13.2) ²
24-36	LS	7.3	0.45	1.11	0.99	4.4	1.6
36-48	LS	7.5	0.41	2.54	0.98	3.6	5.6

¹ NaHCO₃ extractions of phosphorous and NH₄Ac extractions of potassium indicated that these nutrients were present in adequate amounts.

² Accumulated total to 2 feet.

Table 2A

Rape mean total yields; nitrogen, sulfur, phosphorous and potassium contents and uptake; and total N:S ratios at different stages during the growing season.

Plot	Treat. No.	Time (days)	Tot. Wt. (lbs/A)	Analysis				Uptake (lbs/Ac.)				N:S Ratio
				% N	% S	% P	% K	N	S	P	K	
Kitching (Almasippi)	1	(Har.) ¹ 99	2,436	1.25	0.56	0.20	1.44	30.4	13.8	4.9	35.0	2.2
	2	44	1,325	3.04	0.43	-	-	40.2	5.7	-	-	7.1
		65	3,975	1.76	0.38	-	-	70.0	15.1	-	-	4.9
		86	6,033	1.54	0.34	0.22	1.59	93.0	20.6	13.3	95.9	4.5
		(Har.) 99	5,630	1.29	0.52	0.19	1.40	72.5	29.2	10.4	78.6	2.5
	3	44	1,440	3.04	0.59	-	-	43.8	8.5	-	-	5.2
		65	3,539	1.86	0.54	-	-	64.4	19.0	-	-	3.4
		86	6,041	1.41	0.46	0.23	1.65	85.2	27.5	13.9	99.7	3.1
		(Har.) 99	6,115	1.33	0.57	0.20	1.41	81.3	34.9	11.9	86.5	2.3
Armstrong (Almasippi)	1	(Har.) 99	3,514	0.90	0.44	0.22	1.53	31.8	15.3	7.6	53.9	2.0
	2	43	1,037	4.26	0.21	-	-	44.2	2.2	-	-	20.3
		64	3,769	1.92	0.27	-	-	72.3	10.1	-	-	7.1
		87	5,111	1.54	0.28	0.29	1.72	78.7	14.3	14.8	87.9	5.5
		(Har.) 99	6,016	1.25	0.30	0.23	1.53	75.3	18.0	13.6	92.1	4.2
	3	43	1,284	3.30	0.57	-	-	42.4	7.3	-	-	5.8
		64	4,271	1.73	0.44	-	-	73.9	18.7	-	-	3.9
		87	6,617	1.34	0.40	0.29	1.73	88.6	26.5	19.2	114.5	3.4
		(Har.) 99	7,440	0.98	0.47	0.23	1.55	72.9	35.4	17.3	115.3	2.1

¹ Samples taken at harvest time.

Table 3A

Barley mean total yields; nitrogen and sulfur contents, ratios and uptake at different stages during the growing season.

Plot	Treat. No.	Time (days)	Treat. Wt. (lbs/A)	Analysis		N:S Ratios	Uptake (lbs/A)	
				% N	% S		N	S
Toews (Stockton)	1	(Har.) ¹ 84	1,580	1.20	0.19	6.3	18.9	2.8
	2	42	506	4.20	0.33	12.7	21.2	1.7
		63	2,394	1.63	0.17	9.6	39.0	4.0
		(Har.) 84	3,679	1.33	0.13	10.2	48.8	4.6
	3	42	487	4.20	0.44	9.5	20.5	2.1
		63	2,592	1.78	0.24	7.4	46.2	6.1
		(Har.) 84	3,934	1.44	0.18	8.0	56.6	7.2
Kitching (Almasippi)	1	(Har.) 86	2,716	1.09	0.19	5.7	29.7	5.3
	2	44	1,597	2.80	0.29	9.7	44.7	4.6
		65	4,765	1.39	0.20	7.0	66.3	9.5
		(Har.) 86	5,753	1.27	0.18	7.1	73.0	10.3
	3	44	1,416	2.83	0.35	8.1	40.0	4.9
		65	4,691	1.47	0.32	4.6	69.0	14.8
		(Har.) 86	5,424	1.27	0.25	5.1	68.7	14.0
Armstrong (Almasippi)	1	(Har.) 87	3,152	1.17	0.16	7.3	36.8	5.2
	2	43	1,654	3.64	0.23	15.8	60.9	3.8
		64	4,609	1.60	0.13	12.3	73.7	6.1
		(Har.) 87	6,856	1.45	0.12	12.1	99.5	8.1
	3	43	1,687	3.16	0.41	7.7	53.3	7.0
		64	5,029	1.49	0.20	7.5	74.9	7.0
		(Har.) 87	6,913	1.35	0.25	5.4	93.1	17.2

¹ Samples taken at harvest time.

