AMMONIUM THIOSULFATE AS A SOURCE OF SULFUR FOR PLANTS (COMPARED TO OTHER SULFUR CARRIERS)

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by

Murray James Swan
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Abstract

Field and growth chamber studies were conducted in order to examine the response of barley and rapeseed to the addition of different forms of sulfur. Also examined was the oxidation of ammonium thiosulfate as affected by time and soil phosphorus content and the effect of thiosulfate upon the utilization of fertilizer phosphorus by barley and rapeseed.

In a field experiment ammonium sulfate, ammonium thiosulfate, gypsum and a source of elemental sulfur were evaluated for their relative abilities to supply barley and rapeseed with sulfur. In general, grain yield, sulfur concentration and sulfur uptake of barley were not significantly affected by the addition of sulfur in any form. While not always significant, there was a trend towards higher total sulfur uptake and seed yield of rapeseed supplied with sulfur as ammonium sulfate, ammonium thiosulfate or gypsum compared to where sulfur was supplied as elemental sulfur.

In a growth chamber experiment, ammonium thiosulfate, gypsum and elemental sulfur in the form of Agrisul were compared as sources of sulfur for rapeseed. Rapeseed supplied with ammonium thiosulfate or gypsum produced significantly higher dry matter yields and recovered significantly more fertilizer sulfur than treatments supplied with elemental sulfur. Powdering and mixing of elemental sulfur as opposed to banding granules, significantly increased dry matter yield of rapeseed and recovery of fertilizer sulfur. While not always significant, there was

a trend toward higher dry matter yield and higher recovery of fertilizer sulfur where gypsum granules were mixed as opposed to banded and where ammonium thiosulfate was placed in a band as opposed to being mixed throughout the soil.

An incubation experiment carried out on two Manitoba soils showed that the oxidation of ammonium thiosulfate to sulfate occurs over a relatively short period of time (14 days) and that the rate and extent of this oxidation differs among soils. Increasing the available phosphorus content of the soil had no effect upon the rate at which thiosulfate was oxidized.

A second growth chamber experiment was undertaken in order to examine the effect that banding urea or a thiosulfate source with monoammonium phosphate had upon fertilizer phosphorus uptake and dry matter yield of barley and rapeseed. For barley, fertilizer phosphorus uptake and dry matter yield were significantly increased when a thiosulfate source was banded with monoammonium phosphate. Sodium thiouslfate was more effective in increasing fertilizer phosphorus uptake than was ammonium thiosulfate. Banding urea with monoammonium phosphate did not affect fertilizer phosphorus uptake or dry matter yield of barley. Fertilizer phosphorus uptake and dry matter yield of rapeseed were not significantly affected by banding either a thiosulfate source or urea with monoammonium phosphate.

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I Introduction

Sulfur is an essential element required in plant usable forms and sufficient quantities in order to maintain amino acid and protein synthesis, and chlorophyll production in plants. If soils provide insufficient sulfur for optimum plant growth, additions of a fertilizer supplying plant available sulfate must be made. Any fertilizer being considered must provide sulfur in the sulfate form or in a form which is readily oxidized to plant available sulfate.

Other studies have examined the sulfur status of Manitoba soils (Anderson 1966, Bailey 1978) and established the sulfur requirements of various crops (Anderson 1966, Hamm 1969, Ridley 1973, Bailey 1978). Little if any work has been done to evaluate the relative effectiveness of various sulfur fertilizers in providing crops with plant available sulfur.

Field studies were undertaken in which dry matter yield and tissue sulfur concentration of barley and rapeseed were used to evaluate the relative plant availability of four sulfur sources over the course of the growing season. In a growth chamber study, sulfur sources requiring oxidation in order to become plant available and a source which provided sulfur in the sulfate form were compared for their ability to supply rapeseed with sulfur. The effect of banding versus mixing the three sources was also determined.

The rate of oxidation of ammonium thiosulfate in a soil as affected by time and soil phosphorus content was examined in an

incubation experiment. A second growth chamber experiment assessed the effect that banding a thiosulfate source with a phosphorus source had upon fertilizer phosphorus uptake and dry matter yield of barley and rapeseed.

II LITERATURE REVIEW

A. The Oxidation of Reduced Sulfur Compounds

In order to become plant available reduced compounds of sulfur, such as elemental sulfur and thiosulfate, must be oxidized to sulfate. The oxidation of reduced sulfur compounds may occur by purely chemical means in the soil. Gleen and Quastel (1952) reported that soils containing an excessive quantity of adsorbed ferric ions were able to oxidize thiosulfate to sulfate. However, chemical oxidation in soils is usually slow and accounts for only a small portion of the oxidation occuring when compared to that carried out by microorganisms.

Biological oxidation of reduced sulfur compounds may be carried out by three groups of microorganisms found in soils. These include anaerobic photoautotrophs, certain heterotrophs and chemoautotrophic bacteria.

Anaerobic photoautotrophs such as the green sulfur bacteria Chlorobium and Chlorobacterium and the purple sulfur bacteria Thiocystis are able to carry out the oxidation of reduced sulfur compounds. However, Vitolins and Swaby (1969) found photosynthetic, anaerobic oxidation to be unimportant and concluded that oxidation by this process would be rare in opaque, aerobic soils.

Various heterotrophic bacteria have been shown to be capable of oxidizing thiosulfate and elemental sulfur to sulfate.

Pure culture studies have shown that the heterotrophic bacteria Arthrobacter spp., Bacillus spp., Flavobacterium spp. are capable of oxidizing sulfur or thiosulfate to sulfate while Achromobacter stutzeri and Pseudomonas fluorescens have been found to be capable of oxidizing thiosulfate to tetrathionate (Wainwright 1978). In soils incompletely oxidized sulfur compounds, such as tetrathionate, would be oxidized further to sulfate (Starkey 1965).

Most heterotrophic microorganisms prefer a pH range of 6.0 - 7.5. Although oxidation of sulfur by heterotrophs in soils has not received extensive study, presumably oxidation by these organisms is of importance in neutral to slightly alkaline soils.

Pepper and Miller (1978) reported that two nonacidiophilic heterotrophic microorganisms identified only as Isolate 1 and Isolate 5 were capable of the oxidation of thiosulfate and elemental sulfur in soils with a neutral to alkaline pH. Vitolins and Swaby (1969) found that heterotrophic yeasts and heterotrophic facultative autotrophic bacteria were far more numerous in Australian soils than were obligate autotrophs although they were far less efficient at oxidizing sulfur that were the autotrophs. Vitolins and Swaby (1969) felt that the role of the heterotroph in many neutral to alkaline soils is that of a primary oxidizer, reducing pH to the point that secondary oxidation by autotrophic thiobacilli can take place.

The occurence of heterotrophic microorganisms in soil as

sulfur oxidizers is well established, however, the effect of their activity has yet to be quantified. The importance of their role in the oxidation of reduced sulfur compounds in soil and the means by which it is carried out remains unclear.

Autotrophic bacteria of the genus Thiobacillus are the most important oxidizers of sulfur in soils. The thiobacilli are a small group of chemolithotrophic organisms which obtain their energy from the oxidation of elemental sulfur and other reduced sulfur compounds, while obtaining carbon from CO_2 or from inorganic salts.

Wainwright (1978) identified five species of thiobacilli as being important in the oxidation of sulfur in soils.

Thiobacillus novellus, the only one of the five which is not an obligate chemoautotroph, and Thiobacillus thioparus grow best when pH of the media is close to neutrality. Thiobacillus thioparus is well distributed in soils and able to aerobically oxidize thiosulfate, sulfide, elemental sulfur and tetrathionate. Thiobacillus novellus can oxidize thiosulfate to sulfate but is not able to oxidize elemental sulfur (Starkey 1965). Thiobacillus dentrificans is similar to Thiobacillus thioparus but may also oxidize sulfur compounds anaerobically using nitrate as the specific hydrogen acceptor.

Thiobacillus thiooxidans is able to withstand extreme acidity developing best in pH's ranging from 2.0 - 3.0 (Rao and Berger 1971). Starkey (1965) reported little or no development of Thiobacillus thiooxidans at neutral pH's but

in more acid media it was found to oxidize elemental sulfur rapidly and was also capable of oxidizing sulfide, thiosulfate, tetrathionate and sulfite. Similarily Thiobacillus ferrooxidans is extremely acid tolerant, able to oxidize thiosulfate and is also capable of oxidizing ferrous iron.

The thiobacilli are considered to be the most important oxidizers of elemental sulfur in soils. Oxidation of elemental sulfur by these organisms has been shown by a number of workers.

Karavaiko and Pivovarova (1973) found that cultures of Thiobacillus thiooxidans energetically oxidized sulfur as indicated by a decrease in pH and an accumulation of sulfate in the medium. The maximum rate of oxidation occured in the exponential growth phase of the culture and is consistent with data obtained by Lettl et al (1981) who found oxidation of elemental sulfur exhibited a lag phase, the oxidation eventually being induced by a proliferation of thiobacilli.

Although numerous pathways for the aerobic oxidation of elemental sulfur by the thiobacilli have been elucidated, Wainwright (1978) favoured the polythionate pathway for the oxidation of sulfur in soils:

$$S \rightarrow S_2O_3^{2-} \rightarrow S_4O_6^{2-} \rightarrow S_3O_6^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$$

sulfur thiosulfate tetrathionate trithionate sulfite sulfate

Wainwright (1978) provided evidence for the occurrence of thiosulfate as an intermediate in the oxidation of elemental sulfur. An increase was shown in both soil rhodanese activity and sulfate concentration in a soil amended with elemental sulfur. Rhodanese is an enzyme (thiosulfate sulfurtransferase) which catalyses the formation of sulfite from thiosulfate.

Nor and Tabatabai (1977) incubated a number of Iowa soils which were amended with elemental sulfur. Analysis showed that thiosulfate was produced within the first few days of incubation and that tetrathionate accumulated in some soils. The accumulation of these compounds in the soil was found to be transitory in nature. After 28 days all sulfur which had been oxidized was present as sulfate, no thiosulfate or tetrathionate could be detected.

Most evidence to date indicates that elemental sulfur is oxidized to sulfate via the polythionate pathway. Suzuki (1982) proposed that elemental sulfur was oxidized directly to sulfite by thiobacilli and then underwent further oxidation to sulfite. Elemental sulfur normally exists as an S_8 ring structure and the sulfur atoms would be oxidized one by one to sulfite. Accumulations of thiosulfate observed by other workers could be explained by a reaction between sulfide from the broken ring structure and sulfite, which would yield thiosulfate. Whether oxidized directly or via the polythionate pathyway, the literature indicates

that elemental sulfur is energetically oxidized to sulfate by thiobacilli in soils.

Thiosulfate is the form of reduced sulfur which is the most widely oxidized by the thiobacilli (Parker and Prisk 1953). The overall reaction for the aerobic oxidation of thiosulfate is as follows:

$$S_2O_3^{=} + 2O_2 + H_2O \rightarrow 2SO_4^{=} + 2H^+$$

The reaction is highly exergonic and will provide the thiobacilli with their sole source of energy under autotrophic conditions (Aleem 1975).

The mechanisms involved in the oxidation of thiosulfate have been the subject of much research. The literature would indicate that there are three possible pathyways for the oxidation of thiosulfate to sulfate by the thiobacilli.

Peck (1962) proposed a pathway in which the initial reaction would be a reductive cleavage of the thiosulfate molecule to form sulfite and sulfide. The sulfite moiety is then further oxidized to sulfate via a pathway involving adenosine phosphosulfate (APS). The sulfide moiety undergoes oxidation to elemental sulfur which is presumably oxidized to sulfate. Aleem (1975) summarized the reductive cleavage of thiosulfate and subsequent oxidation of the moieties as follows:

$$S_2O_3^{=} \begin{cases} \rightarrow S^{=} \rightarrow S^{\circ} \\ \rightarrow SO_3^{=} \rightarrow APS \rightarrow SO_4^{=} \end{cases}$$

Although the mechanism proposed by Peck (1962) may

appear to be the most direct route for the oxidation of thiosulfate to sulfate, it does not take into account the formation of polythionate observed by many workers. These observations would suggest that a polythionate pathway in which thiosulfate is oxidized to sulfate through the production of the intermediates tetrathionate, trithionate and sulfate occurs.

Vishniac (1952), working with cultures of Thiobacillus thioparus, found that thiosulfate was oxidized to sulfate with the intermediate formation of tetrathionate and trithionate. Precipitation of elemental sulfur in the cultures was noted and thought to arise from the dismutation of tetrathionate to trithionate and pentathionate with the subsequent decomposition of pentathionate to tetrathionate and sulfur.

Gleen and Quastel (1952) perfused a soil with thiosulfate solution. They found that sulfate and tetrathionate were the most common products formed. When concentrations of soil phosphates were high or when thiosulfate concentration was high, the production of sulfate and sulfur was favoured.

London and Rittenberg (1964), citing enzymatic evidence, showed that tetrathionate and trithionate were sequentially formed during the oxidation of thiosulfate to sulfate by Thiobacillus thiooxidans and Thiobacillus thioparus. Mahmoud et al (1979) were able to show the formation of polythionate

in the oxidation of thiosulfate by Thiobacillus thioparus. Tetrathionate in particular was present and this was in keeping with an hypothesis originally proposed by Vishniac (1952) that the oxidation proceeded in two stages, first the complete oxidation of the substrate to tetrathionate followed by the oxidation of tetrathionate to give rise to sulfate.

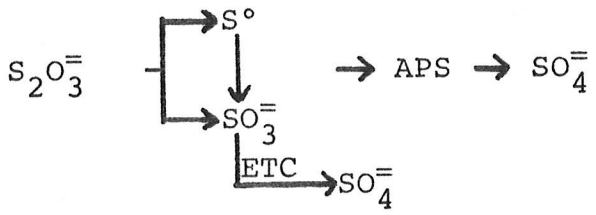
Parker and Prisk (1953) examined four species of thiobacilli and found that all were capable of oxidizing thiosulfate. Thiobacillus thiooxidans, Thiobacillus concretivours and Thiobacillus X first oxidized thiosulfate to tetrathionate and sulfate and then converted the tetrathionate to sulfate. Thiobacillus thioparus oxidized thiosulfate to sulfur and sulfate with the sulfur undergoing a further partial oxidation.

