

**AGRONOMIC EVALUATION OF A HOMOGENEOUS NITROGEN-
PHOSPHORUS-SULPHUR FERTILIZER IN SOUTHERN MANITOBA**

BY

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for the Degree of**

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**Agronomic Evaluation of a Homogeneous Nitrogen-Phosphorus-Sulphur Fertilizer in
Southern Manitoba**

BY

Myron Kroeker

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of
Manitoba in partial fulfillment of the requirement of the degree
Of
Master of Science**

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ABSTRACT

Kroeker, Myron P. M.Sc., The University of Manitoba, May 2005. Agronomic Evaluation of a Homogeneous Nitrogen-Phosphorus-Sulphur Fertilizer in Southern Manitoba. Major Professor; Dr. Don Flaten.

Field studies and a growth chamber study were conducted to evaluate the effect of a homogeneous nitrogen-phosphorus-sulphur (NPS) fertilizer on the emergence and crop utilization of phosphorus (P) and sulphur (S). In the field study, spring wheat (*Triticum aestivum* L. cv. AC Barrie) and spring canola (*Brassica napus* L. cv. DKL 34-55) were grown in southern Manitoba and fertilized with NPS, monoammonium phosphate (MAP) + ammonium sulphate (AS), MAP + elemental S-bentonite (S^o), MAP only and a control (no P or S); and S was applied at 0, 5, 10, 15 and 20 kg ha⁻¹. Wheat and canola emergence was not affected by any of the seed-placed P and S fertilizer sources or S rates used in the study. The NPS and other P fertilizer sources increased dry matter yield 6 – 10% in wheat at midseason but not at maturity; canola yields were not increased by P and S fertilization at any stage. At midseason, all of the phosphate fertilizers increased P uptake by 8 - 13% in wheat and 23 – 45% in canola, while NPS and MAP + AS increased S uptake by wheat 7 – 9%. At maturity, all of the P fertilizers increased total P uptake by 9 – 12% in wheat but not in canola, and all responses to S fertilization had disappeared.

To determine the availability of P, SO₄ and S^o in NPS fertilizer, two S-deficient soils were used for a growth chamber study. Spring canola was fertilized with NPS, MAP + AS, MAP + S^o, MAP only, AS only and a control (no P or S). At 45 days after emergence, the canola was harvested and dry matter yield, P and S uptake were measured. After this harvest, the soils were incubated to simulate potential S^o oxidation conditions between cropping seasons in Manitoba. The pots were then replanted to a second crop of canola to measure residual P and S supplied by NPS fertilizer. In the first canola crop, dry matter yield and apparent P fertilizer use efficiency of NPS fertilizer was 75% and 81% of that for MAP + AS respectively. The apparent S fertilizer use efficiency for NPS was 35% of that for MAP + AS. When the second crop was grown without P and S fertilization, dry matter and residual P and S uptake were highest for the NPS treatment; however, the cumulative dry matter yield (crop 1 + 2) produced with NPS fertilizer was 83% of that for MAP + AS. The apparent P fertilization efficiencies for MAP + AS and NPS fertilizers were 54 – 56% over the two cropping periods. However, the apparent S fertilizer use efficiency of NPS fertilizer was approximately 50% lower than MAP + AS.

Overall, the studies indicated that NPS fertilizer was not detrimental to wheat and canola emergence at the rates used in the study; the availability of P from NPS fertilizer appeared to be at least equivalent to MAP; and that only the SO₄-S portion of NPS fertilizer appeared to be available to crops, with no measurable amount of oxidation of the S^o-S portion.

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FOREWORD

This thesis has been prepared in the manuscript format in adherence with the guidelines established by the Department of Soil Science at The University of Manitoba. The Canadian Journal of Soil Science was used as the reference style in this document. Chapters 3 and 4 will be submitted to the Canadian Journal of Soil Science. I will be the lead author for these papers and co-authorship will be designated accordingly.

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1. INTRODUCTION

Cargill Fertilizers identified phosphorus and sulphur as two nutrients that frequently limit global crop production. For example, in western Canada, soil phosphorus concentrations are often insufficient to optimize crop production (Nyborg et al. 1999), while Doyle and Cowell (1993b) estimated that 30% of the cultivated soils in the prairie provinces were sulphur deficient. Phosphorus and sulphur deficiencies can be further accentuated by unfavourable weather conditions, overall nutrient imbalances (e.g. high nitrogen rates), as well as by growing crops that have high nutrient requirements, such as canola.

To address the crop requirement for both phosphorus and sulphur, Cargill created a unique granular fertilizer that is a homogeneous blend of nitrogen, phosphorus and sulphur (NPS). The nutrient analysis of each fertilizer granule is 13% nitrogen, 33% phosphate, and two sulphur forms, 7.5% S as sulphate and 7.5% S as elemental sulphur (13-33-0-15). The sulphate-sulphur is immediately plant available, while the elemental sulphur requires biological oxidation before it can be utilized by the crop.