Water soluble $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ contents in fallowed and cropped soils during the growing season at the Surminsky site.

Depth (inches)	Sampling Periods ¹				
	1 (seed)	2	3	4	5 (Har.)
<u>Fallow</u>					
	<u>$\text{NO}_3\text{-N}$ (lbs/A)</u>				
0-6	1.0	4.4	8.9	11.0	5.3
6-12	0.2	1.0	0.6	1.3	0.2
12-24	0.4	2.0	2.0	4.4	0.0
24-36	4.4	1.2	1.2	2.4	0.4
36-48	3.6	2.0	1.6	0.8	0.4
	<u>$\text{SO}_4\text{-S}$ (lbs/A)</u>				
0-6	4.0	5.3	7.0	1.0	4.4
6-12	4.0	5.3	3.4	5.3	8.0
12-24	5.2	9.2	9.2	5.2	5.2
24-36	1.6	13.2	11.2	11.2	9.2
36-48	5.6	7.2	9.2	5.2	13.2
<u>Barley Check</u>					
	<u>$\text{NO}_3\text{-N}$ (lbs/A)</u>				
0-6	1.0	2.3	3.6	1.14	4.8
6-12	0.2	1.0	3.8	0.0	0.2
12-24	0.4	1.0	2.0	0.8	1.6
24-36	4.4	1.6	2.0	0.8	0.4
36-48	3.6	8.0	2.4	0.4	0.0
	<u>$\text{SO}_4\text{-S}$ (lbs/A)</u>				
0-6	4.0	0.0	0.0	0.0	0.0
6-12	4.0	3.4	6.3	2.5	6.1
12-24	5.2	5.2	7.2	2.0	3.2
24-36	1.6	7.2	9.2	2.0	5.2
36-48	5.6	2.0	5.2	0.0	0.0
<u>Rape Check</u>					
	<u>$\text{NO}_3\text{-N}$ (lbs/A)</u>				
0-6	1.0	-	2.5	2.3	7.6
6-12	0.2	-	1.0	0.4	0.2
12-24	0.4	-	1.6	0.4	0.4
24-36	4.4	-	0.4	0.0	0.0
36-48	3.6	-	3.2	2.4	0.4
	<u>$\text{SO}_4\text{-S}$ (lbs/A)</u>				
0-6	4.0	-	0.0	5.3	1.5
6-12	4.0	-	5.3	2.5	2.5
12-24	5.2	-	4.0	5.2	10.8
24-36	1.6	-	2.0	7.2	1.2
36-48	5.6	-	12.4	5.2	5.2

¹ See Table 7A for exact sampling dates.

Water soluble NO_3^- -N and SO_4^{2-} -S contents in fallowed and cropped soils during the growing season at the Kitching site.