Aleem (1975) was able to characterize the polythionate pathway of thiosulfate oxidation as follows:

$$S_2O_3^{=} \rightarrow S_4O_6^{=} \rightarrow S_3O_6^{=} \rightarrow SO_3^{=} \rightarrow SO_4^{=}$$

Another mechanism for thiosulfate metabolism in the thiobacilli was proposed by Lyric and Suzuki (1970). In this scheme, the thiosulfate molecule is split to form sulfur and sulfite. The sulfur moiety undergoes further oxidation to sulfite and both sulfites undergo oxidation to sulfate via the electron transport chain or APS reductase. It was felt that the simple splitting of thiosulfate achieved the same result as the polythionate pathway yet was more energy efficient. Aleem (1975) summarized the pathway as

follows:



In view of the data available, Roy and Trudinger (1970) felt that oxidation of thiosulfate by the thobacilli could proceed along any one of the three pathways. The proposed mechanisms are by no means incompatable and it is possible that they could occur simultaneously.

The rate and extent of the conversion of thiosulfate to sulfate by the thiobacilli has been shown to be dependent upon the concentration of phosphate in the media (Peck 1962, Santer 1959, Santer et al 1959, Vishniac and Santer 1957). In the complete absence of phosphate, only a portion of the thiosulfate can be completely oxidized to sulfate. The remainder will be oxidized to a sulfur containing compound short of sulfate.

Santer et al (1959) demonstrated the requirement for inorganic phosphate for the complete conversion of thiosulfate to sulfate by cells of Thiobacillus thioparus. Their data showed that low phosphate concentrations had a rate limiting effect upon the oxidation, that even with very low concentrations of phosphate the conversion of thiosulfate could be carried to completion, and that in the absence of phosphate only about 70% of the theoreticial amount of oxygen required to convert all of the thiosulfate to sulfate is

used.

Subsequent work by Santer (1959) using ^{18}O labelled phosphate supported the hypothesis that phosphate was involved in a substrate level oxidative step in which a sulfur compound was linked to phosphate. Vishniac and Santer (1957) felt that such a compound may donate phosphate to ADP to form ATP in a subsequent energy producing reaction, and that one of the oxygen atoms of each of the sulfur molecules is derived from the phosphate.

Santer's work indicates that in a liquid media, increasing the phosphate concentration increased the rate of thiosulfate oxidation to sulfate. Similar work was carried out by Lettl et al (1981) in their examination of the oxidative capacity of a number of forest soils towards thiosulfate. Increasing amounts of potassium phosphate or superphosphate were added to the soils. As the phosphorus concentration of the soils was increased the rate of conversion of thiosulfate to sulfate increased over control soils which received no additional phosphorus.

The literature indicates that a phosphorus requirement for the complete oxidation of thiosulfate to sulfate in liquid media can be shown and that this requirement may be extended to the oxidation of thiosulfate in soils. Thus it is possible that the thiosulfate oxidizing capacity of a soil could be enhanced by increasing concentrations of inorganic phosphorus.

B. The Effect of Elemental Sulfur and Sulfate Addition on Phosphorus Availability to Plants

Research by several workers has shown that the addition of a sulfur source with a phosphorus source may increase the plant availability and uptake of phosphorus. This effect has been related to an increase in the solubility of the phosphorus source (Mitchell et al, 1952), to an increase in the availability of phosphorus reaction products (Menary and Hughes, 1967, Barrow, 1967) and to an alteration in the physiology of the plant such that it is better able to utilize phosphorus.

Mitchell et al (1952) showed that mixing small amounts of elemental sulfur with dicalcium phosphate-nitrate increased the uptake of phosphorus by wheat. In order for the elemental sulfur to be effective in increasing phosphorus uptake, conditions conducive to the oxidation of elemental sulfur had to exist. It was felt that the increased uptake of phosphorus was due to the reduction of pH in the area of the fertilizer granule thus resulting in a reduced rate of fixation or an increased solubility of the phosphorus fertilizer.

Menary and Hughes (1967) were able to provide evidence for a sulfur-phosphorus interaction in work with tomato plants. In field trials, tomato plants showed a response to sulfur banded with monocalcium phosphate when the plants were phosphorus deficient. No response was noted when the plants were adequately supplied with phosphorus suggesting

that sulfur deficiency was not a factor. While no further explanation was offered, the authors noted that the response to sulfur was independent of the form applied; in this case elemental sulfur, calcium sulfate or sodium sulfate.

In greenhouse trials, Menary and Hughes noted an increase in phosphorus uptake by tomato plants when sodium sulfate and monocalcium phosphate were mixed together throughout the soil. When sodium sulfate was applied alone, there was no influence upon phosphorus uptake even under extreme phosphorus deficiency conditions. Menary and Hughes concluded that sulfate influences phosphorus uptake only in the presence of applied phosphorus and attributed the increased uptake of phosphorus to a reduced fixation of phosphate in the presence of sulfate.

Aitken and Hughes (1980) investigated the effect of the addition of sulfate upon phosphorus uptake by greenhouse grown tomatoes when three phosphate fertilizers (monocalcium phosphate, monoammonium phosphate or diammonium phosphate) were either banded or mixed into a high P-fixing soil. The results showed that availability of phosphorus from all sources was increased in the presence of potassium sulfate as long as the plants were not severely phosphorus deficient. A second crop of tomatoes grown without any further addition of phosphorus showed that only plants receiving phosphorus as banded monocalcium phosphate had phosphorus concentrations near the critical level. In this case both yield and

phosphorus concentration were significantly increased in those treatments which received potassium sulfate along with the monocalcium phosphate.

Aitken and Hughes felt that in this experiment sulfate increased phosphorus availability and that this increase was the result of sulfate effectively competing with phosphate for fixation sites on soil minerals. A response to sulfate due to a sulfur deficiency was discounted as soil and plant tissue analysis indicated sufficient levels of sulfur were present.

Kumar and Singh (1980) were able to show that the addition of sulfur as potassium sulfate had a synergistic effect upon the P content of greenhouse grown soybeans. Addition of sulfur significantly increased phosphorus concentration in plant parts and an increase in grain yield was observed when sulfate was applied at 40 ppm.S. Kumar and Singh accounted for this effect as being the result of the fact that sulfur and phosphorus are related in a number of metabolic processes in plants. If sulfur concentration is increased, the P requirement of the plant would be higher.

C. Elemental Sulfur as a Fertilizer

At normal pressures and temperatures elemental sulfur exists as a solid, orthorhombic eight membered ring which is essentially insoluble in water. Although elemental sulfur may be considered as having the potential for being 100% plant nutrient, its insoluble nature renders it unavailable for plant use until oxidation to sulfate occurs.

The oxidation of elemental sulfur in soils can be related to a number of factors. Soils with a water content near field capacity, under aerobic conditions and with a temperature range of 23°C - 40°C have been shown to have the highest oxidation rates (Wainwright 1978). Soil texture and organic matter content have shown no well defined effect upon the oxidation of sulfur although among soils there may be variation in the species and numbers of sulfur oxidizing organisms which would in turn influence the amount of sulfur oxidized to sulfate.

Studies have shown that the rate of oxidation of elemental sulfur is directly related to its exposed surface area and thus to particle size (Li 1964, Fox et al 1965, Attoe and Olson 1966, Li and Caldwell 1966, Felinger et al 1972, Wainwright 1978). Fox et al (1965) showed that as the particle size was decreased, sulfur fractions were more effective in supplying sulfur to young corn grown in the greenhouse. Li (1964) obtained similar results in soil incubation work and concluded that the oxidation of sulfur

is a surface phenomenon dependent upon the amount of exposed surface area. When the amount of sulfur added is the same, the finer particles will have the greater surface exposed to bacteria and will thus be oxidized faster.

The direct relationship between surface area of sulfur particles and the amount of sulfur oxidized has been shown to be due to the necessity for direct contact between the oxidizing organisms and the sulfur particle (Vogler and Umbreit 1941, Schaeffer et al 1963). Umbreit et al (1941) showed that cells of Thiobacillus thiooxidans came into contact with sulfur particles by means of a fat-like globule located at the end of the cell. Upon contact, the sulfur was dissolved in the fat and in this way insoluble sulfur was brought within the boundries of the cell for controlled oxidation.

Schaeffer et al (1963) obtained electron micrographs of sulfur crystals before and after attack by Thiobacillus thiooxidans. The results showed that the individual cell eroded portions of the crystal immediately adjacent to themselves.

Because the rate of oxidation of elemental sulfur to sulfate is so much faster when the particle size is reduced, it would follow that applying sulfur in its finest form, as a flour, would be most conducive in making it available to plants. Applying sulfur as a fine flour on a large scale is however, inherently difficult. Some utilization of sulfur-bentonite assemblages have been made in order that

elemental sulfur can be applied as a granule. Presumably upon contact with soil moisture the bentonite component will swell causing disintegration of the granule into finer particles (Burns 1967).

Feilinger et al (1972) examined a number of granular sulfur fertilizers and found that a sulfur-bentonite $-Na_2SO_4$ assemblage was as beneficial to growth of alfalfa as was finely powdered elemental sulfur. However, oxidation in the soil of the sulfur-bentonite $-Na_2SO_4$ assemblage was very low unless it was pretreated by shaking with water.

An increase in the rate of application of elemental sulfur will increase the total surface area available for oxidation to plant available sulfate. Li (1964) increased the application rate of sulfur from 100 to 1000 ppm and found that an increasing amount of sulfur was oxidized while percent oxidation remained approximately the same for all five levels of application. Similarily results obtained by Nor and Tabatabai (1977) showed that increasing amounts of elemental sulfur were oxidized when the rate of application was increased from 50 to 100 ug/g soil and that the percentage of the sulfur oxidized in the soil remained fairly constant.

Placement of elemental sulfur in a band will effectively reduce the amount of surface area available for direct contact with microorganisms and thus reduce the amount of sulfur oxidized to sulfate. Sulfuric acid is a product of

the microbial oxidation of sulfur. When sulfur is banded, the buffering effect of the soil will be reduced. In acid soils, concentrations of H_2SO_4 high enough to discourage plant root and microbial growth could accumulate in the band. In a calcareous soil, the lower pH may have beneficial effects; for example, in increasing the plant availability of phosphorus.

Fox et al (1965) showed that when sulfur flour was mixed throughout an acid soil, it could be as effective a source of sulfur for young green house grown corn as was gypsum. However, when sulfur flour was sidebanded it was not as effective unless a small amount of calcium carbonate was added with it. This may indicate the accumulation of a harmful concentration of H_2SO_4 in the band which was neutralized by the calcium carbonate.

D. Gypsum as a Fertilizer

Gypsum is a sparingly soluble sulfur fertilizer which may contain from 13 - 19% sulfur by weight depending upon the water of hydration. In order for the sulfate supplied by gypsum to become plant available, it must first enter into the soil solution. The rate of dissolution of gypsum, and thus plant availability, will be governed firstly by the rate of movement of the solid into solution and secondly by the transport of the dissolved material away from the surface (Barrow 1975).

Williams (1971) used superphosphate, which contains its sulfur component as calcium sulfate, to study the movement of sulfate into soils. It was found that both fertilizer particle size and soil moisture influenced the rate of solution of calcium sulfate. The rate of solution of the gypsum and its movement into the soil under constant moisture conditions was enhanced by decreasing the particle size of gypsum. Leaching of the soil also increased the solution of sulfate.

Williams (1971) also studied the dissolution of sulfate provided by superphosphate as affected by soil pH. Three acid soils and one calcareous soil were examined. It was found that the amount of sulfate entering the calcareous soil was only 37% of that for the acid soil. This would indicate a lower solubility of calcium sulfate in calcareous soils possibly due in part to the common ion effect on

solubility. In this case the common ion would be the calcium components of $CaSO_4$ and $CaCO_3$.

Aylmore et al (1971) studied the dissolution of gypsum and superphosphate in soil. Their studies showed that the rate of dissolution of gypsum was directly proportional to the size of the fertilizer particle. When soils were leached with the equivalent of 15 inches of rainfall, negligible amounts of sulfate ions were lost from superphosphate particles >2mm in diameter. More than 60% was lost from powdered superphosphate while there was a virtual 100% loss from powdered gypsum. Aylmore et al (1971) thus suggested that it was the external surface area exposed by the granules per unit mass which governed the rate of dissolution. In other words, rate of dissolution of superphosphate and gypsum was increased by decreasing the particle size.

McLachlan and De Marco (1968) investigated the response of pasture (subterranean clover) to the application of different amounts and particle sizes of gypsum. At low rates of application the yield of pasture in the first year of application was influenced by particle size. At high rates of application there was no significant effect of particle size. It was found that gypsum applied as a very fine powder at 56 lb/ac could be as effective in increasing dry matter yields as applications of up to 224 lb/ac of a coarser material (>5.0mm). McLachlan and De Marco felt that the increases in net uptake observed with the finer particle fra-

ctions were associated more with increases in the rate of solution than with a change in the number of particles and their proximity to plant roots.

Williams and Lipsett (1969) were able to show that the uptake of sulfur by pasture plants (subterranean clover) from finely powdered superphosphate was three times that from a single particle. They were also able to show that the availability of sulfate from superphosphate was unaffected by the distance of the particle to the plant, at least to a distance of 2 inches. Sulfate was not strongly absorbed in the soils under study thus suggesting that the availability of sulfate was mainly affected by its rate of solution from superphosphate.

E. Ammonium Thiosulfate as a Fertilizer

Ammonium thiosulfate is a clear liquid fertilizer which is gaining wider usage as a source of sulfur for agricultural crops. Thiosulfate has a tetrahedral structure similar to that of sulfate but with a sulfur atom substituting for an oxygen. Oxidation of the thiosulfate molecule is required to convert it to plant available sulfate. While the use of thiosulfates as sulfur fertilizers has been recognized (Burns, 1967), reported literature on methods of use and relative efficiency is rather scanty and inconclusive.