The homogeneous NPS fertilizer granule may have several potentially beneficial attributes for both Cargill as well as agricultural producers. The unique properties of this fertilizer allow Cargill to separate this product from the existing phosphate and sulphur fertilizer in the market place today. The inclusion of elemental sulphur increases the nutrient concentration of the NPS fertilizer by 20% compared to conventional monoammonium phosphate and ammonium sulphate fertilizers. Therefore, 20% less

fertilizer is transported and handled by the producer at planting, translating into lowered production costs. Elemental S is a by-product of many industrial processes and is inexpensive relative to ammonium sulphate; therefore, the inclusion elemental S fertilizer in NPS fertilizer decreases the retail price by 12% compared to MAP + ammonium sulphate (at 44 kg P ha⁻¹ and 20 kg S ha⁻¹).

The inclusion of nitrogen and sulphur with phosphorus may improve the efficiency of phosphate fertilizer. Typically, conventional phosphate fertilizer efficiency is low in western Canada, often less than 20% for wheat in the year of application (Doyle and Cowell 1993a). Therefore, the potential for improved fertilizer efficiency could reduce fertilizer application rates and thus reduce crop production costs (Hammond 1997).

Numerous studies in western Canada have demonstrated that the addition of ammonium-nitrogen may enhance the chemical availability of phosphate as well as a host of biological processes responsible for phosphate uptake by the crop (Beever 1987; Flaten 1989; Miller and Ohlrogge 1958; Thien and McFee 1970). Sulphate fertilizers may also improve phosphate fertilizer efficiency by increasing the chemical availability of phosphate, though biological benefits are possible, as well (Goos and Johnson 2001; Kumaragamage et al. 2004; Singh et al. 1998). The oxidation of elemental sulphur may also improve phosphate fertilizer solubility and provide a slow release of sulphate as well (Doyle and Cowell 1993b; Kashirad 1972; Mitchell et al. 1952). In addition, researchers have found that placing ammonium sulphate and phosphate fertilizer granules in physical contact with each other increased the efficiency of the phosphate fertilizer (Hammond 1997; He et al. 2002). Overall, the combination of phosphate and sulphur may provide a balance of nutrients required for vigorous crop growth.

The overall research question that we sought to answer in this project was: how does the NPS fertilizer perform in wheat and canola when applied at typical rates and using simulated airseeder technology under Manitoba conditions. Specifically, we wanted to determine: the potential risk of seed-placed NPS fertilizer relative to other conventional P and S fertilizers; and the availability of P and S from NPS, including the availability of the elemental-S portion of the NPS fertilizer.

2. LITERATURE REVIEW

Cargill Fertilizer has developed a unique phosphorus-sulphur fertilizer which combines ammonium (NH_4^+), orthophosphate (H_2PO_4^-), sulphate (SO_4^{2-}) and elemental sulphur (S^0) into a single homogeneous granule. Each granule contains 13% ammonium, 33% phosphate, 7.5% sulphate and 7.5% elemental sulphur. The purpose of this chapter is to review: the importance of phosphorus and sulphur to crop production; factors affecting the efficiency of these nutrients, such as the potential benefits of combining different fertilizer ions on phosphorus availability; as well as possible crop production risks associated with fertilizer use, for example, fertilizer toxicity to germinating seeds.

2.1 Phosphate Behavior in Plants and Soils

2.1.1 Function and Uptake of Phosphorus in the Plant

Phosphorus (P) is a vital crop nutrient for all processes that require energy, synthesis of structural components, and transfer of genetic material. Phosphorus is a key component in adenine triphosphate (ATP), the energy currency of the cell. The energy is used for biosynthesis of metabolic and structural constituents required for plant growth and maintenance.

Phosphorus is also an important structural component in plants. It is an essential component of phospholipids membranes that surround cells, and the organelles within

each cell. Coenzymes, nucleotides, phosphoproteins and sugar phosphates all require P for synthesis. Genetic material, such as DNA and RNA contain large quantities of P in the backbone of the molecule (Lehninger et al. 1997). Therefore, P is essential for the reproductive function of a plant.

Agronomically, P fertilization can improve early season growth in cool soils by increasing early season P uptake. Adequate P nutrition also increases frost tolerance, resistance to root rot diseases, the rate of ripening and grain yields (Doyle and Cowell 1993a; Hanway and Olson 1980; Havlin et al. 1999; McKenzie et al. 2003). Thus, P is essential for physiological processes and agronomic crop management.

Plants absorb P as H_2PO_4^- and HPO_4^{2-} from the soil solution. Soil pH determines which form of phosphate exists in solution, at $\text{pH} < 7.2$, H_2PO_4^- dominates and at $\text{pH} > 7.2$, HPO_4^{2-} is the prevalent form (Barber 1984). Solution P moves to the root surface primarily by diffusion, over distances < 2 mm. Transport of soluble P may also occur by mass flow; however, this mechanism typically accounts for $< 1\%$ of P uptake due to retention by the soil (Sheppard and Racz 1980). Once at the root surface, P moves into the root by active transport (Grossman and Takahashi 2001; Schachtman et al. 1998). Root uptake of P lowers the P concentration in the rhizosphere, causing a shift in equilibrium from solid phase to solution P, replenishing P available for uptake (Sheppard and Racz 1980). The ability of the soil to replace solution P is dependent on immobilization and mineralization rates, P transport rates, adsorption and desorption rates and changes in the solubility of P minerals (Hammond 1997; Sheppard and Racz 1980).