Depth (inches)	Sampling Periods					
	1 (seed)	2	3	4	5 (Har.)	6 (Oct.)
<u>Fallow</u>						
	<u>NO_3^--N (lbs/A)</u>					
0-6	2.5	4.1	8.8	3.6	4.5	3.1
6-12	5.2	1.6	2.6	2.2	0.2	4.6
12-24	5.4	6.8	3.6	3.6	0.0	5.4
24-36	2.3	1.7	3.1	1.7	0.4	2.0
36-48	3.0	2.3	3.0	1.9	0.8	1.9
	<u>SO_4^{2-}-S (lbs/A)</u>					
0-6	5.8	5.9	8.5	1.4	0.9	0.5
6-12	6.8	8.4	2.6	6.4	5.4	6.4
12-24	16.2	10.4	5.9	1.4	1.4	18.9
24-36	32.4	14.4	32.0	20.3	10.5	38.6
36-48	111.3	61.6	117.8	87.4	131.5	85.1
<u>Barley Check</u>						
	<u>NO_3^--N (lbs/A)</u>					
0-6	2.5	3.6	2.9	2.7	0.9	2.9
6-12	5.2	7.4	0.6	0.8	1.0	3.2
12-24	5.4	11.3	1.8	0.9	0.9	3.6
24-36	2.3	5.1	2.0	0.8	0.4	0.8
36-48	3.0	5.7	6.1	2.3	1.9	4.2
	<u>SO_4^{2-}-S (lbs/A)</u>					
0-6	5.8	4.9	7.6	6.7	4.1	0.5
6-12	6.8	18.2	2.6	2.6	9.4	13.4
12-24	16.2	8.1	5.9	8.1	10.4	10.4
24-36	32.4	5.1	67.9	12.5	16.4	21.8
36-48	111.3	77.5	228.0	36.9	58.5	76.0
<u>Rape Check</u>						
	<u>NO_3^--N (lbs/A)</u>					
0-6	2.5	-	4.1	0.9	2.0	2.5
6-12	5.2	-	0.6	0.6	1.4	2.2
12-24	5.4	-	3.2	1.4	1.4	3.6
24-36	2.3	-	2.0	7.8	7.8	2.7
36-48	3.0	-	3.8	2.3	1.1	1.9
	<u>SO_4^{2-}-S (lbs/A)</u>					
0-6	5.8	-	9.4	4.1	1.4	0.9
6-12	6.8	-	12.4	8.4	8.4	11.2
12-24	16.2	-	12.2	14.4	10.4	12.6
24-36	32.4	-	28.1	12.5	18.3	12.9
36-48	111.3	-	53.2	57.8	64.6	59.3

Table 6A

Water soluble $\text{NO}_3^- \text{N}$ and $\text{SO}_4^{2-} \text{S}$ contents in fallowed and cropped soils during the growing season at the Armstrong site.

Depth (inches)	Sampling Periods						
	1 (seed)	2	3	4	5 (Har.)	6 (Oct.)	7 (spring)
<u>Fallow</u>				<u>$\text{NO}_3^- \text{N}$ (lbs/A)</u>			
0-6	7.0	11.7	11.7	5.2	0.9	4.0	10.7
6-12	2.4	2.4	5.0	4.8	0.6	5.2	10.4
12-24	5.0	4.5	4.1	9.0	0.0	6.8	6.0
24-36	10.8	4.5	2.7	1.4	0.5	4.1	1.8
36-48	15.3	4.1	7.7	5.0	3.6	4.5	4.2
				<u>$\text{SO}_4^{2-} \text{S}$ (lbs/A)</u>			
0-6	4.1	0.0	0.0	0.0	0.0	0.0	2.3
6-12	4.0	1.4	0.6	1.6	1.6	1.2	3.6
12-24	3.2	10.4	1.4	3.6	8.1	1.4	0.9
24-36	5.9	10.4	5.4	9.0	8.1	10.4	5.9
36-48	5.0	5.4	8.1	14.4	8.1	8.1	10.4
<u>Barley Check</u>				<u>$\text{NO}_3^- \text{N}$ (lbs/A)</u>			
0-6	7.0	9.5	3.4	1.4	0.0	3.1	2.0
6-12	2.4	4.0	1.4	1.0	0.2	4.4	2.3
12-24	5.0	10.4	1.8	0.9	0.0	8.6	5.1
24-36	10.8	10.4	2.4	0.5	0.5	3.2	8.3
36-48	15.3	9.9	5.4	3.6	0.0	4.1	14.8
				<u>$\text{SO}_4^{2-} \text{S}$ (lbs/A)</u>			
0-6	4.1	0.0	0.0	0.0	0.0	0.0	0.0
6-12	4.0	4.6	0.0	0.6	2.4	2.4	2.6
12-24	3.2	8.1	6.8	3.6	8.1	15.8	4.5
24-36	5.9	6.8	3.2	3.6	10.4	8.1	10.4
36-48	5.0	10.4	8.1	9.0	8.1	8.1	10.4
<u>Rape Check</u>				<u>$\text{NO}_3^- \text{N}$ (lbs/A)</u>			
0-6	7.0	-	3.6	2.2	0.7	3.6	2.4
6-12	2.4	-	1.6	1.0	0.2	4.8	1.4
12-24	5.0	-	3.2	0.9	0.5	4.5	4.2
24-36	10.8	-	3.2	0.5	0.0	4.5	4.2
36-48	15.3	-	6.3	1.4	0.5	2.7	4.2
				<u>$\text{SO}_4^{2-} \text{S}$ (lbs/A)</u>			
0-6	4.1	-	0.0	0.0	0.0	0.0	0.4
6-12	4.0	-	0.0	0.0	0.6	1.2	5.6
12-24	3.2	-	8.1	10.4	9.0	2.7	5.9
24-36	5.9	-	10.4	10.4	3.6	6.8	0.9
36-48	5.0	-	12.2	9.0	13.5	8.1	8.1