III Methods of Analysis

Experimental procedures carried out for individual studies are discussed with the results obtained for each of the individual studies. The analytical procedures described here were employed for all studies.

Soil Analysis

Soil Texture - Soil texture was estimated by hand on unground soil samples.

Calcium Carbonate Content - Free lime content ($CaCO_3$) was estimated on the basis of the degree of reaction (effervescence) of a soil sample to a 1:3 HCl - water solution.

Soil pH - Soil pH was determined using a glass calomel electrode to measure the pH of a water soil paste.

Soil Salinity - Soil salinity was determined by measuring the electrical conductivity of a soil-water paste

with a Fisher Combination electrode on a Radiometer conductivity meter.

Soil Nitrate Nitrogen - Fifty ml. of 0.5M $NaHCO_3$ extracting solution (pH 8.5) and 1 gm. of activated charcoal were added to 2.5 gm. of soil in 125 ml. Erlenmeyer flasks and shaken for 30 minutes on a Eberbach reciprocating shaker on slow speed. The soil extract was filtered through Whatman no. 30

paper and NO_3-N level in the extract determined by a modification of the colorimetric procedure of Kamphake et al (1967).

Exchangeable Potassium - Twenty-five ml. of neutral 1M NH_4OAC and 2.5 gm. of soil were shaken for 30 minutes and filtered through Whatman no. 1 paper. Potassium content of the extract was then determined by flame photometry using lithium as an internal standard.

Available Phosphorus - One gram of pretreated charcoal and 100 ml. of 0.5M $NaHCO_3$ (pH 8.5) solution were added to 5 gm. of soil. The samples were shaken for 30 minutes, filtered through Whatman no. 30 paper and the P content in the extract determined colorimetrically by the acid molybdate-ascorbic acid method (Murphy and Riley 1962).

Calcium Chloride Extractable Sulfate Sulfur - fifty ml. of 0.001 M $CaCl_2$ extracting solution was added to 25 gm. of soil and shaken for 30 minutes. The suspension was filtered through Whatman no. 42 paper and sulfate-sulfur concent determined using the barium chloride turbidimetric method as described by Lazrus et al (1966).

Plant Analysis

Total Nitrogen - Total nitrogen content of plant material was determined by the Kjeldahl-Gunning method as described by Jackson (1958).

Total P - Phosphorus concentration of plant material was determined by the method described by Stainton et al (1974). Plant material was oven dried (85°C), ground and digested. In the digestion, 1 gm. of plant material was mixed with 5 ml. of concentrated nitric acid and 2.5 ml. of concentrated perchloric acid and heated. After allowing sufficient time for complete digestion, the material was filtered through Whatman no. 42 paper and P content of the filtrate determined colorimetrically by the acid molybdate-ascorbic acid method (Murphy and Riley 1962).

Total Sulfur - For the determination of sulfur concentration, plant material was oven dried (85°C) and ground. The ground material was then digested by mixing 5 ml. of concentrated nitric acid and 2.5 ml. of concentrated perchloric acid and heated. After allowing sufficient time for complete digestion, the material was filtered through Whatman no. 42 paper and the filtrate analysed for sulfate sulfur content colorimetrically by the barium chloride turbidimetric method as described by Lazrus et al (1966).

IV Field Trials: The Effect of Sulfur Fertilizers on the Yield and Chemical Composition of Rapeseed and Barley

Introduction

Plants utilize sulfur mainly as sulfate; thus in order for a crop to utilize sulfur, it must be available in the soil solution in the sulfate form. Fertilizers such as ammonium sulfate contain all of their sulfur in the sulfate form, are highly soluble and thus become quickly available for use by plants. Other fertilizers such as gypsum contain all of their sulfur as sulfate but are only sparingly soluble thus reducing their plant availability. Fertilizers such as ammonium thiosulfate or Agrisul contain their sulfur in a form which must undergo oxidation to sulfate in order to become plant available.

Previous work in Manitoba (Anderson 1966) identified soils which contain amounts of sulfur inadequate for the production of rapeseed. Other work (Anderson 1966, Hamm 1969, Ridley 1973) has shown that barley and rapeseed grown on these sulfur deficient soils will respond to the addition of sulfur fertilizers.

The field experiment reported here was established in order to determine what effect sulfur fertilization had upon the yield and sulfur uptake of rapeseed and barley grown on soils considered to be sulfur deficient. Also examined is the relative plant availability of sulfur sup-

plied as ammonium sulfate, gypsum, ammonium thiosulfate and Agrisul.

Methods and Materials

Plot sites for the field experiment were established in the spring of 1979 at two locations in Manitoba. One site was established near Sidney, Manitoba on a soil of the Firdale association (Orthic Dark Grey Chernozem (Ehrlich et al, 1957)) and a second site was located near Neepawa, Manitoba on a soil of the Stockton association (Orthic Black Chernozem (Ehrlich et al, 1957)). The plot sites chosen were well drained and relatively uniform with a soil texture ranging from very fine sandy loam to loamy very fine sand. In selecting sites for the field experiments emphasis was placed on those soils designated as being sulfur deficient. Sulfur availability at both sites was determined by the Manitoba Provincial Soil Testing Laboratory as being in the low to moderate category.

Soil samples were taken in early spring to a depth of 60 cm. A summary of characteristics of both soils is given in Table 1. The trials at each site and for each crop were of a randomized complete block design consisting of ten treatments and six replicates. Treatments for each crop are listed in Tables 2 - 7. Plot dimensions were 10 m. in length and 1.6 m. wide.

All fertilizers except for phosphorus were broadcast by hand over individual plots prior to seeding. Barley plots received 150 kg. N/ha and rapeseed plots 200 kg. N/ha mostly as commercial grade NH_4NO_3 (34-0-0). Some of

the sulfur sources used for treatments in this experiment contain nitrogen in their formulation and the amount of NH_4NO_3 applied was calculated so that all treatments received equivalent amounts of nitrogen. Soil tests indicated that additional potassium was required at the Neepawa site and this was supplied at 50 kg. K/ha as KCl (0-0-60).

For the sulfur treatments, prilled ammonium sulfate (21-0-0-24), prilled gypsum (0-0-0-18) and granular Agrisul (0-0-0-90 - 1979 product) were broadcast by hand over appropriate plots prior to seeding. Liquid ammonium thiosulfate (12-0-0-26) was diluted with tap water and sprayed over individual plots prior to seeding.

Phosphorus requirements for both crops at both sites were met by sidebanding 26.9 kg. P/ha as $NH_4H_2PO_4$ (11-55-0) at seeding. Nitrogen added as $NH_4H_2PO_4$ (13.3 kg. N/ha) was in addition to that which had been supplied as NH_4NO_3.

Avadex BW, a preemergence herbicide for the control of wild oats, was applied to barley plots at a rate of 1.7 kg. active ingredient/ha in 112 l. water/ha via a pressurized boom sprayer. Treflan applied in a similar manner and at a rate of 1.12 kg. active ingredient/ha in 112 l. water/ha was used for weed control in rapeseed. Prior to seeding, all plots were rotovated in order to incorporate the nitrogen, potassium and sulfur sources and preemergence herbicides.

A nine row seeder with row spacings of 22.9 cm. was used to seed barley (Hordeum vulgare var. Conquest) and

rapeseed (Brassica campestris var. Torch) at rates of 102 kg/ha and 5.2 kg/ha respectively. Both crops at both sites were seeded June 3, 1979. Furaden, an insecticide used for the control of flea beetles in rapeseed, was also applied at seeding. A 50:50 mix of rapeseed and granular Furaden was drilled through the seedbox at a rate of 10.4 kg/ha.

Midseason samples for barley were taken on July 20 at the Sidney site and July 26 at the Neepawa site when the majority of the barley plants had formed heads. Midseason samples for rapeseed at the Sidney site were taken on July 31 when the majority of plants had formed pods. Sampling procedure consisted of cutting plants from 3 m. of a single row of a few centimeters above the soil surface. The samples were then air dried, weighed and ground to pass a 2 mm. sieve.

The second harvest was taken at maturity and consisted of two 3 m. samples taken from two rows. Total dry weight was determined and the samples were threshed. Grain yield was determined and barley was ground to pass a 2 mm. sieve in order to facilitate laboratory analysis.

Rapeseed at the Neepawa site was severely damaged by toxic pesticides early in the season and thus not sampled. The source of the toxicity would appear to have been spray drift from adjacent farmers fields as rapeseed at Sidney showed no signs of chemical damage.

Tissue analysis for midseason barley from the Neepawa site is not available as the samples were inadvertantly destroyed prior to analysis.

Table 1: Chemical and physical properties of soils used in the field experiment (1979).

Characteristics	Site and Crop		
	Sidney Barley	Sidney Rapeseed	Neepawa Barley
Texture (0-15cm)	VFSL	VFSL	LVFS
Carbonate Content (0-15cm)	absent	absent	absent
pH (0-15cm)	7.0	7.1	7.4
Salinity (0-15cm) (ds m-1)	0.23	0.27	0.12
NO_3-N (0-60 cm) (ppm)	13.0	13.6	8.5
NaHCO, ext. P (0-15cm) (ppm)	13.7	12.1	8.0
Exchangeable K (0-15cm) (ppm)	177	217	131
Water Soluble SO_4 (0-60cm) (ppm)	9.0	7.3	4.1

Results and Discussion

Midseason dry matter yields for barley from either the Sidney or Neepawa sites (Tables 2 and 3) were not affected by the addition of sulfur in any form. Analysis of plant tissue from the Sidney site (Table 2) showed that sulfur concentration of midseason barley was significantly increased when 20 or 40 kg S/ha as ammonium sulfate or ammonium thiosulfate or 40 kg. S/ha as gypsum were applied compared to those treatments which received no sulfur, 10 kg. S/ha as ammonium sulfate 20 or 80 kg. S/ha as Agrisul or 20 kg. S/ha as gypsum. Barley from treatments receiving 40 kg. S/ha as ammonium sulfate, ammonium thiosulfate or gypsum had both the highest tissue sulfur concentration and the highest total sulfur uptake indicating that by early heading significantly larger amounts of sulfur were being utilized where 40 kg. S/ha as ammonium sulfate, ammonium thiosulfate, or gypsum were applied compared to treatments which received no sulfur or 20 or 80 kg. S/ha as Agrisul. Application of 10 kg. S/ha as ammonium sulfate produced total sulfur uptake in barley which was significantly higher than when no sulfur was added or where Agrisul was applied at 20 kg. S/ha.

Where Agrisul was applied, sulfur concentration and total sulfur uptake by barley did not differ significantly from the treatment which received no sulfur. This would

suggest that by early heading, oxidation of Agrisul may not have occured to the point that barley was able to utilize significant amounts of sulfur from this source. Barley which received ammonium thiosulfate as its sulfur source had values for sulfur concentration and total sulfur uptake which were significantly higher than those obtained for treatments where no sulfur was applied or where Agrisul was applied. This would indicate that the oxidation of thiosulfate had occured to the point that by midseason, significant amounts of sulfate-sulfur were available to barley. Neither sulfur concentration or total sulfur uptake were affected when 20 kg. S/ha as gypsum was applied and this may be a reflection of the relatively low solubility and hence plant availability of sulfur supplied as gypsum compared to ammonium sulfate.

Grain yields of barley from either site were not affected by the addition of sulfur in any form (Tables 4 and 5). Analysis of grain from the Sidney site (Table 4) showed that barley supplied with 40 kg. S/ha as gypsum had the lowest concentrations of sulfur in its grain and the lowest total sulfur uptake. Although these results would suggest that barley utilized less sulfur from gypsum at 40 kg. S/ha this is rather unlikely as treatments which were supplied with 20 kg. S/ha as gypsum did not differ from any of the other treatments. With the exception of the 40 kg

S/ha gypsum treatment, there were no significant differences among treatments for sulfur concentration or sulfur content of grain. Root growth in the period from early heading to maturity may partially account for the lack of difference in sulfur concentration and content of the grain. Up until early heading, the barley roots had explored a limited soil volume and total sulfur uptake and concentration of the tissue may have been influenced to a greater degree by the availability of sulfur from fertilizer sources. As the roots reached greater depth, soil sulfur from a larger soil volume would become available to the plant and the availability of sulfur from fertilizer sources would have less effect upon total sulfur content. Translocation of sulfur within the plant from vegetative material to grain may also in part account for the lack of difference in sulfur concentration noted in the barley grain.

At the Neepawa site, concentration of sulfur in the barley grain did not differ significantly among treatments (Table 5). Total sulfur uptake of the grain was significantly higher when barley was supplied with 20 kg. S/ha as ammonium sulfate as opposed to no sulfur or 20 kg. S/ha as Agrisul. No other significant differences were noted.

The lack of a yield response to the addition of sulfur in any form would indicate that sufficient amounts of soil sulfur for the production of barley were available

at both the Sidney and Neepawa sites. Hamm (1969) had determined the critical soil sulfur content for the production of cereal crops to be 11.2 kg. /ha water extractable sulfate sulfur to a depth of 60 cm. The Manitoba Provincial Soil Testing Laboratory (1982) currently employs a value of 12.0 kg./ha water extractable sulfate sulfur to 60 cm. to indicate sulfur sufficiency for the production of cereals. Soil at the Sidney site was well in excess of this critical value with a water extractable sulfate sulfur content to 60 cm. of 28.3 kg/ha (Table 1). At the Neepawa site the sulfate sulfur content (water extractable to 60 cm.) was 12.7 kg./ha, only slightly in excess of the previously determined critical levels. On the basis of the critical soil sulfur value determined by Hamm (1969) and the Manitoba Provincial Soil Testing Laboratory (1982), a yield response by barley to the addition of sulfur would not be expected at either site. The fact that barley did not respond to the addition of sulfur at either site and in particular the lack of response at the Neepawa site would indicate that a value of 12.0 kg. SO_4-S/ ha (water extractable to 60 cm.) as is in use by the Manitoba Provincial Soil Testing Laboratory is a reasonable indicator of sulfur sufficiency for the production of barley.