In addition to soil characteristics, plants have a significant influence on P uptake due to morphological and physiological characteristics as well as nutritional requirements. Crops may also increase P uptake by forming symbiotic relationships with

mycorrhizal fungi, for example wheat forms mycorrhizal associations, while canola does not (Harris et al. 2002; Yao and Christie 2001). Most annual crops require substantial amounts of P in their early stages of growth. For example, wheat and other cereals rapidly take up P, especially after the plant reaches the two leaf stage (Clarke et al. 1990). In contrast, Strong and Soper (1974b) reported that P uptake in wheat was more gradual and consistent throughout the growth cycle. Oilseed crops, such as canola, generally require more P than cereal crops. The rate of P uptake and accumulation within the plant may often be highest during the period from late vegetative growth to mid-flowering (Johnston et al. 2003).

2.1.2 Dissolution of Phosphate Fertilizer

Monoammonium phosphate (MAP) is the primary source of P in crop production in Western Canada (Korol 2002). Phosphate fertilizers such as MAP are highly water soluble and are an efficient nutrient source (Havlin et al. 1999; Sample et al. 1980; Zhang et al. 2000), even under low soil moisture conditions (Lawton and Vomocil 1954).

Fertilizer salts from the MAP granule create a solution that approaches saturation (Sample et al. 1980). The highly concentrated fertilizer solution produces an osmotic potential gradient relative to the surrounding dilute soil solution. Thus, water moves to the dissolved fertilizer granule, the fertilizer reaction zone, by vapour or capillary transport. Simultaneously, P diffuses away from the site of application due to capillary flow, decreasing the concentration of P at the site of application (Doyle and Cowell 1993a; Sample et al. 1980). As the capillary transport of water and the diffusion of P continues, the osmotic potential gradient diminishes, slowing and eventually stopping further movement of water.

Monoammonium phosphate is an acid forming fertilizer with a pH of 4.7 when dissolved in pure water (Dowling 1998). In soil, the pH around the granule may decrease slightly after dissolution, and theoretically could alter P adsorption and precipitation reactions in the soil. However, Racz and Soper (1967) suggested that MAP did not lower soil pH sufficiently to cause changes in P reaction products.

The dissolution of multiple fertilizer granules in a band produces a concentrated P solution. As this solution moves through the soil, it may dissolve soil minerals, releasing considerable concentrations of Al, Fe, Mg and Ca. In theory, cations on the exchange sites of soil minerals and soil organic matter may also be dislodged into soil solution by high concentrations of fertilizer cations. These exchange cations may then react with the fertilizer P to form compounds that are less available to plants (Akinremi and Cho 1991; Cho 1991; Sample et al. 1980; Soper and Racz 1980). In general, these reactions with the soil are limited to a small area around the site of application (Bell and Black 1970).

2.1.3 Phosphate Fertilizer Retention in Soils

The efficiency of fertilizer P in the year of application is low in many soils. For example, fertilizer P uptake by cereals in the year of application is at best 20% to 25%, while uptake by rape may be 50% in the year of application (Soper and Kalra 1969). This indicates that P availability is limited by retention processes in the soil, namely precipitation and adsorption reactions, as well as microbial immobilization (Doyle and Cowell 1993a). These competing soil reactions have been recognized for over 150 years and the negative effects of these reactions on fertilizer P efficiency and P nutrition have been extensively studied (Sample et al. 1980).

2.1.3.1 Phosphate Fertilizer Precipitation Reactions In P precipitation reactions, phosphate is bonded to cations to form secondary P minerals, resulting in decreased P availability to growing crops. The degree to which fertilizer P is precipitated is dependent on the ability of plants to compete for P with reactive cations present in soil solution. In acidic soils, P forms precipitates with Al and Fe forming variscite or strengite. In calcareous soils, P forms precipitates with Ca and/or Mg forming dicalcium phosphates and magnesium phosphates. These reactions of P occur primarily near the site of the granule or band, in the zone of high solution P concentration (Soper and Racz 1980).

Precipitation reactions occur rapidly in most soils, though the rate of reaction may depend on soil pH, moisture and temperature (Bailey et al. 1980). Racz and Soper (1967) found that the majority of the initial reaction products formed rapidly, primarily in the first 4 to 8 weeks. Over a period of months to years, dicalcium phosphate dihydrate (DCPD) is slowly converted to octacalcium phosphate, (OCP) and eventually to hydroxyapatite (HA) (Soper and Racz 1980). The DCPD remains relatively plant available, or labile, over the duration of a cropping season. However, as DCPD is converted to OCP and HA, the P is increasingly unavailable, or non-labile (Strong and Racz 1970).