Table 7A

Sampling dates for soil and plant material in field experiment; and rainfall received during the sampling period as recorded at Graysville, Man. by the Dept. of Transport, Meteorology Branch.

Sampling Period							
Soil	1	2	3	4	5	6	7
Plants	-	-	1	2	3	4	-

Surminsky (Stockton)

May 20 June 7 June 29 July 19 Aug. 9 - -

Kitching (Almasippi)

May 22 June 9 July 5 July 26 Aug. 16 Oct. 21 -

Armstrong (Almasippi)

May 22 June 9 July 4 July 25 Aug. 16 Oct. 21 May 18('68)

Precipitation (inches) between sampling periods

.58 4.18 .89 2.69 2.40 -

Table 8A

Water soluble $\text{SO}_4\text{-S}$ contents to different depths, total sulfur contents, and yield increases due to added sulfur on Rape trials at 3 Manitoba locations.

Plot Designation	Water soluble $\text{SO}_4\text{-S}$ (lbs/A) to			Sulfur Treatment (lb./A)	Total S	
	12"	24"	36"		(%) @ Flowering ²	% yield
Armstrong-1967 (Almasippi)	8.1	11.3	17.2	30	.21	71.1
¹ Anderson-1965 (Stockton)	7.1	16.6	19.8	20	.29	84.1
Kitching-1967 (Almasippi)	12.6	28.8	61.2	30	.43	84.9

¹ Results from field trial conducted by Anderson (2).

² Nitrogen and phosphorous check treatment.

Table 9A

Moisture contents to which soils belonging to the textural groups in the incubation experiment were brought prior to incubation.

Textural Group	Moisture Content (% Dry Wt.)	
	Above W.P.	Below F.C.
Course (S-LS)	18	5
Medium (LVFS-L)	28	8
Fine (CL-C)	38	18

Table 10A

Designation of soils according to conditions during incubation.

Temperature (°C)	Laboratory Soil Nos.	
	Above W.P.	Below F.C.
10°C	11, 12, 16, 18, 19	11, 12, 16, 19
18°C	11, 12, 16 - 21	1 - 21
30°C	11, 12, 16 - 21	11, 12, 16 - 21

Table 11A

NO₃ nitrogen and SO₄ sulfur contents at intervals during incubation experiment¹.