Rapeseed grown at Sidney and sampled at early flowering showed no significant dry matter yield response to the application of sulfur in any form (Table 6). Tissue analy-

sis of rapeseed at early flowering showed that sulfur concentration was signficantly increased when sulfur was added at 20 or 40 kg. S/ha as ammonium sulfate or 20 kg. S/ha as ammonium thiosulfate compared to where no sulfur was added or where Agrisul was added at 20 or 80 kg. S/ha. Addition of ammonium thiosulfate at 40 kg. S/ha significantly increased tissue sulfur concentration compared to rapeseed which received 20 kg. S/ha as Agrisul.

The tissue analysis indicates that by early flowering rapeseed was obtaining a portion of its sulfur requirement from ammonium sulfate or ammonium thiosulfate applied at 20 or 40 kg. S/ha. Sulfur concentration of plant tissue from these treatments was higher than from treatments which received no sulfur being well in excess of the critical value of 0.25% as determined by Hamm (1969) to be indicative of sulfur sufficiency in rapeseed. By midseason, Agrisul appeared to be supplying rapeseed with very little if any of its sulfur requirement. This is reflected by tissue concentrations of sulfur which were well below the critical value and which did not differ from sulfur concentration in rapeseed which received no additional sulfur. By early flowering, gypsum at 40 kg. S/ha was providing a portion of the sulfur requirement of rapeseed as evidenced in sulfur concentrations which were above the critical value. When gypsum was supplied at 20 kg. S/ha, sulfur concentrations in rapeseed were slightly below the criti-

cal value, showing that solubility of this fertilizer is low enough to somewhat limit its plant availability.

Total sulfur uptake by rapeseed at early flowering was significantly greater when ammonium thiosulfate was applied at 40 kg. S/ha as compared to where no sulfur was applied or where Agrisul was applied at 80 kg. S/ha. There were no other significant differences in total sulfur uptake by rapeseed at midseason although a trend did exist toward higher values in treatments supplied with sulfur as ammonium sulfate, ammonium thiosulfate or gypsum as opposed to treatments receiving no sulfur or having sulfur supplied as Agrisul.

Seed yield of rapeseed at final harvest was significantly increased when 40 kg. S/ha as ammonium sulfate or gypsum were added (Table 7). Rapeseed supplied with 40 kg. S/ha as ammonium sulfate produced seed yields significantly higher than treatments supplied with Agrisul at 20 kg. S/ha. No other significant differences were noted for seed yields although there was a trend toward increased yield where sulfur was added as ammonium sulfate, ammonium thiosulfate or gypsum compared to where Agrisul was added or where no sulfur was added. Sulfur concentration in the seed was not affected by addition of sulfur in any form. Values for total sulfur uptake by the seed were significantly higher when 40 kg. S/ha gypsum was added as opposed to treatments receiving no

sulfur or Agrisul at 20 kg. S/ha. Addition of 20 kg. S/ha as ammonium thiosulfate produced sulfur uptake by seed which was significantly higher than that obtained where no sulfur was added. Although not always significant, there was a trend towards higher total sulfur uptake by the seed when sulfur was added as ammonium sulfate, ammonium thiosulfate or gypsum as opposed to Agrisul being supplied at 20 kg. S/ha or where no sulfur was added.

The results show that over the course of the growing season, sulfur supplied as ammonium sulfate, ammonium thiosulfate or gypsum was plant available and was being utilized by rapeseed. Rapeseed appeared to utilize little of the sulfur supplied by Agrisul at 20 kg S/ha indicating that the oxidation of Agrisul to plant available sulfate was slow. By final harvest, Agrisul at 80 kg. S/ha was able to provide rapeseed with amounts of sulfate comparale to that supplied by other carriers; however, these carriers were being applied at a rate of one quarter to one half that of the Agrisul. This is a further indication that over the time period studied, only a portion of the sulfur supplied as Agrisul was being oxidized to a plant available form.

The response of rapeseed to the addition of sulfur, as reflected in values for midseason tissue concentration of sulfur and in the higher final seed yields obtained

when sulfur was supplied in an available form, would indicate that soil sulfur content at the Sidney site was somewhat inadequate for the production of rapeseed. Hamm (1969) had determined that a soil sulfate sulfur content of 22.4 - 28.0 kg./ha (water soluble to 60 cm.) would provide sufficient sulfur for the production of rapeseed. Ridley (1973) showed a significant yield response by rapeseed to sulfur fertilization on soils containing up to 31.4 kg. SO_4-S/ha to 60 cm. and an increase in seed sulfur concentration when soils containing 33.6 kg. SO_4-S/ha to 60 cm had sulfur added. Currently the Manitoba Provincial Soil Testing Laboratory (1982) uses a critical value of 23 kg./ha water extractable sulfate sulfur to 60 cm. to indicate sufficient soil sulfur for rapeseed production. At the Sidney site, the average soil sulfur content (water extractable to 60 cm.) was 21.1 kg. SO_4-S/ha. On the basis of the value determined by Hamm (1969) and in use by the Manitoba Provincial Soil Testing Laboratory, this site would be deemed as being slightly deficient in its ability to supply rapeseed with sulfur. The seed yield response obtained at this site along with the values for midseason tissue concentration of sulfur are a further indication that a response by rapeseed to the addition of sulfur may be expected on soils containing 21.1 kg SO_4-S/ha (water extractable to 60 cm.).

From the observations in this study, it is apparent

that rapeseed grown on soils considered to be sulfur deficient showed a response to the addition of sulfur in terms of seed yield and composition and that this response was dependent upon the form of sulfur added. In general, it would appear that over the time period studied, the oxidation of thiosulfate to plant available sulfate occured to such an extent that it was comparable to ammonium sulfate or gypsum in its sulfur supplying power to rapeseed. Oxidation of Agrisul to sulfate did not occur to the same extent thus limiting its plant availability and utilization by rapeseed.

Table 2: Dry matter yields and tissue analyses for barley at the early heading stage from the Sidney site.

Carrier	Rate kg/ha	Yield kg/ha	Sulfur Concentration (%)	Total Sulfur Uptake (kg/ha)
Check	0	3140 a*	0.156 a	4.7 a
$(NH_4)_2SO_4$	10	3547 a	0.180 a	6.4 bc
$(NH_4)_2SO_4$	20	3440 a	0.190 b	6.3 abc
$(NH_4)_2SO_4$	40	3381 a	0.212 b	7.2 c
Agrisul	20	3209 a	0.153 a	4.9 a
Agrisul	80	3334 a	0.150 a	5.0 ab
$(NH_4)_2S_2O_3$	20	3103 a	0.200 b	6.3 abc
$(NH_4)_2S_2O_3$	40	3456 a	0.209 b	7.2 c
$CaSO_4 5H_2O$	20	3584 a	0.177 a	6.3 abc
$CaSO_4 5H_2O$	40	3559 a	0.212 b	7.5 c

Table 3: Dry matter yields for barley at the early heading stage from the Neepawa site.

Carrier	Rate kg/ha	Yield kg/ha
Check	0	3453 a
$(NH_4)_2SO_4$	10	3750 a
$(NH_4)_2SO_4$	20	4263 a
$(NH_4)_2SO_4$	40	3753 a
Agrisul	20	3403 a
Agrisul	80	3800 a
$(NH_4)_2S_2O_3$	20	3906 a
$(NH_4)_2S_2O_3$	40	3834 a
$CaSO_4 5H_2O$	20	4478 a
$CaSO_4 5H_2O$	40	3328 a

* Duncan's Multiple Range: Numbers followed by the same letter are not significantly different at P = 0.05.

Table 4: Final grain yield and analyses for barley from the Sidney site.

Carrier	Rate kg/ha	Yield kg/ha		Sulfur Concentration (%)		Total Sulfur Uptake (kg/ha)	
Check	0	3211	a*	0.146	ab	4.7	ab
$(NH_4)_2SO_4$	10	3023	a	0.141	ab	4.3	ab
$(NH_4)_2SO_4$	20	2886	a	0.139	ab	4.1	ab
$(NH_4)_2SO_4$	40	3157	a	0.150	ab	4.8	b
Agrisul	20	3023	a	0.149	ab	4.4	ab
Agrisul	80	2917	a	0.157	b	4.5	ab
$(NH_4)_2S_2O_3$	20	3011	a	0.142	ab	4.3	ab
$(NH_4)_2S_2O_3$	40	2814	a	0.146	ab	4.1	ab
$CaSO_4 5H_2O$	20	3090	a	0.148	ab	4.5	ab
$CaSO_4 5H_2O$	40	3001	a	0.127	a	3.8	a

Table 5: Final grain yield and analyses for barley from the Neepawa site.

Carrier	Rate kg/ha	Yield kg/ha		Sulfur Concentration (%)		Total Sulfur Uptake (kg/ha)	
Check	0	2451	a	0.138	a	3.3	a
$(NH_4)_2SO_4$	10	2528	a	0.172	a	4.4	ab
$(NH_4)_2SO_4$	20	2895	a	0.181	a	5.2	b
$(NH_4)_2SO_4$	40	2862	a	0.174	a	5.0	ab
Agrisul	20	2228	a	0.147	a	3.3	a
Agrisul	80	2520	a	0.186	a	4.2	ab
$(NH_4)_2S_2O_3$	20	2703	a	0.177	a	4.7	ab
$(NH_4)_2S_2O_3$	40	2286	a	0.166	a	3.9	ab
$CaSO_4 5H_2O$	20	3106	a	0.162	a	5.1	ab
$CaSO_4 5H_2O$	40	2214	a	0.178	a	4.0	ab

* Duncan's Multiple Range: Numbers followed by the same letter are not significantly different at P = 0.05.

Table 6: Dry matter yields and tissue analyses for rapeseed at the early flowering stage from the Sidney site.

Carrier	Rate kg/ha	Yield kg/ha		Sulfur Concentration (%)		Total Sulfur Uptake (kg/ha)	
Check	0	3031	a*	0.202	a	4.5	a
$(NH_4)_2SO_4$	10	2287	a	0.280	abc	6.3	ab
$(NH_4)_2SO_4$	20	2269	a	0.306	c	6.7	ab
$(NH_4)_2SO_4$	40	2084	a	0.308	c	6.7	ab
Agrisul	20	2662	a	0.202	a	5.6	ab
Agrisul	80	1975	a	0.212	ab	4.4	a
$(NH_4)_2S_2O_3$	20	2350	a	0.315	c	7.5	ab
$(NH_4)_2S_2O_3$	40	3037	a	0.294	bc	9.3	b
$CaSO_4 5H_2O$	20	2234	a	0.246	abc	5.9	ab
$CaSO_4 5H_2O$	40	2359	a	0.290	abc	7.9	ab

Table 7: Final seed yields and analyses for rapeseed from the Sidney site.

Carrier	Rate kg/ha	Yield kg/ha		Sulfur Concentration (%)		Total Sulfur Uptake (kg/ha)	
Check	0	1287	a	0.473	a	6.0	a
$(NH_4)_2SO_4$	10	1526	abc	0.565	a	8.5	abc
$(NH_4)_2SO_4$	20	1570	abc	0.563	a	8.9	abc
$(NH_4)_2SO_4$	40	1783	c	0.550	a	9.2	abc
Agrisul	20	1392	ab	0.525	a	7.0	ab
Agrisul	80	1451	abc	0.571	a	8.2	abc
$(NH_4)_2S_2O_3$	20	1426	abc	0.661	a	9.5	bc
$(NH_4)_2S_2O_3$	40	1578	abc	0.552	a	8.6	abc
$CaSO_4 5H_2O$	20	1564	abc	0.504	a	7.8	abc
$CaSO_4 5H_2O$	40	1714	bc	0.636	a	10.8	c

* Duncan's Multiple Range: Numbers followed by the same letter are not significantly different at P = 0.05.

V Growth Chamber Experiment 1: The effect of method of application of a source of elemental sulfur, gypsum and ammonium thiosulfate on yield and uptake of sulfur by rapeseed.

Introduction

In the previous study, rapeseed grown on a moderately sulfur deficient soil was shown to respond to sulfur fertilization and this response was related in some degree to the type of sulfur fertilizer added. Plant availability of fertilizer sulfur is dependent upon the form of sulfur present in that fertilizer. For example, sulfur supplied as elemental sulfur or ammonium thiosulfate must be oxidized to sulfate in order to become plant available and sulfate supplied as gypsum must first move into the soil solution before being utilized by plants. The amount of fertilizer sulfur available for use from these sources has also been shown to be related to the amount of sulfur applied and to the method of application (Li 1964, Fox et al 1965, McLachlen and De Marco 1968, Nor and Tabatabai 1977).

In the work reported here, elemental sulfur in the form of Agrisul, ammonium thiosulfate and gypsum were compared for their relative effectiveness in supplying sulfur to rapeseed (Brassica napus var. Regent) grown in a growth chamber on a sulfur deficient soil. Also examined in the experiment was the effect that banding versus mixing throughout the soil would have upon the plant availability of sulfur from these sources.

Methods and Materials

Soil from the top 15 cm. of a sulfur deficient Stockton very fine sandy loam was collected in October 1979. Soil characteristics are listed in Table 8. The soil was stored in a frozen condition until December whereupon it was air dried, sieved and mixed thoroughly. 5,000 grams of air dry soil was then placed in each of 46 polyethylene pots.

All soils received a basal application of potassium, phosphorus, zinc and copper. Potassium and phosphorus were added as KH_2PO_4 at 100 ppm P to give 126.3 ppm K (all nutrient concentrations are on an air dry soil basis). Potassium phosphate was dissolved in deionized water and a sufficient amount of the resulting solution to treat soil from an individual pot was placed in a spray bottle. This was further diluted with less than 10 ml. of deionized water, sprayed onto the soil as a fine mist and mixed throughout.

Zinc and copper were applied at 8 ppm Zn as $ZnCl_2$ and at 5 ppm Cu as $CuCl_2$. The $ZnCl_2$ and $CuCl_2$ were dissolved together in deionized water and applied to soil from individual pots in a similar manner to the potassium phosphate.