2.1.3.2 Phosphate Fertilizer Adsorption Reactions In adsorption reactions, P is bonded to the surface of soil colloids, with the cations attached to clay particles and the surfaces of calcium carbonates or iron and aluminum hydroxides (Larsen 1967; Soper and Racz 1980). Phosphate adsorption reactions occur less frequently than precipitation reactions in P fertilized calcareous soils. Sample et al. (1980) reported that adsorption

accounted for 20% of P retention near the granule. However, as the fertilizer P became more dilute with increased distance from the granule, adsorption accounted for 84% of P retention. Thus, the combination of precipitation and diffusion outward from the fertilizer reaction zone decreases the P concentration, to a point where adsorption reactions dominate near the periphery of the P fertilizer reaction zone.

Adsorption reactions in acidic soils are dominated by Al and Fe hydroxides, though these cations are less important in neutral to alkaline soils (Barber 1984). Soper and Racz (1980) determined that the rate of adsorption in acid soils was directly related to P concentration and temperature, and inversely related to pH.

Adsorption reactions in calcareous soils are dominated by Ca and Mg carbonates, but adsorption to Fe compounds may also occur (Bhadoria et al. 2002). Racz and Soper (1967) demonstrated that the P adsorption to Ca carbonates occurred in significant amounts in Manitoba soils but was dependent on the proportion of Ca and Mg carbonates present in the soil.

Adsorbed P may undergo desorption reactions, releasing P into soil solution. In general, P is less strongly sorbed to Ca carbonates than other oxides or hydroxides and is relatively easy to desorb (Soper and Racz 1980). Depending on the strength of the surface bonding, P adsorbed to Al and Fe may have limited desorption in acidic soil (Soper and Racz 1980).

In practice, it is difficult to differentiate between precipitation and adsorption reactions. Both reactions occur simultaneously and the reaction products are difficult to distinguish (Sample et al. 1980). In western Canada, precipitation reactions probably are the dominant reaction for fertilizer P in most soils; however, adsorption reactions may also be significant.

2.1.3.3 Phosphate Fertilizer Immobilization Microbial absorption of inorganic nutrients such as P is known as immobilization. Phosphorus requirements for microbial growth and reproduction are low compared to other nutrients. For example, immobilization occurs only with relatively high carbon (C) to P ratios (>300:1) compared to C to N ratios (30:1). Therefore, immobilization of fertilizer P is relatively minor compared to precipitation and adsorption reactions (Sheppard and Racz 1980).

2.1.4 Residual Phosphate Fertilizer

Repeated additions of P fertilizers in excess of crop removal may result in an accumulation of fertilizer P residues over time. Even if applications are equal to crop removal, retention reactions and the limited degree of root exploration may mean that a portion of the fertilizer P will remain in the soil. McKenzie and Roberts (1990) and Doyle and Cowell (1993a) indicated that up to 75% of P fertilizer may not be used by the initial crop and may remain in a form that is moderately available to subsequent crops. Therefore on occasion, farmers may not apply P fertilizers and rely solely on residual P for a single crop year.

As previously stated, the initial P adsorption and precipitation reaction products remain relatively labile during the first several months following application. This characteristic is important for continued P supply to the current crop as well as subsequent crops. As P is removed from solution by plants, solid labile P compounds are rapidly solubilized to replenish solution P. The depletion of solid phase labile P causes a shift in equilibrium with non-labile P. The non-labile P solubilizes into labile P; however, this reaction is relatively slow in comparison to the dissociation of labile P (Barrow 1980;

McKenzie and Roberts 1990). For example, octacalcium phosphate (non-labile) may dissociate to form soluble P which is then adsorbed to soil colloids (labile P) (Havlin et al. 1999).

Much of the research conducted on residual P availability to crops used very large applications of fertilizer P (Halvorson and Black 1985; Read et al. 1977; Spratt and Read 1980). In these studies, residual effects of P on crop uptake and yield were observed up to 5 to 10 years after the initial application. Annual application of moderate amounts of P fertilizer may also provide residual release of P when fertilizer application is discontinued (Selles 1993; Wagar et al. 1986). For example, Spratt and McCurdy (1966) and Spratt and McIver (1978) reported that annual applications of 15 kg P ha⁻¹ as MAP, or more, significantly increased solution P for subsequent crops, even after P fertilization was terminated. The amount of residual P left for successive crops may decrease depending on the type of crop grown and the degree to which retention reactions occur (Doyle and Cowell 1993a).

2.2 Sulphur Behavior in Plants and Soils

In the early 1970s, researchers assumed that sulphur (S) deficiency was limited to well drained, coarse textured and Luvisolic soils. However, in subsequent years, increased soil testing for S revealed that considerably more land in Manitoba was S deficient than previously thought (Beaton and Soper 1986).