Soil Association or Series	Mois- ture	Temp. (°C)	NO ₃ -N (ppm) Time (weeks)					SO ₄ -S (ppm) Time (weeks)				
			0	1	3	6	12	0	1	3	6	12
Osborne	FC	18	9.4	14.0	15.4	18.3	25.5	37.2	-	-	-	37.2
Poppleton B	FC	18	9.9	29.1	39.7	48.1	64.8	27.1	-	31.2	29.7	32.0
Poppleton C	FC	18	3.1	9.9	-	26.1	33.2	0.7	1.8	1.8	-	3.2
Sandilands	FC	18	1.1	5.7	11.7	17.2	28.4	0.3	0.3	0.8	-	1.3
Poppleton A	FC	18	2.2	9.4	18.3	33.2	0.8	-	-	-	-	2.3
Poppleton D	FC	18	0.5	2.3	4.0	8.9	19.9	1.2	-	2.0	2.7	1.9
Thalberg	FC	18	28.4	37.4	36.6	49.6	61.7	9.9	8.7	7.7	7.3	7.3
Caliento	FC	18	4.4	10.4	15.9	19.3	25.5	1.2	1.5	2.0	1.5	1.5
Libau	FC	18	12.3	26.1	26.9	36.3	38.8	5.2	2.3	7.3	6.5	7.5
Almasippi A	WP	10	1.1	-	0.7	1.6	3.8	0.0	-	0.0	0.3	0.4
	FC	10	1.1	-	3.5	7.4	15.3	0.0	-	0.0	0.3	1.0
	WP	18	1.1	1.3	1.8	7.3	22.1	0.0	0.0	0.0	0.8	2.3
	FC	18	1.1	1.3	11.4	-	30.9	0.0	1.7	0.8	-	2.3
	WP	30	1.1	4.2	10.4	31.2	34.6	0.0	0.8	0.3	0.8	1.5
	FC	30	1.1	11.1	28.4	33.7	52.4	0.0	2.3	2.3	3.2	3.3
	WP	10	1.0	-	2.3	2.7	1.9	0.0	-	0.0	0.0	0.3
	FC	10	1.0	-	3.5	4.9	7.0	0.0	0.0	0.5	0.0	0.0
Almasippi B	WP	18	1.0	2.3	3.0	4.9	11.9	0.0	0.0	0.0	0.3	0.2
	FC	18	1.0	3.3	5.2	8.2	17.6	0.0	0.0	0.0	0.7	1.6
	WP	30	1.0	5.4	8.3	20.7	25.9	0.0	0.0	0.3	0.7	0.9
	FC	30	1.0	8.0	13.7	22.0	38.8	0.0	0.3	1.5	-	3.2
	FC	18	17.3	26.1	32.8	47.1	52.4	1.3	2.7	2.3	5.2	4.9
	FC	18	5.7	8.8	-	13.7	21.0	2.3	5.2	3.5	5.5	6.3
	WP	10	5.2	-	7.8	7.6	11.9	1.0	-	2.3	2.0	2.3
	WP	18	5.2	7.8	9.9	15.2	22.4	1.0	2.0	2.3	2.0	3.2
Erickson A	WP	30	5.2	15.3	23.1	-	67.9	1.0	-	1.7	-	3.3
	FC	30	5.2	1.1	30.2	-	-	1.0	2.0	2.7	-	-
	WP	18	3.4	6.1	5.7	10.3	13.5	0.7	2.0	2.3	3.2	5.7
	WP	30	3.4	12.2	29.5	36.3	104.9	0.7	2.0	6.3	4.0	7.3
	FC	30	3.4	0.9	38.9	44.0	235.4	0.7	1.5	2.7	3.8	7.8
Erickson B												

Table 11A (Con't.)

Soil Association or Series	Mois- ture	Temp. (°C)	NO ₃ -N (ppm) Time (weeks)					SO ₄ -S (ppm) Time (weeks)				
			0	1	3	6	12	0	1	3	6	12
Granville	WP	10	5.5	-	8.6	9.2	10.5	0.6	-	0.8	1.2	2.0
	WP	18	5.3	7.8	9.9	-	29.2	0.6	1.5	2.0	-	2.2
	FC	18	5.5	9.4	12.8	23.6	34.6	0.6	0.0	1.2	2.7	3.7
	WP	30	5.5	16.1	22.0	55.3	78.1	0.6	-	0.3	1.5	2.0
	FC	30	5.5	25.8	45.3	-	140.8	0.6	2.7	4.3	-	6.2
Clarkesville A	WP	10	11.7	-	19.9	23.6	27.6	0.4	-	0.3	1.2	1.2
	FC	10	11.7	-	21.3	26.9	47.3	0.4	-	0.3	3.7	1.3
	WP	18	11.7	18.4	26.9	29.2	32.8	0.4	0.8	2.3	3.2	3.7
	FC	18	11.7	18.1	28.4	46.8	94.6	0.4	3.7	2.3	5.7	5.2
	WP	30	11.7	33.6	40.8	73.2	128.5	0.4	4.2	5.2	6.2	6.7
Clarkesville B	FC	30	11.7	34.5	58.6	106.5	185.0	0.4	3.2	3.7	7.2	9.0
	WP	18	4.4	9.9	12.8	20.7	26.7	0.3	0.3	0.8	1.3	1.4
	FC	18	4.4	8.8	15.4	25.6	61.7	0.3	0.0	0.3	1.3	3.4
	WP	30	4.4	19.2	33.6	52.2	59.6	0.3	0.8	3.0	3.0	3.7
	FC	30	4.4	23.5	42.0	82.4	111.0	0.3	3.0	3.0	5.2	5.2
Newdale	WP	18	2.1	3.7	5.7	5.4	20.7	3.9	4.7	-	4.7	4.7
	WP	30	2.1	7.0	15.9	38.9	37.0	3.9	5.2	-	5.7	6.7
Wellwood	FC	18	2.0	3.7	-	7.8	14.1	0.0	1.8	2.3	2.9	3.9