Three sulfur sources were investigated in this experiment. Gypsum ($CaSO_4 \cdot 5H_2O$) and ammonium thiosulfate ($(NH_4)_2 S_2O_3$) were applied at rates of 10 ppm S and 20 ppm S. Agrisul (90%S) was applied at rates of 10 ppm S, 20 ppm S and 40 ppm S. All sulfur treatments were applied in two ways; as a band or mixed

throughout the soil. In the band treatments, granules of Agrisul or gypsum or a concentrated liquid band of ammonium thiosulfate was placed 3 cm. below the 2 cm. to the side of a seed row. For the mixed treatments, Agrisul was powdered with a mortar and pestle to a flour-like consistency and the required amount was mixed throughout the soil. Those treatments in which gypsum was used had granules of gypsum mixed thoroughly throughout the soil. For the thiosulfate treatments, the required amount of liquid ammonium thiosulfate was placed in a spray bottle, diluted with less than 20 ml. of deionized water, sprayed as a fine mist on soil from an individual pot and mixed thoroughly throughout the soil.

Treatments which received a sulfur source were replicated three times while check treatments, which received all nutrients applied except for sulfur, were replicated four times for a total of 46 pots in a completely randomized design.

Rapeseed was seeded to a depth of 2 cm. in a single row at a rate of 10 to 15 seeds per pot. Rapeseed plants were thinned to four plants per pot one week after emergence. The initial watering took place on January 29, 1980. Sufficient deionized water was added to each pot to wet the upper 3 cm. of soil. Once good seedling growth was established (approximately one week after emergence), all treatments were brought to field capacity on a daily basis through watering with deionized water.

Nitrogen requirements were met through the addition of 300 ppm N in three 100 ppm N aliquots. Sufficient NH_4NO_3 to give 100 ppm N was dissolved in deionized water. This solution was further diluted with the daily watering requirement and added to individual pots on the day of the initial watering, on day 20 and on day 28 of the study to give a total of 300 ppm N per pot.

Rapeseed from all treatments was harvested on March 9, 1980 when most of the plants were at the early flowering stage. Plants were cut a few millimeters above the soil surface, dried in a forced air oven at 85°C and ground to pass a 2 mm. sieve in a hammermill.

Conditions in the growth chamber were set as follows: Temperature: 15°C (night) 20°C (day); day length: 15 hours; Humidity: 80% (night) 51% (day). Light intensity measured seven days after planting ranged from 630 - 642 microeinsteins m^{-2} sec^{-1} at the topmost height of the canopy.

Results & Discussion

Dry matter yields of rapeseed (Table 9) were significantly affected by the form of sulfur applied, the method of application and the amount of sulfur applied. Yield response was generally larger when sulfur was supplied as ammonium thiosulfate or gypsum compared to where it was supplied as elemental sulfur. In most cases, rapeseed showed visible signs of sulfur deficiency, regardless of the form of sulfur applied.

Table 8: Soil properties for surface soils used in growth chamber and incubation experiments.

	SOILS	
	Stockton	Elm River
Carbonate Content	absent	High
pH	7.2	7.6
Salinity dSm^{-1}	0.2	0.3
NO_3-N (ppm)	6.8	9.4
$NaHCO_3$extP (ppm)	13.6	4.0
Exchangeable K (ppm)	217	325
Water Soluble SO_4-S (ppm)	1.8	4.8

Table 9: Dry matter yield, tissue analyses and percent recovery of fertilizer by rapeseed in the growth chamber.

Carrier	Method of Application	Rate S (ppm)	Dry Matter Yield (gm)	Sulfur Conc. %	N/S Ratio	% Recovery of S	Standard Deviation
Control	--	--	8.0 a*	.109 ab	36.0 abcde	--	--
Agrisul	banded	10	8.7 a	.118 b	40.8 cdef	0.7 a	0.7
		20	7.7 a	.100 ab	50.1 f	0.0 a	0.0
		40	10.6 a	.087 ab	50.1 ef	0.2 a	0.3
	mixed	10	22.5 bcd	.098 ab	34.0 abcde	24.7 bcde	12.7
		20	21.0 b	.080 ab	45.3 def	6.6 abc	2.3
		40	26.3 bcde	.096 ab	34.0 abcde	7.7 ab	2.1
Gypsum	banded	10	23.0 bc	.088 ab	35.0 abcdef	20.6 bcd	0.0
		20	31.0 efg	.120 b	26.1 abc	27.1 de	12.2
	mixed	10	30.0 efg	.102 ab	29.7 abcd	42.3 e	17.2
		20	34.7 gh	.119 b	23.0 a	31.4 de	8.0
Thiosulfate	banded	10	31.0 df	.090 ab	35.1 abcdef	35.8 de	11.7
		20	36.3 h	.107 ab	24.9 ab	29.1 de	8.3
	mixed	10	27.7 cf	.077 a	39.6 bcdef	21.9 bcd	4.5
		20	35.0 gh	.097 ab	27.9 abc	24.0 cd	7.2

* Duncan's Multiple Range: Numbers followed by the same letter are not significantly different at P = 0.05.

Where Agrisul was banded at 10, 20 or 40 ppm S, dry matter yields for rapeseed did not differ significantly from treatments which received no sulfur. Where Agrisul was powdered and mixed throughout the soil, dry matter yields were consistently and significantly higher than those obtained for the check or the banded Agrisul treatments.

All treatments which received gypsum as their sulfur source produced dry matter yields which were significantly higher than the banded Agrisul treatments for the check, and dry matter yield increased as the amount of sulfur applied as gypsum was increased from 10 to 20 ppm S. Mixing of gypsum granules throughout the soil at 10 ppm S. significantly increased dry matter yields compared to the banded 10 ppm S. gypsum treatments. When gypsum was mixed at 20 ppm S., the dry matter yield was significantly higher than that obtained in any treatments receiving sulfur as Agrisul.

Where ammonium thiosulfate was used, comparable dry matter yields were obtained when rapeseed was supplied with equivalent amounts of sulfur as thiosulfate or gypsum with the exception of the banded thiosulfate treatments which produced higher dry matter yields than the banded gypsum treatments. Rapeseed which received 10 ppm S. as thiosulfate produced dry matter yields which were significantly higher than those obtained when no additional sulfur was supplied or where sulfur was supplied as banded Agrisul. When thiosulfate was mixed or banded 20 ppm S., dry matter yields were significantly higher

than any obtained for rapeseed supplied with sulfur as Agrisul. Although not significant, treatments where thiosulfate was placed in a band had slightly higher yields than treatments where thiosulfate was mixed.

Values for the recovery of fertilizer sulfur (Table 9) reflected the trends noted for dry matter yield, with percent recovery increasing as yield increased.

Where rapeseed was supplied with banded Agrisul, very little, if any of the fertilizer sulfur was recovered. When Agrisul was powdered and mixed through the soil, utilization of fertilizer sulfur by rapeseed was improved considerably. Rapeseed was able to recover 24.68% of the fertilizer sulfur supplied in the 10 ppm S. mixed Agrisul treatments, significantly more than in any of the banded Agrisul treatments.

The improved recovery of fertilizer from the mixed Agrisul treatments indicates that oxidation of elemental sulfur in this form, to plant available sulfate, occurs more quickly when it is mixed as opposed to banded. The fact that a greater percentage of fertilizer sulfur was recovered from the 10 ppm S mixed Agrisul treatment than the 20 or 40 ppm S treatment may indicate that the amount of microbial oxidation occuring was the most limiting factor in the availability of Agrisul to plants. Nor and Tabatabai (1966) incubated elemental sulfur in a number of soils and found that after 56 days of incubation, even when large amounts of sulfur were applied, oxidation to sulfate by microorganisms occurred

in approximtely the same proportions. The recovery of a larger percentage of fertilizer sulfur in the 10 ppm S mixed Agrisul treatment than at 20 or 40 ppm S would indicate that, in the time period studied, the rate of microbial oxidation was the limiting factor in the plant availability of Agrisul applied in this manner.

In treatments which received gypsum, recovery of fertilizer sulfur by rapeseed was significantly higher when gypsum was banded at 20 ppm or mixed at 10 or 20 ppm than it was in any Agrisul treatment except where Agrisul was mixed at 10 ppm S. Where gypsum was banded at 10 ppm, percent recovery did not differ from the mixed Agrisul treatments but was significantly higher than any of the banded Agrisul treatments. Mixing of gypsum at 10 ppm S as opposed to banding significantly increased the percent recovery of fertilizer S by rapeseed.

When sulfur was supplied as ammonium thiosulfate, recovery of fertilizer sulfur by rapeseed was similar to that obtained with gypsum. While no real differences existed between the gypsum and ammonium thiosulfate treatments in terms of fertilizer recovery, placement of the sources did show some effect. In general, there was a trend toward higher fertilizer recoveries from the mixed gypsum treatments compared to the banded treatments. For thiosulfate, banding produced a trend toward higher recoveries than those obtained when it was mixed. Fertilizer recoveries obtained in mixed gypsum treatments were more comparable to banded thiosulfate treatments and those

obtained for mixed thiosulfate treatments were more comparable to banded gypsum treatments.

While definite trends were noted, the effect of placement upon the recovery of fertilizer sulfur from gypsum and ammonium thiosulfate remains unclear. In most cases, placement had no significant effect upon recovery although this lack of significance may be due in part to the large error associated with the measurement of percent recovery of fertilizer sulfur.

Tissue analysis for sulfur concentration (Table 9) indicated that no rapeseed grown in this experiment was adequately supplied with sulfur. Hamm (1969) determined that a total sulfur concentration of less than 0.25% at early flowering or a total N/total S ratio in tissue greater than 12 was indicative of sulfur deficiency in rapeseed. N/S ratios are often a more accurate indication of sulfur sufficiency in a plant than sulfur concentration alone. In Brassica sp. sulfur occurs not only in protein but also in the form of glucosinolates thus producing a relatively narrow N/S ratio. In the data reported here, N/S ratios were high and well in excess of Hamm's critical value of 12 thus indicating that rapeseed from all treatments was deficient in sulfur. Tissue concentration of sulfur for rapeseed from all treatments was well short of the 0.25% which Hamm determined as being the critical value, again indicating that no rapeseed in this experiment was adequately supplied with sulfur.

Inspection of the rapeseed through the course of the experiment showed that visual symptoms characteristic of sulfur deficiency in rapeseed occured in most treatments. Anderson (1966) described severely sulfur deficient rapeseed as being smaller than plants receiving adequate sulfur, exhibiting chlorosis, having a thickening of the leaves to give a leathery feel and an upward cupping of the leaves. Visual deficiency symptoms occured much earlier in the experiment for check and Agrisul treatments than they did for the gypsum or ammonium thiosulfate treatments.

Figure 1 shows rapeseed, supplied with 40 ppm S as Agrisul, twenty days after seeding. Where the Agrisul was banded, rapeseed is sulfur deficient indicating that by this time very little if any sulfur from banded Agrisul was being utilized by the plant. Rapeseed from the mixed Agrisul treatment shows no visible sign of sulfur deficiency indicating that up until day 20 rapeseed was utilizing more sulfur from the mixed Agrisul treatment than it was from the banded treatment. Aside from the banded Agrisul treatments and the check, no sulfur deficiency symptoms were visible for any of the other treatments at this time.

The series 2 figures show rapeseed 29 days after seeding. Figure 2a shows that by 29 days, rapeseed supplied with Agrisul at 40 ppm S was exhibiting visible symptoms of sulfur deficiency indicating that by this time inadequate amounts of sulfur from this source were available to the plant. Rapeseed supplied with 10 ppm S as gypsum or thiosulfate (Figures 2b and 2c) were also exhibiting sulfur deficiency symptoms indicating

insufficient sulfur from these sources.

Figures 3a and 3b show rapeseed 37 days after seeding, just prior to final harvest. Rapeseed in Figure 3a was supplied with 10 ppm banded sulfur. Where the sulfur was supplied as gypsum or thiosulfate, rapeseed shows signs of a moderate sulfur deficiency. Where sulfur was supplied as Agrisul, rapeseed was extremely stunted and chlorotic exhibiting symptoms of severe sulfur deficiency. This is a further indication that although 10 ppm S in any of the forms applied was insufficient sulfur for the rapeseed, sulfur supplied as gypsum or thiosulfate was considerably more available for plant use over the course of the experiment than that from Agrisul.

Figure 3b shows rapeseed supplied with 20 ppm mixed sulfur. Where sulfur was supplied as gypsum or thiosulfate, no symptoms of sulfur deficiency were visible. However, when supplied with 20 ppm S as mixed Agrisul, rapeseed was extremely sulfur deficient, again indicating that sulfur from this source is not utilized by rapeseed to the same extent as sulfur from gypsum or thiosulfate is.

In comparing the three carriers as suppliers of sulfur for rapeseed, it is obvious that Agrisul did not perform as well as either the gypsum or ammonium thiosulfate fertilizers. Dry matter yields and percent recovery of fertilizer sulfur was, for the most part, much lower for the Agrisul treatments as compared to the other two treatments. Even when Agrisul at

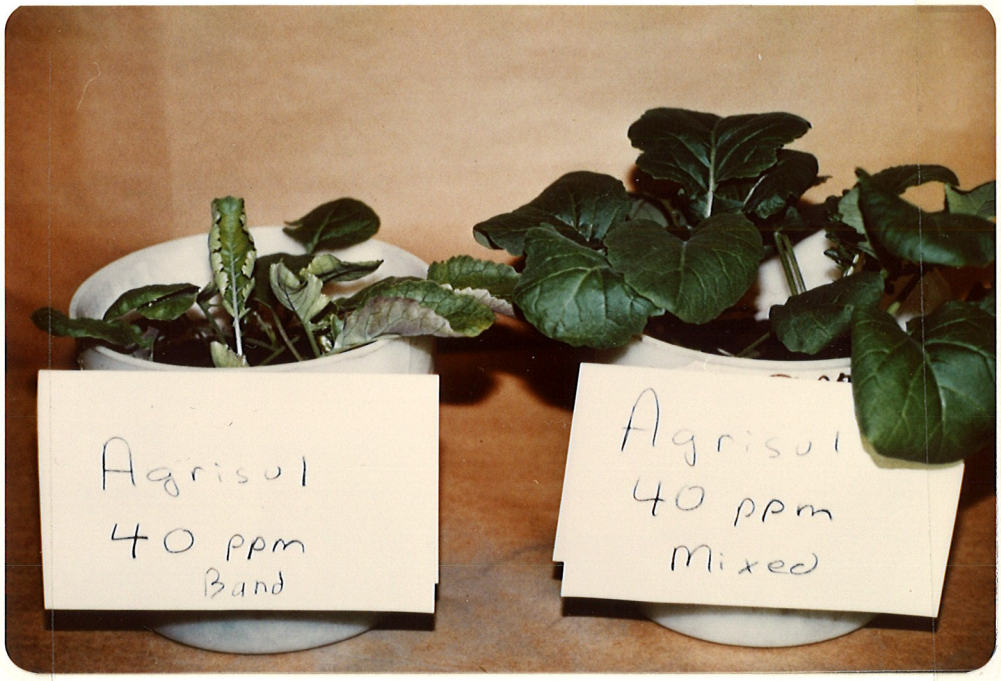


Figure 1: Rapeseed supplied with 40 ppm S as Agrisul twenty days after seeding.