2.2.1 Uptake and Function of Sulphur in the Plant

Most S in plants is required for synthesis of: amino acids such as cysteine and methionine; vitamins such as thiamine and biotin; coenzyme A, essential for respiration and the synthesis and breakdown of fatty acids; and structural components such as sulpholipids (Salisbury and Ross 1991). Sulphur may also be used to synthesize defense mechanisms against pests and can contribute to the taste characteristics of the tissue and seed, such as glucosinolates in canola and mustard (Bennett and Wallsgrove 1994; Duke and Reisenauer 1986; Zhao et al. 1997).

Plants absorb S primarily as sulphate (SO_4^{2-}) from soil solution. Unlike P movement, mass flow is of major importance in SO_4^{2-} transport; therefore, a much larger volume of soil can supply SO_4^{2-} to the crop. Once at the root surface, SO_4^{2-} is actively transported into the roots, reduced and incorporated into amino acids (Grossman and Takahashi 2001), unlike phosphate which remains oxidized after uptake. In soils with low to moderate SO_4^{2-} supply, replenishment of solution SO_4^{2-} is similar to that of P. As SO_4^{2-} is absorbed by plants, solid phase SO_4^{2-} dissolves or is desorbed into solution to re-establish solid-solution phase equilibrium (Bohn et al. 1986).

Canola requires adequate levels of SO_4^{2-} relatively early in crop development. Nuttall and Ukrainetz (1991) reported that canola yields decreased significantly when application of SO_4^{2-} was delayed until 14, 18 and 42 days after seeding in Saskatchewan. In the same study, canola varieties also differed in the critical development stage at which SO_4^{2-} was required.

Agronomically, S fertilization can improve crop growth, increase flowering, increase seed yield and improve crop quality. Early season growth and flower initiation are improved by sufficient S nutrition, while insufficient S nutrition just prior to or during

flowering may result in indeterminate flowering (Duke and Reisenauer 1986), pod abortion, decreased seed set and yield (Doyle and Cowell 1993b; Zhao et al. 1997).

Beaton and Soper (1986) reviewed fertilizer S responses of crops in western Canada. They reported wheat yield increased up to 345% when S fertilizer was applied to deficient soils, though in S-sufficient soils no yield response was observed. The yield response of canola to fertilizer S is generally larger and more consistent than that of wheat (Ridley 1972).

Sulphur fertilization in itself may not increase yield. The nitrogen (N) and S interaction is important, as S assimilation is directly linked to N availability (Janzen and Bettany 1981). Therefore, canola yields are optimized by a proper N to S ratio in the plant (Grant 1991). Janzen and Bettany (1984b) determined that the optimum N to S ratio was approximately 7; values greater or less than this resulted in inefficient use of nutrients or decreased yield. Thus, S fertilization is a strategy to balance nutrients supplied to the crop.

Sulphur fertilization may also alter seed quality characteristics for processing. Addition of S fertilizer may increase oil yield, protein and glucosinolate content of canola seed. For example Zhao et al. (1997) determined that S fertilization in wheat improved bread making qualities such as loaf volume, and increased glucosinolate concentrations in canola oil.

2.2.2 Reactions of Sulphate Fertilizer in Soils

Sulphate fertilizers, such as ammonium sulphate (AS), dissolve readily in soil solution. Solution sulphate has several possible fates in the soil including immediate

uptake by plant roots, adsorption onto soil constituents, precipitation, and leaching out of the rooting zone.

2.2.2.1 Sulphate Fertilizer Adsorption Reactions Many soils have at least some capacity to adsorb fertilizer SO_4^{2-} (Harward and Reisenauer 1966). In general, adsorption reactions are most significant at soil pH 4.0 to 6.0 (Barrow 1970; Scott 1976). Sulphate is predominantly adsorbed to Al oxides, though adsorption to Fe oxides and to edges and surfaces of clay particles occurs as well (Barber 1984; Bohn et al. 1986). Sulphate adsorption reactions occur slowly in most soils (Barrow 1967); however, over time the strength of retention increases and desorption is less likely to occur (Sanders and Tinker 1975). In acidic soils, adsorption reactions may account for a significant reduction in plant available sulphate, while in calcareous soils other retention mechanisms are more important. In Manitoba's typically neutral to alkaline soils, SO_4^{2-} adsorption plays a minor role in retaining S (Anderson 1966).

2.2.2.2 Sulphate Fertilizer Coprecipitation and Precipitation Reactions

Coprecipitation of sulphate with calcium carbonate (CaCO_3), forming $\text{CaCO}_3\text{-CaSO}_4$, is an important fraction of S within calcareous soils (Williams and Steinbergs 1962; Williams et al. 1960). The rate of coprecipitation reactions increase as the soil becomes more alkaline, as the specific surface area of the CaCO_3 particles increases and as soil moisture decreases (Havlin et al. 1999).

In addition to coprecipitation reactions, SO_4^{2-} may also form ion pairs with Ca^{2+} , Mg^{2+} or Na^+ in soil solution and at sufficient concentrations, form precipitates. Of these,

only gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is of sufficiently low solubility that precipitates normally form (Barber 1984).