¹ The physical structure of soils #8, 16, 17, and 21 at near FC moisture conditions were destroyed on preparation, and were eliminated from the experiment after the 3rd week.

Table 12A

Net changes in $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ contents and ratios of release at intervals during incubation experiment¹.

Soil Association or Series	Mois- ture	Temp. (°C)	$\text{NO}_3\text{-N}$ changes (ppm)				$\text{SO}_4\text{-S}$ changes (ppm)				Ratio of release ²			
			Time (weeks)				Time (weeks)				Time (weeks)			
			1	3	6	12	1	3	6	12	1	3	6	12
Osborne	FC	18	4.6	6.0	8.9	16.1	0.0	0.0	0.0	0.0	-	-	-	-
Poppleton B	FC	18	19.2	29.2	38.3	54.9	-	4.2	2.7	5.0	-	7.2	14.4	11.1
Poppleton C	FC	18	6.8	-	23.0	30.1	1.2	1.2	-	2.5	5.9	-	-	12.0
Sandilands	FC	18	4.6	10.6	16.1	27.3	0.0	0.5	-	1.1	-	21.7	-	27.3
Poppleton A	FC	18	7.2	-	16.1	31.0	-	-	-	1.6	-	-	-	19.5
Poppleton D	FC	18	1.8	3.5	8.4	19.5	-	0.8	1.5	0.8	-	4.3	5.6	25.6
Caliento	FC	18	6.0	11.5	14.9	21.1	0.3	0.8	0.3	0.4	17.8	13.8	43.8	60.3
Libau	FC	18	6.0	11.5	14.9	21.1	0.3	0.8	0.3	0.4	-	6.7	18.0	11.3
Libau	FC	18	13.8	14.6	24.1	26.5	-	2.2	1.3	2.3	-	-	1.5	5.3
Almasippi A	WP	10	-	-	0.5	2.2	-	-	0.3	0.4	-	-	-	-
	FC	10	-	2.2	6.4	14.2	-	-	0.3	1.0	-	-	18.7	14.2
	WP	18	0.2	0.7	6.2	21.0	0.0	0.0	0.8	2.3	-	-	7.5	9.0
	FC	18	0.2	10.2	-	29.8	1.7	0.8	-	2.3	0.1	12.3	-	12.7
	WP	30	3.1	9.3	30.1	33.5	0.8	0.3	0.8	1.5	3.7	27.4	36.3	22.3
	FC	30	9.9	27.3	32.7	51.3	2.3	2.3	3.2	3.3	4.2	11.7	10.3	15.4
Almasippi B	WP	10	-	1.2	1.7	1.8	0.0	0.0	0.0	0.3	-	-	-	7.0
	FC	10	-	2.5	4.0	6.0	0.0	0.5	0.0	0.0	-	4.8	-	-
	WP	18	1.2	2.0	4.0	10.9	0.0	0.0	0.3	0.2	-	-	11.6	64.1
	FC	18	2.3	4.2	7.2	16.6	0.0	0.0	0.7	1.6	-	-	10.9	10.4
	WP	30	4.4	7.3	19.7	25.9	-	0.3	0.7	0.9	-	21.4	29.9	28.4
	FC	30	8.0	12.7	22.0	37.7	0.3	1.5	-	3.3	23.4	8.4	-	11.7
Winkler	FC	18	8.9	15.5	29.9	35.2	1.3	1.0	3.8	3.6	6.6	15.5	7.8	9.8
Red River	FC	18	3.1	-	8.0	15.3	2.9	1.3	3.2	4.9	1.1	-	2.5	3.8
Erickson A	WP	10	-	2.6	2.4	6.7	-	1.3	1.0	1.4	-	1.9	2.4	5.0
	WP	18	2.6	4.7	10.0	17.2	1.0	1.3	1.0	2.2	2.6	3.5	10.0	7.9
	WP	30	10.0	17.9	-	62.6	-	0.7	-	2.3	-	27.2	-	27.8
	FC	30	-	25.2	-	-	1.0	1.7	-	-	-	15.0	-	-
Erickson B	WP	18	2.8	2.4	7.4	10.1	1.3	1.7	2.5	5.0	2.1	1.4	3.0	2.0
	WP	30	8.8	26.1	33.0	101.5	1.3	5.7	3.3	6.7	6.6	4.6	9.9	15.2
	WP	30	-	35.5	40.7	232.0	0.8	2.0	3.1	7.2	-	17.7	13.0	32.4