Figure 2a: Rapeseed supplied with 40 ppm S as mixed Agrisul 29 days after seeding.

Figure 2b: Rapeseed supplied with 10 ppm S as mixed gypsum 29 days after seeding.

Figure 2c: Rapeseed supplied with 10 ppm S as mixed thiosulfate 29 days after seeding.

Figure 3a: Rapeseed supplied with 10 ppm banded sulfur 37 days after seeding.

Figure 3b: Rapeseed supplied with 20 ppm mixed sulfur 37 days after seeding.

40 ppm S was powdered and mixed throughout the soil, dry matter yields were produced which compared only to the lowest yields obtained by the other carriers. This is consistent with data obtained by Noellemeyer et al (1981) for rapeseed grown in the growth chamber. In their experiment rapeseed showed little response to elemental sulfur fertilizers applied up to 150 ppm S while application of sulfur from a readily available source, in this case ammonium sulfate at 30 or 75 ppm S, greatly increased yields of rapeseed.

When Agrisul was powdered and mixed throughout the soil, dry matter yields and percent recovery of fertilizer sulfur were improved. This is consistent with work done by Li (1964) who found that oxidation of elemental sulfur to sulfate occurs more quickly when the particle size is smaller. By applying Agrisul as a well mixed powder, surface area contact with oxidizing microorganisms is greatly increased hence speeding oxidation to sulfate. It would be expected that elemental sulfur applied in this manner would be more quickly oxidized to sulfate than if a similar amount were applied as banded granules.

Doubling or quadrupling the amount of sulfur added as Agrisul did not increase dry matter yields to the extent expected. Presumably by increasing the amount of Agrisul applied surface area available for microbial oxidation should be increased. This should in turn increase the amount of sulfate available to the plant. Li (1964) and Nor and Tabatabai (1977)

were able to show that the amount of elemental sulfur oxidized was a function of the rate of application. As more elemental sulfur was applied, increasing amounts of sulfur were oxidized, the percent oxidation remaining approximately the same for all levels of application. In this experiment, the percent recovery of oxidized sulfur did not increase proportionally to the amount of elemental sulfur added. This would suggest that oxidation of elemental sulfur and hence plant availability was limited by the reduced action or population of oxidizing microorganisms rather than by the amount of sulfur added.

In the results reported here, gypsum treatments produced substantially higher fertilizer recoveries and dry matter yields than the Agrisul treatments. Plant availability of the sulfate component of gypsum is governed by the movement of this sulfate into the soil solution. In the time period studied it is apparent that the dissolution of gypsum occurred to a greater extent than did the oxidation of elemental sulfur and this is reflected in the higher dry matter yields and fertilizer recoveries obtained in the gypsum treatments compared to the elemental sulfur treatments.

While not always significant, mixing of gypsum granules throughout the soil showed a trend toward higher dry matter yields and fertilizer sulfur recovery compared to where gypsum granules were banded. In the banded treatments, the common ion effect of the high calcium concentrations associated with the band may have reduced the dissolution of gypsum and hence

plant availability of the sulfate component. By mixing individual granules throughout the soil, calcium concentration in the area of the granule would be reduced thus enhancing the solution and plant availability of sulfur from gypsum.

Rapeseed supplied with sulfur as ammonium thiosulfate produced dry matter yields and recoveries of fertilizer sulfur which were comparable with those obtained in the gypsum treatments and somewhat higher than those obtained in the Agrisul treatments. The increased plant utilization of sulfur supplied as ammonium thiosulfate compared to sulfur supplied as Agrisul would indicate that the oxidation of thiosulfate to sulfate proceeds more quickly than does the oxidation of elemental sulfur in the form of Agrisul. Thiosulfate has been identified as an intermediate in the oxidation of elemental sulfur to sulfate (Nor and Tabatabai 1977, Wainwright 1978). It would therefore follow that the oxidation of thiosulfate to sulfate would occur over a shorter period of time than would the oxidation of elemental sulfur to sulfate. Thus, sulfur supplied as ammonium thiosulfate should become plant available earlier than sulfur supplied as Agrisul.

Although not significant, there was a trend toward higher dry matter yields and fertilizer sulfur utilization where ammonium thiosulfate was banded compared to where it was mixed. The apparently increased availability of thiosulfate placed in the band may be due in part to the following. At pH's near

neutrality, the majority of thiosulfate oxidation is carried out by heterotrophic bacteria. Vitolins and Swaby (1969) found that production of sulfate from heterotrophic thiosulfate oxidation was far less than that produced in oxidation by autotrophic bacteria. At more acid pH's oxidation of thiosulfate could be carried out by a broader range of thiobacilli. For example, Thiobacillus thiooxidans, a major oxidizer of sulfur in soils, develops best in pH's ranging from 2.0 - 3.0 (Rao and Berger 1971); however Starkey (1965) reported little or no development of this organism at near neutral pH's. In the banded treatments, heterotrophic microorganisms would act as primary oxidizers of thiosulfate. As products from the heterotrophic oxidation of thiosulfate accumulate and lower the pH in the area of the band, conditions conducive to the more efficient oxidation of thiosulfate by thiobacilli would exist. Thus oxidation to sulfate would occur more quickly. When the thiosulfate was applied over a large volume of soil (i.e. mixed throughout), the effect on pH would be negligible, thus oxidation of thiosulfate would be carried out by the less efficient heterotrophic microorganisms.

The results obtained in this experiment would indicate that elemental sulfur in the form of Agrisul is a poor supplier of plant available sulfur over the time period studied. Even where Agrisul was added in a form most conducive to increasing its oxidation and ultimately its plant availability, (i.e. as a well mixed flour) the results achieved were not as good as those

for either gypsum or ammonium thiosulfate. The results would also indicate that oxidation of ammonium thiosulfate occurs quickly enough and to such an extent that thiosulfate may be considered comparable to gypsum in its ability to supply rapeseed with sulfur.

VI Incubation Experiment: The effect of time and soil phosphorus content upon thiosulfate oxidation.

In order for its sulfur component to become plant available, ammonium thiosulfate must first be oxidized to sulfate. To date, the rate and extent of this oxidation in soils has not been well documented. Preliminary incubation work, which is not reported here, had been carried out on seven Manitoba soils in order to determine whether differences in soil pH, texture, calcium carbonate content or organic matter content could affect the rate of thiosulfate oxidation. No relationship could be shown between thiosulfate oxidation and these factors although some correlation was shown to exist between thiosulfate oxidation and the amount of available phosphorus in a soil. This is consistent with work by Lettl et al (1981) who showed that the oxidation of thiosulfate was increased as the phosphorus content of a forest soil was increased through the addition of KH_2PO_4.

In the work reported here, the oxidation of ammonium thiosulfate in soils was examined with regard to time, soil type and soil phosphorus content.

Methods and Materials

Two soils chosen for their differences in soil pH, carbonate content, available phosphorus and sulfate sulfur content were used in the incubation experiment. A Stockton very fine sandy loam (Orthic Black Chernozem (Ehrlich et al, 1957)) which had been stored in an air dry state for a period of eighteen months, was sieved, moistened to field capacity with deionized water and incubated for two weeks in order to stimulate microbial activity. The same soil was then air dried and sieved once again prior to the incubation experiment. An Elm River silty loam (Cumulic regosol (Michalyna and Smith, 1972)) was taken directly from the field, air dried and sieved for use in the experiment.

Both the Elm River and Stockton soils were handled in exactly the same manner through the course of the experiment and each soil was treated as follows: 200 gms. of air dry soil was placed into each of forty-five pots. The pots were split into three groups of 15, group one being incubated for one day, group two for five days and group three for 14 days. Each group of 15 pots was further subdivided into three subgroups of five pots, subgroup one receiving no sulfur, subgroup two receiving 20 ppm S. as ammonium thiosulfate and subgroup three receiving 100 ppm S. as ammonium thiosulfate. Within each subgroup, phosphorus content of soil in the individual pots was increased through

the addition of 10 ppm P, 25 ppm P, 50 ppm P and 100 ppm P with one pot receiving no additional phosphorus.

For treatments receiving additional phosphorus, sufficient KH_2PO_4 was dissolved in deionized water and applied dropwise through the soil. The soil was then air dried and thoroughly mixed with a mortar and pedestal.

For those treatments receiving sulfur, ammonium thiosulfate at 20 ppmS or 100 ppmS was diluted with sufficient deionized water to bring the soil to field capacity and then added directly to the soil in the pots. Where no thiosulfate was added, deionized water only was used to bring soil in the pots to field capacity.

All treatments were maintained at a temperature of 20°C and at field capacity through the course of the experiment. Sampling technique was as follows. For the one day incubation, samples were allowed to stand long enough for the water added to thoroughly infiltrate the soil. The soil was then removed from the pot, spread in a thin layer and allowed to air dry prior to analysis. Where the samples were incubated for 5 or 14 days, soil was removed from the pots on the morning of the fifth or fourteenth day, spread in a thin layer and allowed to air dry.

Percent thiosulfate oxidized to sulfate is based upon the difference in the sulfate sulfur content of soils treated with ammonium thiosulfate and those which had no thiosulfate added. Sulfate sulfur content in excess of that obtained

in the check pots is assumed to be the result of oxidation of ammonium thiosulfate. Soil phosphorus content reported in Table 10 is on the basis of $NaHCO_3$ extractable phosphorus present on the date of sampling.

Results and Discussion

Results from the incubation experiment are reported in Table 10. Increasing the phosphorus content of the soil had no effect upon the rate at which thiosulfate was oxidized to sulfate in either the Elm River or Stockton soil. Oxidation of thiosulfate increased with time and the two soils differed both in the rate of thiosulfate oxidation and in the total amount of thiosulfate oxidized to sulfate in the time period studied.

In Elm River soil incubated for one day, the rate of thiosulfate oxidation was affected by the amount of thiosulfate added to the soil. A greater percentage of the thiosulfate applied was oxidized in the 100 ppmS treatment (50.7%) than in the 20 ppmS treatment (20.4%). By day five of the incubation this effect had disappeared and thiosulfate was being oxidized in approximately the same proportions for both the 100 ppmS treatment and the 20 ppmS treatment. Similarily by day 14, sulfate sulfur was being recovered in approximately the same proportions for both the 20 ppmS treatment and the 100 ppmS treatment.

The oxidation of thiosulfate in relatively the same proportions, regardless of the amount initially added, has also been found to occur where elemental sulfur undergoes active microbial oxidation. Li (1964) and Nor and Tabatabai (1977) had found that when increasing amounts of elemental sulfur were added to a soil, oxidation by micro-

organisms increased so that the oxidation occured in relatively the same proportions. The same would seem to be true for the oxidation of thiosulfate in the Elm River soil.

In the Stockton soil the rate of thiosulfate oxidation was lower than that in the Elm River soil with the exception of the 20 ppmS treatment incubated for one day. The amount of thiosulfate added affected thiosulfate oxidation to a greater degree in the Stockton soil, with a higher percentage being oxidized to sulfate in the 20 ppmS treatment than in the 100 ppmS treatment by day five of the study. By day 14 this effect was no longer evident with the percent thiosulfate oxidized to sulfate being slightly higher in the 100 ppmS treatment compared to the 20 ppmS treatment.

These results would indicate that the oxidative capacity of the Stockton soil towards thiosulfate was less than that of the Elm River soil. Previous work had shown no correlation between the oxidation of thiosulfate and soil pH, calcium carbonate content or organic matter content. Attoe and Olson (1966), in reviewing the oxidation of elemental sulfur in soils found no well defined relationship between soil type and sulfur oxidation but felt that the oxidation of sulfur in soils was more related to the number of sulfur oxidizing organisms within a soil. If this is true, the results obtained in this experiment could be explained as follows. In the Elm River soil, large numbers of viable microorganisms capable of oxidizing thiosulfate

may have been present. This would account for the higher total amount of thiosulfate oxidized in the Elm River soil compared to the Stockton soil and also for the fact that by day five in the Elm River soil, thiosulfate was being oxidized in the same proportions whether supplied at 20 ppmS or 100 ppmS.

In the Stockton soil, populations of oxidizing microorganisms may have been low enough that up until day five of the study, thiosulfate from the 100 ppmS treatment was not oxidized to sulfate in the same proportions as that from the 20 ppmS treatment. After 14 days of incubation, the population of oxidizing microorganisms may have increased to the extent that percent oxidation of thiosulfate was similar for both the 20 ppmS and 100 ppmS treatment but not to the extent that it was comparable with the oxidation occuring in the Elm River soil.

The data reported here indicates that phosphorus, at the levels examined in this experiment, and at the levels of ammonium thiosulfate added to the two soils considered, had no effect upon the rate or total amount of thiosulfate oxidation. Presumably inorganic phosphorus levels were high enough in the soils for the oxidation of thiosulfate by microorganisms to proceed quickly and completely. Although increasing the amount of phosphorus to the levels indicated had no effect upon oxidation of ammonium thiosulfate, the data would indicate that in soils, ammonium thiosulfate is

oxidized to sulfate in a relatively short period of time. The rate and extent of this oxidation differs among soils and this difference is perhaps due to the numbers and types of sulfur oxidizing organisms originally present in the soil.