2.2.2.3 Sulphate Fertilizer Leaching Leaching is potentially the largest single cause of SO_4^{2-} depletion in well drained soils (Tisdale et al. 1986). Soils with low adsorption, low coprecipitation, low precipitation capacity and sufficient precipitation for downward movement of water are prone to SO_4^{2-} leaching. For example, lysimeter studies in Illinois and Wisconsin measured up to $64 \text{ kg SO}_4^{2-} \text{ ha}^{-1}$ leached annually in fallow fields (Stauffer and Rust 1954). In addition, high concentrations of anions, such as phosphate ions, in solution can displace adsorbed SO_4^{2-} , which is then free to leach (Barrow 1975). Rainfall in western Canada is generally lower than in the Midwest; however, leaching may be a concern on some Western Canadian soils, especially in lower landscape positions and coarse textured soils in Parkland regions.

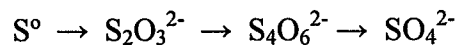
2.2.3 Reactions of Elemental Sulphur Fertilizer in Soils

Elemental sulphur (S^0) fertilizer, for example 90% S^0 and 10% bentonite, is an alternative S fertilizer source in western Canada. However, the S^0 must undergo biological oxidation to SO_4^{2-} before it is plant available.

2.2.3.1 Dissolution of S^0 -Bentonite Fertilizer When bentonite-containing S^0 fertilizer is applied to the soil, the bentonite portion of the granule attracts and absorbs water causing the granule to disintegrate. Disintegration of the granule produces finely divided particles which are then oxidized to SO_4^{2-} (Havlin et al. 1999). Generally, S^0 -bentonite has limited crop availability in the year of application due to slow oxidation to SO_4^{2-} . The

mechanisms of oxidation and factors affecting oxidation rates will be discussed in the following sections.

2.2.3.2 Oxidation of S⁰ in Soil Soil microorganisms are responsible for the majority of SO₄²⁻ oxidation; however, a limited amount of abiotic S⁰ oxidation also occurs in the soil. Biological oxidation occurs in the following sequence of reactions:



Elemental sulphur is a reduced form, while SO₄²⁻ is the most oxidized form. Sulphur oxidation is exclusively a surface process, limited to those atoms that are directly exposed to microorganisms. Oxidation is initiated when bacteria and fungi colonize the surface of the S⁰ particle and enzymatic degradation begins (Germida and Janzen 1993). In general, S⁰ oxidation is relatively slow and the rate of oxidation is dependent on numerous environmental and soil factors.

Chemoautotrophic and heterotrophic bacteria and fungi are the most important S⁰ oxidizing groups and are ubiquitous in most soils (Germida and Janzen 1993).

Chemoautotrophic bacteria such as *Thiobacillus* are capable of complete and relatively rapid oxidation of S⁰ to SO₄²⁻ which is in contrast to most heterotrophic oxidizers (Germida and Janzen 1993; Lawrence and Germida 1991b).

Populations of *Thiobacillus* may increase quickly with the addition of S⁰. For example, populations increased from 10 to 10⁸ in only ten weeks in a New Zealand study (Lee et al. 1987). Therefore, SO₄²⁻ production may start slowly and increase exponentially over a period of weeks to months.

Historically, *Thiobacillus* have been assumed to be the predominant S⁰ oxidizers; however, studies in the last 15 years indicate that heterotrophic microorganisms appear to

dominate in agricultural soils in Saskatchewan and the U.S. (Germida and Janzen 1993; Lawrence and Germida 1988; Lindemann et al. 1991). Lawrence and Germida (1991a) also determined that populations of S⁰ oxidizing microorganisms were ubiquitous in Saskatchewan agricultural soils and non-limiting to S⁰ oxidation, and the lack of suitable oxidizers did not explain the slow release of sulphate from S⁰ fertilizers.

These heterotrophic organisms may be able to oxidize S⁰ completely, though it is more likely that one group of microorganisms will produce an intermediate S compound, while one or more groups will oxidize the intermediate S compound to SO₄²⁻ (Germida and Janzen 1993). Two or more microbial populations acting together in this manner, incidental or not, is known as a consortium and is likely to be the dominant process of S⁰ oxidation in the prairie provinces.

2.2.3.3 Factors Influencing S⁰ Fertilizer Oxidation Numerous studies have correlated various biological, physical, chemical and environmental factors to S⁰ oxidation rates (Janzen and Bettany 1987; McCaskill and Blair 1987; Wainwright 1978).

Influence of Plants Plants may excrete considerable quantities of organic carbon into the rhizosphere providing heterotrophic microorganisms organic C for respiration.

Therefore, it is conceivable that different plant species could affect heterotrophic S⁰ oxidation near the root. Grayston and Germida (1990) found that S⁰ oxidizing heterotrophic populations were 10 to 32% and 8 to 19% higher in the rhizosphere as compared to the bulk soil for wheat and canola respectively. This indicates that S⁰ oxidation may be higher near the root compared to the bulk soil and that greater populations existed in wheat than canola rhizospheres. However, Janzen (1990) reported

that S° oxidation rates in the rhizosphere did not vary significantly between barley and canola.