Table 12A (Con't.)

Soil Association or Series	Mois- ture	Temp.	NO ₃ -N changes (ppm)				SO ₄ -S changes (ppm)				Ratio of release ²			
			Time (weeks)				Time (weeks)				Time (weeks)			
			1	3	6	12	1	3	6	12	1	3	6	12
Granville	WP	10	-	3.1	3.7	5.0	-	0.3	0.6	1.4	-	12.3	6.3	3.5
	WP	18	2.3	4.4	-	23.7	0.9	1.4	-	1.6	2.4	3.1	-	14.9
	FC	18	3.9	7.3	18.0	29.1	-	0.6	2.1	3.1	-	12.3	8.6	9.5
	WP	30	10.7	16.5	49.8	72.6	-	-	0.9	1.4	-	-	53.5	51.1
	FC	30	20.3	39.8	-	135.3	2.1	3.8	-	5.7	9.7	10.6	-	24.2
Clarkesville A	WP	10	-	8.2	11.8	15.8	-	-	0.8	0.8	-	-	15.6	20.8
	FC	10	-	9.6	15.2	35.6	-	-	3.3	0.9	-	-	4.6	38.3
	WP	18	6.7	15.2	17.5	21.1	0.4	1.9	2.8	3.3	16.0	7.9	6.3	6.4
	FC	18	6.4	16.7	35.1	82.9	3.3	1.9	5.3	4.5	2.0	8.7	6.7	18.5
	WP	30	21.9	29.0	61.5	116.8	3.8	4.8	5.8	6.3	5.8	6.1	10.7	18.7
Clarkesville B	FC	30	22.8	46.9	94.8	173.3	2.8	3.3	6.8	8.6	8.2	14.1	14.0	20.2
	WP	18	5.5	8.4	16.3	22.3	0.0	0.5	1.0	1.0	-	17.1	16.3	22.3
	FC	18	4.4	11.0	21.2	57.3	-	0.0	1.0	2.0	-	-	21.2	28.5
	WP	30	14.8	29.2	47.8	55.2	0.5	2.7	2.7	3.3	30.1	10.9	17.8	16.5
	FC	30	19.1	37.6	78.0	106.6	2.7	2.7	4.8	4.8	7.1	14.0	16.2	22.0
Newdale	WP	18	1.6	2.6	3.3	18.6	0.8	-	0.8	0.8	2.1	-	4.4	24.8
	WP	30	4.9	13.8	36.8	34.9	1.2	-	1.8	2.8	3.9	-	21.0	12.7
Wellwood	FC	18	1.7	-	5.8	12.1	1.8	2.3	2.9	3.9	0.9	-	2.0	3.1

¹Only soils in which positive changes occurred are listed here.

²Where applicable