Table 10: Percent recovery of sulfate from ammonium thiosulfate as affected by available phosphorus, time and soil.

		Elm River Soil			Stockton Soil		
Incubation Time (days)	Sulfur Added (ppm)	Avail P (ppm)	% Recovery as SO_4-S	Average % recovery as SO_4-S	Avail P (ppm)	% Recovery as SO_4-S	Average % recovery as SO_4S
1	20	4.8	20.9	20.4	15.2	--	22.6
		7.0	19.2		21.4	--	
		17.9	21.4		29.1	24.5	
		20.2	19.0		45.8	20.4	
		65.5	21.7		40.7	23.0	
	100	4.3	47.0	50.7	14.6	14.6	19.0
		10.4	58.5		20.4	18.1	
		21.4	44.5		28.9	21.7	
		41.4	51.0		44.3	20.4	
		72.1	52.6		76.5	20.2	
5	20	4.1	83.4	83.6	11.5	53.1	59.1
		11.2	83.0		25.1	61.9	
		10.2	81.6		27.1	64.8	
		31.6	87.2		43.6	59.5	
		54.8	82.7		77.5	56.3	
	100	5.3	81.7	84.5	9.4	25.3	25.4
		10.4	85.7		18.2	26.5	
		24.0	85.2		12.2	26.6	
		41.8	85.0		40.2	24.6	
		80.2	84.9		77.5	24.2	
14	20	4.6	64.1	85.2	15.6	66.5	71.2
		11.5	91.5		23.0	71.1	
		21.4	87.2		30.2	73.1	
		40.6	93.8		45.3	63.6	
		79.5	89.2		77.8	81.6	
	100	5.1	91.8	88.2	15.6	79.1	78.8
		11.2	84.3		23.0	85.8	
		20.7	88.8		30.2	66.7	
		40.2	84.2		45.3	77.0	
		81.8	91.8		77.8	85.6	

VII Growth Chamber Experiment 2: The effect of ammonium thiosulfate on phosphorus availability and uptake by plants.

Several workers (Mitchell et al 1952, Menary and Hughes 1967, Kumar and Singh 1980) have shown that the addition of a sulfur source with a phosphorus source may increase the plant availability and utilization of phosphorus. Mitchell et al (1952) were able to relate the oxidation of elemental sulfur and the subsequent reduction of pH to the increased uptake and utilization of fertilizer phosphorus by wheat. Ammonium thiosulfate is oxidized in soils in a similar manner to elemental sulfur. Thus the addition of ammonium thiosulfate with a phosphorus source may result in a similar increase in plant availability and utilization of fertilizer phosphorus.

In this experiment, barley and rapeseed were examined for their response to the placement of monoammonium phosphate in a band with ammonium thiosulfate. Also examined were responses to banding monoammonium phosphate with sodium thiosulfate, urea, or urea and ammonium thiosulfate.

Methods and Materials

Rapeseed (Brassica campestris var. Torch) and barley (Hordeum vulgare var. Conquest) were grown in a growth chamber on a sulfur and phosphorus deficient Elm River silty loam soil (Cumulic Regosol (Michalyna and Smith 1972)) (Table 8). Soil from the 0 - 15 cm. depth was collected in June of 1981, air dried and sieved. 6,000 grams of air dry soil was then placed

into each of 48 plastic pots. There were a total of 8 treatments replicated three times in a completely randomized design.

Nitrogen, phosphorus and sulfur were supplied to barley and rapeseed in six of the eight treatments. Phosphorus was supplied at 40 ppm P as monoammonium phosphate. Sulfur was supplied at 20 ppm S as either ammonium thiosulfate or sodium thiosulfate. Urea was added so that a total of 100 ppm N was supplied from all sources.

In order to examine the effect of carrier placement upon phosphorus utilization, nitrogen, phosphorus and sulfur sources were placed in different combinations in various bands. Figure 4 illustrates the relative position of fertilizer bands in the pot. All bands were placed at a 7 cm. depth and band 2 lay directly below the seed row.

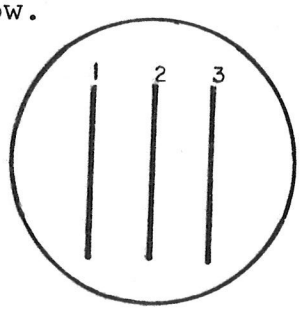


Figure 4: Top view of fertilizer band placement in pot.

Treatments consisted of placing urea, monoammonium phosphate and ammonium thiosulfate in separate bands; placing urea and ammonium thiosulfate in a single band and banding monoammonium phosphate separately; placing urea and monoammonium

phosphate in a single band and banding ammonium thiosulfate separately; placing monoammonium phosphate and ammonium thiosulfate in a single band and banding urea separately; placing monoammonium phosphate and sodium thiosulfate in a single band and banding urea separately; or placing urea, monoammonium phosphate and ammonium thiosulfate in a single band. The two additional treatments consisted of placing urea and ammonium thiosulfate in a single band with no phosphorus source added and placing urea and monoammonium phosphate in a single band with no sulfur source added. The relative locations of the bands in the pot for each treatment are listed in tables 11 and 12.

All nutrients applied in a band were added as liquid solution. Monoammonium phosphate, ammonium thiosulfate or sodium thiosulfate and urea were dissolved in sufficient deionized water so that the volume of solution applied to each of the required bands was 10 ml. Where more than one nutrient was applied in a single band, the required amounts of those nutrients were dissolved in 10 ml. of deionized water and then banded.

Prior to use in the experiment, monoammonium phosphate was labelled with ^{32}P. One millicurie of ^{32}P obtained from New England Nuclear was added to a liquid solution containing monoammonium phosphate which was then diluted to a 500 ml. volume with deionized water. 60 mls. of this solution was placed in a 100 ml. volumetric flask and when brought to volume, 10 ml. of the resulting solution would supply an individual pot with 40 ppm P

on a dry soil weight basis.

Copper and zinc were required and were supplied at 4 ppm Cu and 8 ppm Zn. Sufficient $CuCl_2$ and $ZnCl_2$ were dissolved in deionized water and added in the first daily watering after seeding. Further nitrogen requirements were met through the addition of two subsequent aliquots, each supplying 100 ppm N as dissolved urea, on day 24 and day 34 of the study.

Seeding took place on July 28, 1981 when 10 seeds per pot were placed in a single row 1 cm. deep, directly above fertilizer band 2. The number of plants per pot was thinned to 5 after emergence. The watering regime consisted of daily watering to field capacity with deionized water. Plants from all treatments were harvested on September 15, 1981 when rapeseed was in the early flowering stage and barley in the early heading stage. At harvest, plants were cut a few millimeters above the soil surface, dried in a forced air oven (85°C) and ground in a Wiley mill to pass a 2 mm. sieve. Conditions in the growth chamber were set as follows: Temperature: 18°C (night) - 24°C (day); Day length 15 hours; Humidity 90%.

In this experiment ^{32}P labelling was used in order to determine percent phosphorus derived from fertilizer which was in turn used to calculate fertilizer phosphorus uptake. The procedure for the determination was as follows: 1 gm. of plant material was mixed with 5 ml. of concentrated nitric acid and 2.5 ml. of perchloric acid and heated. After allowing sufficient time

for complete digestion, the material was filtered through Whatman no. 42 paper. A 15 ml. portion of the filtrate was pipetted into the required container and radioactive counts were taken by a Beckman LS 7500 Liquid Scintillation counter. The standard for this procedure was prepared by diluting 0.1 ml. of the 40 ppm. solution in 15 ml. water. Plant material containing no labelled P was digested to provide blanks in order that background radiation could be obtained.

Percent phosphorus derived from fertilizer was calculated as follows: $$\% \text{ Pdff} = \frac{\text{Specific Activity of Sample}}{\text{Specific Activity of Standard}} \times 100$$

Specific Activity = counts/min/mg P/ml. of solution

Results and Discussion

Carrier placement significantly affected total fertilizer phosphorus uptake, total phosphorus uptake and dry matter yield of barley. (Table 10). Where phosphorus was added total phosphorus uptake and dry matter yield of barley were increased significantly compared to the treatment where no additional phosphorus was supplied. Dry matter yield of barley was significantly increased by the addition of sulfur except where sulfur was supplied as ammonium thiosulfate in a band with urea and monoammonium phosphate.

Placement of thiosulfate in a band with monoammonium phosphate significantly increased total fertilizer phosphorus uptake, total phosphorus uptake and dry matter yield of barley. Total

phosphorus uptake in treatments where monoammonium phosphate was banded with either sodium or ammonium thiosulfate were comparable and significantly higher than that obtained in any other treatment.

Where sodium thiosulfate was banded with monoammonium phosphate, total fertilizer phosphorus uptake was significantly higher than that obtained in any other treatment and was in particular 158% of that obtained in the treatment where urea, ammonium thiosulfate and monoammonium phosphate were each placed in separate bands. Banding ammonium thiosulfate with monoammonium phosphate produced total fertilizer phosphorus uptake which was lower than that obtained when sodium thiosulfate was banded with monoammonium phosphate, but significantly higher than that obtained in any other treatment. The effect of ammonium thiosulfate upon the uptake of fertilizer phosphorus by barley is reflected inthe value for total fertilizer phosphorus uptake which is 123% of that obtained in the treatment where the phosphorus, nitrogen and sulfur sources were banded separately. Fertilizer phosphorus uptake was not significantly affected by the placement of monoammonium phosphate in a band with any other carrier.

Dry matter yield of barley was significantly increased by banding monoammonium phosphate with either sodium or ammonium thiosulfate compared to where the nitrogen, phosphorus and sulfur sources were banded separately. Any other combination of carriers in a band did not have a similar effect.

The fact that higher dry matter yields and total phosphorus uptake may be associated with increased fertilizer phosphorus uptake by barley in treatments where a thiosulfate source was banded with monoammonium phosphate would indicate that thiosulfate effectively increased either plant availability or plant utilization of phosphorus or both. In the previous experiment it was shown that thiosulfate undergoes oxidation to sulfate in soil. The overall reaction for the aerobic oxidation of thiosulfate is an acid forming process (Aleem 1975). This may in part account for the increased utilization of fertilizer phosphorus placed in a band with thiosulfate. As oxidation of thiosulfate proceeds, the pH in the area of the band would be lowered which may in turn result in a reduced fixation or an increased solubility of the phosphate fertilizer thus making it more available for plant use.

Mitchell et al (1952) showed an increase in phosphorus uptake by wheat when small amounts of elemental sulfur were mixed with dicalcium phosphate. This effect was attributed to a reduction of pH in the area of the band associated with the oxidation of elemental sulfur, the lower pH resulting in a reduced rate of fixation or an increased solubility of the phosphate fertilizer. Menary and Hughes (1967) noted an increased uptake of fertilizer phosphorus by tomato plants when sodium sulfate was banded with mono-calcium phosphate and attributed this effect to a reduced fixation of fertilizer phosphorus in

the presence of sulfate. Similarily Aitkens and Hughes (1980) showed an increase in phosphorus availability to tomato plants when monocalcium phosphate, monoammonium phosphate or dicalcium phosphate were banded in the presence of a sulfate source.

Banding urea with monoammonium phosphate did not affect the plant uptake of fertilizer phosphorus in the same way that thiosulfate did. Where urea was placed in a band with monoammonium phosphate, uptake of fertilizer phosphorus, total phosphorus and dry matter yield of barley did not differ significantly from the treatment where the nitrogen, phosphorus and sulfur sources were banded separately. Both total fertilizer phosphorus uptake and total phosphorus uptake were significantly lower when urea was banded with monoammonium phosphate than when either sodium or ammonium thiosulfate were banded with monoammonium thiosulfate.

Where urea was placed in a band with monoammonium phosphate and ammonium thiosulfate, total fertilizer phosphorus uptake, total phosphorus uptake and dry matter yield of barley were comparable to that obtained in the treatment where the three carriers were banded separately and significantly lower than that obtained in treatments where monoammonium phosphate was banded with either ammonium thiosulfate or sodium thiosulfate. Although thiosulfate was present in the band with phosphate and urea, the increased uptake of fertilizer phosphorus associated with other thiosulfate-phosphate treatments was not observed.

The lower uptake of fertilizer phosphorus noted for treatments where urea was banded with monoammonium phosphate may

relate to ammonia toxicity in the area of the band. Flaten and Racz (1982) had shown that when monoammonium phosphate was banded with urea, there was an initial depression in phosphorus uptake by wheat. This depression was attributed to concentrations of ammonia ion in the band which were toxic to root growth. In treatment where urea, monoammonium phosphate and ammonium thiosulfate were all placed in the same band a total of 100 ppm N was supplied from all sources and concentrations of ammonia ion may have been high enough to be toxic to root growth thereby preventing plant utilization of fertilizer phosphorus. For barley, the high level of ammonia associated with the triple band would prevent root access to the point that the beneficial effects of an intimate association of thiosulfate and phosphate in the band would be negated. This is reflected in values for dry matter yield and phosphorus uptake which did not differ or were significantly lower than those obtained in the treatment where the nitrogen, phosphorus and sulfur sources were banded separately. Further evidence that ammonia toxicity in the area of the band may have reduced fertilizer phosphorus uptake comes from the fact that total fertilizer phosphorus uptake by barley was significantly lower when monoammonium phosphate was banded with ammonium thiosulfate as opposed to sodium thiosulfate.

Rapeseed responded to the addition of phosphorus as reflected in values for total fertilizer phosphorus uptake, total

phosphorus uptake and dry matter yield (Table 11) which were significantly higher for treatments receiving phosphorus compared to the treatment which received no phosphorus. Addition of sulfur significantly increased total fertilizer phosphorus uptake, total phosphorus uptake and dry matter yield of rapeseed compared to where no sulfur was added.

Unlike barley, carrier placement did not significantly affect total fertilizer phosphorus uptake, total phosphorus uptake or dry matter yield of rapeseed. In particular, placement of monoammonium phosphate in a band with either ammonium or sodium thiosulfate did not significantly increase total fertilizer phosphorus uptake compared to treatments where monoammonium phosphate was banded alone, banded with urea or banded with urea and ammonium thiosulfate.