Influence of Fertilizer Properties Several important physical and chemical properties of S° fertilizers influence oxidation rates. Factors that increase soil-S° fertilizer contact, such as decreased particle size and improved dispersion upon wetting, increased contact between microorganisms and increased oxidation rates (Germida and Janzen 1993; Janzen and Bettany 1986; McCaskill and Blair 1987).

Previous application of S° fertilizer to the soil increases potential oxidation rates. This may be due to a preferential selection for S oxidizing heterotrophic and chemoautotrophic microbes which can populate the soil quickly when S° fertilizer is subsequently added to the soil (Doyle and Cowell 1993b).

Influence of Soil and Environmental Factors

Temperature Temperature has a significant influence on oxidation rates. Below 5° C oxidation is minimal, while optimum oxidation rates occur at 30 to 40°C in prairie soils (Germida and Janzen 1993). Therefore, placement of S° fertilizer in a band below the soil surface will limit heat available for oxidation, while placement at or near the surface will provide more favorable temperatures for oxidation.

Water and Aeration The proper balance between adequate soil moisture and aeration is critical in agricultural soils. Moisture must be sufficient for microbial activity, but must not interfere with the oxygen requirement for microbial respiration. Maximum S° oxidation occurs near field capacity and then decreases rapidly with either higher or lower water potentials (Figure 2.1).

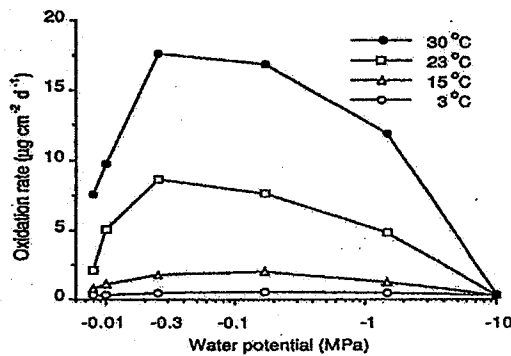


Figure 2.1 S° oxidation rate as influenced by water potential and temperature (Germida and Janzen 1993).

Soil Texture and pH The effect of soil texture on S° oxidation rates may be related to soil moisture and aeration. Soil textures, such as loamy soils, that promote high total porosity, good aeration and water holding capacity favour S° oxidation (Germida and Janzen 1993). However, the effect of soil texture as a single, direct factor is probably not important (McCaskill and Blair 1987).

Alkaline soils are more favorable for S° oxidation than acidic soils. Nor and Tabatabai (1977) reported that S° oxidation rates were on average 17% higher in alkaline soils with pH 6.6-8.0 than acidic soils with pH 5.4-6.4. The positive correlation between pH and oxidation may be related to the ability of high pH soils to buffer against acidification, which can inhibit oxidation (Germida and Janzen 1993).

Loss Mechanisms Elemental sulphur is not prone to retention losses; however, once oxidized to sulphate, the sulphate ion is subject to the same retention or leaching loss mechanisms as sulphate fertilizers. Janzen and Bettany (1986) have suggested that due to slow oxidation of S°, less SO₄²⁻ will accumulate in the soil from S° than from AS decreasing the potential for substantial leaching losses during a single event. Therefore,

applying S^o fertilizer in soils with high leaching potential may improve S nutrition to a crop.

2.3 Fertilizer Use Efficiency

Increasing fertilizer costs and concerns of surface and ground water contamination associated with fertilizer use require that P and S fertilizers be applied in an efficient manner. Fertilizer use efficiency is influenced by crop type, fertilizer source, placement, timing and environmental conditions.

2.3.1 Crop Type

Nutrients such as P and S are not homogeneously distributed in agricultural soils. When fertilizer is banded or seed-placed, the localized concentration of nutrients is confined to a small volume of soil. Crops vary in their ability to exploit these nutrient rich zones, especially for non-mobile nutrients such as P (Robinson 1996). For example, fertilizer P use efficiency of wheat is approximately 20% (Doyle and Cowell 1993a; Holford and Doyle 1993; Spinks and Barber 1948), while canola may have fertilizer P use efficiency as high as 65% in growth chamber studies (Hammond 1997). Fertilizer use efficiency also varies between different cultivars of wheat and barley (Gahoonia et al. 1997; Gahoonia et al. 1999; Yao and Christie 2001). Differences in S efficiency between hybrid and open-pollinated canola cultivars have also been observed (Karamanos et al. 2002).