The lack of a response by rapeseed to carrier placement may be due in part to the ability of rapeseed to extract and utilize phosphorus. Kalra and Soper (1968) showed that rapeseed generally absorbs more total phosphorus than crops such as oats and flax. Rapeseed has also been shown to be highly efficient in extracting banded fertilizer phosphorus and this has been related to an extensive proliferation of roots within the fertilizer zone (Kalra, 1971; Strong and Soper, 1974). In the data reported here, the more efficient extraction of phosphorus by rapeseed is reflected in the higher overall phosphorus contents of rapeseed compared to barley. Any increase in the availability of fertilizer phosphorus associated with the monoammonium phosphate-

thiosulfate double band would seem to have been masked by the more efficient extraction and uptake of phosphorus by rapeseed.

From the results obtained in this experiment it is apparent that total phosphorus uptake and dry matter yield of barley may be significantly increased by supplying phosphorus as monoammonium phosphate in a band with either ammonium or sodium thiosulfate and that these increases may in turn be related to the effect of thiosulfate upon the availability of fertilizer phosphorus to barley. Rapeseed responded to the addition of phosphorus in terms of total phosphorus uptake and dry matter yield, however, placement of monoammonium phosphate in a band with either sodium or ammonium thiosulfate had no further effect upon this response. This may be due in part to the ability of rapeseed to extract and utilize phosphorus.

Table 11: Treatments, dry matter yield and phosphorus uptake by barley.

Band 1	Band 2	Band 3	Dry Weight (gms.)	Total P (mg.)	Total Fertilizer P (mg.)
NS			4.6 a*	7.5 a	--
NP			18.2 b	39.5 b	33.8 a
P	N	S	25.3 cd	44.9 bc	39.3 ab
NS		P	26.0 de	44.0 bc	39.2 ab
NP		S	26.5 def	49.9 c	40.6 b
PS	N		27.9 ef	66.7 d	48.3 c
PS(Na)	N		31.0 f	66.7 d	62.1 d
NPS			21.6 bc	49.5 bc	37.9 ab

Table 12: Treatments, dry matter yield and phosphorus uptake by rapeseed.

Band 1	Band 2	Band 3	Dry Weight (gms.)	Total P (mg.)	Total Fertilizer P (mg.)
NS			15.7 a*	29.2 a	--
NP			19.4 b	43.7 a	35.9 a
P	N	S	34.6 cd	98.5 b	80.1 b
NS		P	35.8 cd	112.4 b	86.0 b
NP		S	33.6 cd	109.8 b	74.9 b
PS	N		32.7 c	110.8 b	80.7 b
PS(Na)	N		33.0 c	102.4 b	83.8 b
NPs			32.7 c	100.8 b	78.2 b

* Duncan's multiple range: Numbers followed by the same letter are not significantly different at P = 0.05.

VIII Summary and Conclusions

A field study was conducted in order to determine what effect sulfur fertilization had upon the yield and sulfur uptake of barley and rapeseed grown on soils considered to be sulfur deficient. Also examined was the relative plant availability of sulfur supplied as ammonium sulfate, ammonium thiosulfate, gypsum and Agrisul. The field experiments were located near Sidney and Neepawa, Manitoba.

Midseason dry matter yields of barley from either site were not affected by the addition of sulfur in any form. Plant tissue analysis from the Sidney site indicated that by early heading barley was utilizing significantly larger amounts of sulfur where 40 kg S/ha as ammonium sulfate, ammonium thiosulfate or gypsum were applied compared to treatments which received 20 or 80 kg S/ha as Agrisul, or no sulfur. Yield, sulfur concentration and total sulfur uptake by barley were, in general, not significantly affected by the addition of sulfur in any form. The lack of a yield response would indicate that soils containing 12.0 kg SO_4-S/ha (water extractable to 60 cm.) contain sufficient sulfur for the production of barley. Midseason samples of rapeseed from the Sidney site showed no significant dry matter yield response to the application of sulfur in any form. While not always significant, by early flowering there was a trend towards higher sulfur uptake in rapeseed supplied with sulfur as ammonium sulfate, ammonium thiosulfate or gypsum compared to

rapeseed which received no sulfur or had sulfur supplied as Agrisul.

By maturity a similar, although not necessarily significant trend was noted toward increased sulfur uptake and seed yield of rapeseed where sulfur was supplied as ammonium sulfate, ammonium thiosulfate or gypsum compared to where Agrisul was added. The seed yield response obtained at the Sidney site along with the values for midseason tissue concentration of sulfur indicate that rapeseed grown on soils containing 21.1 kg SO_4-S/ha (water extractable to 60 cm.) will respond to the addition of sulfur.

The results from the field study led to the initiation of a growth chamber experiment in which gypsum, ammonium thiosulfate and Agrisul were compared for their abilities to supply rapeseed with sulfur. Rapeseed supplied with gypsum or ammonium thiosulfate had significantly higher fertilizer sulfur recoveries and dry matter yields compared to rapeseed which was supplied with Agrisul. Dry matter yields and fertilizer sulfur recovery by rapeseed were significantly increased when Agrisul was powdered and mixed throughout the soil as opposed to being applied as banded granules. Similarily there was a trend in the gypsum treatments toward higher fertilizer sulfur recovery where it was mixed throughout the soil as opposed to being banded. In treatements where ammonium thiosulfate was applied, there was a trend toward higher fertilizer sulfur recovery in banded treatments compared to mixed treatments.

The results from the field and growth chamber experiments show that over the time period studied, the oxidation of elemental sulfur in the form of Agrisul does not proceed quickly enough to adequately supply rapeseed with sulfur. Over the same time period, the oxidation of ammonium thiosulfate occured to such an extent that it was comparable to ammonium sulfate or gypsum in its ability to provide the rapeseed with sulfur.

The oxidation of thiosulfate was studied further in an incubation study carried out using two Manitoba soils. Increasing the phosphorus content of the soil had no effect upon the rate at which thiosulfate was oxidized to sulfate. The results did show that in soils, ammonium thiosulfate is oxidized to sulfate in a relatively short period of time (14 days) and that the rate and extent of this oxidation differs among soils.

In a second growth chamber experiment, fertilizer phosphorus uptake, total phosphorus uptake and dry matter yield of barley and rapeseed were used to examine the effect of banding urea or a thiosulfate source with a phosphorus source. For barley, total phosphorus uptake and dry matter yield were significantly increased by banding a thiosulfate source with monoammonium phosphate. Sodium thiosulfate was more effective in increasing total fertilizer phosphorus uptake than was ammonium thiosulfate.

Banding urea with monoammonium phosphate did not significantly affect total fertilizer phosphorus uptake or dry matter yield of barley. This was attributed in part to an initial depression in fertilizer phosphorus uptake due to the effects

of ammonia toxicity in the area of the band.

Total phosphorus uptake and dry matter yield of rapeseed was not significantly affected by banding either urea or a thiosulfate source with monoammonium phosphate. This was attributed to the ability of rapeseed to more efficiently extract and utilize phosphorus.

Table 1A: Tissue analyses for barley at the early heading stage from the Sidney site.

Carrier	Rate kg/ha	Nitrogen Concentration (%)	Total Nitrogen Uptake kg/ha	N/S
Check	0	2.45 ab*	76.5 a	15.9 c
$(NH_4)_2SO_4$	10	2.43 ab	86.3 a	14.0 abc
$(NH_4)_2SO_4$	20	2.53 b	84.9 a	13.9 abc
$(NH_4)_2SO_4$	40	2.50 ab	79.1 a	12.0 ab
Agrisul	20	2.40 ab	76.9 a	15.8 c
Agrisul	80	2.39 ab	79.9 a	16.8 c
$(NH_4)_2S_2O_3$	20	2.48 ab	76.9 a	12.6 ab
$(NH_4)_2S_2O_3$	40	2.31 a	80.0 a	11.2 a
$CaSO_4 5H_2O$	20	2.46 ab	88.2 a	14.6 bc
$CaSO_4 5H_2O$	40	2.40 ab	85.5 a	11.5 a

Table 2A: Tissue analyses for barley grain from the Sidney site.

Carrier	Rate kg/ha	Nitrogen Concentration (%)	Total Nitrogen Uptake kg/ha	N/S
Check	0	2.23 a	71.4 a	15.4 ab
$(NH_4)_2SO_4$	10	2.27 a	68.4 a	16.4 ab
$(NH_4)_2SO_4$	20	2.19 a	62.9 a	16.1 ab
$(NH_4)_2SO_4$	40	2.21 a	69.8 a	15.0 ab
Agrisul	20	2.27 a	68.1 a	15.4 ab
Agrisul	80	2.18 a	63.6 a	13.2 a
$(NH_4)_2S_2O_3$	20	2.19 a	65.9 a	15.7 ab
$(NH_4)_2S_2O_3$	40	2.24 a	62.9 a	15.6 ab
$CaSO_4 5H_2O$	20	2.26 a	69.6 a	15.4 ab
$CaSO_4 5H_2O$	40	2.21 a	66.3 a	17.6 b

* Duncan's Multiple Range: Numbers followed by the same letter are not significantly different at P = 0.05.

Table 3A: Analyses for barley grain from the Neepawa site.

Carrier	Rate kg/ha	Nitrogen Concentration (%)	Total Nitrogen Uptake kg/ha	N/S
Check	0	2.28 a*	55.5 a	16.8 b
$(NH_4)_2SO_4$	10	2.23 a	56.3 a	13.2 ab
$(NH_4)_2SO_4$	20	2.26 a	64.5 a	12.8 a
$(NH_4)_2SO_4$	40	2.23 a	63.5 a	13.9 ab
Agrisul	20	2.33 a	51.0 a	15.9 ab
Agrisul	80	2.28 a	57.6 a	13.5 ab
$(NH_4)_2S_2O_3$	20	2.26 a	61.2 a	13.1 a
$(NH_4)_2S_2O_3$	40	2.30 a	52.4 a	14.0 ab
$CaSO_4 5H_2O$	20	2.19 a	67.9 a	13.8 ab
$CaSO_4 5H_2O$	40	2.33 a	51.0 a	13.4 ab

Table 4A: Analyses for rapeseed at the early flowering stage from the Sidney site.

Carrier	Rate kg/ha	Nitrogen Concentration (%)	Total Nitrogen Uptake kg/ha	N/S
Check	0	1.86 a	37.5 a	9.9 ab
$(NH_4)_2SO_4$	10	2.22 b	50.7 a	8.1 ab
$(NH_4)_2SO_4$	20	2.19 b	48.5 a	7.4 a
$(NH_4)_2SO_4$	40	2.18 b	45.0 a	7.4 a
Agrisul	20	2.04 ab	54.4 a	11.4 b
Agrisul	80	2.01 ab	39.1 a	10.4 ab
$(NH_4)_2S_2O_3$	20	2.22 b	50.7 a	7.7 ab
$(NH_4)_2S_2O_3$	40	2.09 ab	62.6 a	8.2 ab
$CaSO_4 5H_2O$	20	2.06 ab	46.3 a	8.6 ab
$CaSO_4 5H_2O$	40	2.08 ab	54.7 a	7.2 a

* Duncan's Multiple Range: Numbers followed by the same letter are not significantly different at P = 0.05.

Table 5A: Analyses for seed from the Sidney rapeseed site.

Carrier	Rate kg/ha	Nitrogen Concentration (%)	Total Nitrogen Uptake kg/ha	N/S
Check	0	3.22 a*	41.6 a	8.0 a
$(NH_4)_2SO_4$	10	3.46 cd	52.7 abcd	6.5 a
$(NH_4)_2SO_4$	20	3.48 cd	54.7 bcd	7.7 a
$(NH_4)_2SO_4$	40	3.55 d	63.6 d	8.2 a
Agrisul	20	3.30 ab	46.1 ab	7.3 a
Agrisul	80	3.35 bc	48.5 abc	6.3 a
$(NH_4)_2S_2O_3$	20	3.49 cd	50.0 abc	5.7 a
$(NH_4)_2S_2O_3$	40	3.57 d	56.1 bcd	8.1 a
$CaSO_4 5H_2O$	20	3.37 bc	52.8 abcd	8.2 a
$CaSO_4 5H_2O$	40	3.48 cd	59.6 cd	5.7 a

* Duncan's Multiple Range: Numbers followed by the same letter are not significantly different at P = 0.05.

Table 6a: Tissue nitrogen concentration for rapeseed grown in the growth chamber.

Carrier	Method of Application	Rates (ppm)	% N
Control	--	--	3.80 cd
Agrisul	banded	10	4.73 e
		20	4.89 e
		40	4.33 de
	mixed	10	3.28 abc
		20	3.51 bcd
		40	3.24 abc
Gypsum	banded	10	3.01 abc
		20	2.85 ab
	mixed	10	3.01 ab
		20	2.68 ab
Thiosulfate	banded	10	3.14 abc
		20	2.58 a
	mixed	10	3.01 ab
		20	2.63 ab

Table 7a: Treatments, nitrogen and sulfur uptake by barley in the second growth chamber experiment.

Band 1	Band 2	Band 3	Total N (mg.)	Total S (mg.)
NS			230 a*	21.0 a
NP			738 b	17.0 a
P	N	S	995 d	62.2 c
NS		P	1008 d	65.2 c
NP		S	1022 de	71.7 cd
PS	N		1109 ef	79.7 d
PS(Na)	N		1139 f	80.6 d
NPS			894 c	47.5 b

Table 8a: Treatments, nitrogen and sulfur uptake by rapeseed in the second growth chamber experiment.

Band 1	Band 2	Band 3	Total N (mg.)	Total S (mg.)
NS			705 a*	67.2 b
NP			813 ab	8.4 a
P	N	S	1336 bc	85.4 b
NS		P	1303 c	83.0 b
NP		S	1209 c	73.0 b
PS	N		1037 bc	84.0 b
PS(Na)	N		1279 c	86.4 b
NPS			1226 c	74.6 b

* Duncan's multiple range: Numbers followed by the same letter are not significantly different at P = 0.05.

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