The efficiency of P fertilizers, and to a lesser degree S fertilizers, may be improved by plant plasticity mechanisms such as: root growth rate and architecture

(Pregitzer et al. 1993); nutrient uptake kinetics (Jackson et al. 1990); exudation (Jungk and Claasen 1989); mycorrhizal association (Yao and Christie 2001); and root hair density (Meisner and Karnok 1991). An example of modifying root architecture to increase P uptake is root proliferation. Most plants have at least some ability for root proliferation, effectively increasing root surface area and absorption potential in nutrient rich pockets in the soil (Jackson and Caldwell 1996; Robinson 1994). Soper and Strong (1974a) found that canola had much greater root proliferation in P fertilizer reaction zones than wheat. The importance of root proliferation for SO_4^{2-} uptake was not found in literature; however, if SO_4^{2-} uptake is similar to nitrate, root proliferation may not be an important mechanism of SO_4^{2-} uptake from fertilizer bands (Robinson 1996; Robinson 1994).

Plants may also respond to nutrient rich zones in the soil by increasing the number of nutrient ion transporters on the root surface, increasing the rate of nutrient uptake. Jackson and Caldwell (1996) reported that increases in nutrient uptake kinetics are important in N and P uptake. No information was found with regards to increased uptake kinetics in response to SO_4^{2-} .

Low molecular weight organic acids excreted by plant roots can decrease rhizosphere pH and increase the solubility and uptake of P. Researchers found that canola root exudates decreased the pH of the rhizosphere by 0.8 to 2.4 units and in contrast, wheat exudates decreased the pH by only 0.4 units (Grinsted et al. 1982; McKenzie et al. 1995). McKenzie et al. (1995) suggested that exudate acidification of the rhizosphere was important for P uptake by canola but not by wheat.

Root hairs also increase the nutrient absorbing surface area of roots and thus, increase the nutrient uptake efficiency of a crop (Barber 1984). Gahoonia et al. (1999)

found that increased root hair length and density increased fertilizer P uptake in cereal crops. However, when the rate of P fertilizer was increased to 20 kg P ha⁻¹, the importance of root hairs for P uptake and efficiency was decreased.

The hyphae of arbuscular mycorrhizal fungi increase the effective surface area and nutrient absorbing capacity of roots (Harrison 1999). Crops vary in their ability to form mycorrhizae associations. For example, wheat may form mycorrhizal associations while canola does not (Harris et al. 2002; Yao and Christie 2001). The majority of mycorrhizae nutrient uptake research has focused on immobile nutrients like P. While arbuscular mycorrhizae increase P uptake in P deficient soils, P fertilization appears to decrease mycorrhizae association in flax, red clover and barley (Kahiluoto et al. 2001; Khaliq and Sanders 1997). Arbuscular mycorrhizae have also been implicated in improved S uptake at low soil-S concentrations (Banerjee et al. 1999; Cooper and Tinker 1978; Rhodes and Gerdemann 1978), while others indicated that mycorrhizae had no effect on S uptake (Harley and Smith 1983; Morrison 1962). In general, root hairs and arbuscular mycorrhizae associations contribute more to nutrient use efficiency in nutrient deficient soils than in fertilized soils.

2.3.2 Fertilizer Source

Research by Mitchell (1946) and Dion et al. (1949) demonstrated that MAP was a superior source of fertilizer P in calcareous western Canadian soils compared to calcium phosphate fertilizers, such as triple superphosphate. The fertilizer P use efficiency of MAP is approximately 20% to 50% for wheat and canola respectively (Soper and Kalra 1969). However, as soil P concentrations and fertilizer P applications increase, the fertilizer use efficiency of MAP declines significantly (Dion et al. 1949).

Cargill's homogeneous NPS fertilizer contains 33% P_2O_5 , hence is more dilute than MAP, which contains 52% P_2O_5 . Therefore, 58% more NPS fertilizer is required for the equivalent rate of P as MAP. More NPS granules may increase the probability of root exploitation of the fertilizer band and P uptake. Sander and Eghball (1988) determined that P uptake increased as fertilizer particle size decreased and number of fertilizer particles increased. The difference in P uptake was attributed to increased root interception due to the greater number of fertilizer particles. However, the effect of increased P distribution was not significant at fertilizer rates exceeding 25 kg P ha⁻¹.

Ammonium sulphate fertilizers are readily available sources of SO_4^{2-} and have high fertilizer use efficiencies, relative to other S sources (Grant et al. 2000; Karamanos et al. 1987; Nuttall et al. 1990). In growth chamber studies, Noellemeyer et al. (1981) measured 63% ammonium sulphate fertilizer use efficiency by rapeseed. However, in the field, Karamanos et al. (1987) measured fertilizer use efficiencies of < 50%.

The fertilizer use efficiency of S^o or S^o-bentonite fertilizers is generally much lower than AS fertilizer (Grant et al. 2003b; Karamanos et al. 1987; Noellemeyer et al. 1981). Karamanos and Janzen (1991) found that the S^o-bentonite fertilizer had only 10% fertilizer use efficiency in the year of application in field studies in Alberta. However, Nuttall et al. (1990) found that S^o provided equivalent SO_4 -S to a crop as ammonium sulphate in a field study. The results were mostly likely attributed to the fine particle size used in the latter study.

2.3.3 Fertilizer Placement

There are several methods of applying fertilizer to the soil; however, only subsurface banding and broadcasting will be explored in this review. Banding, including

seed placement, side banding and deep banding, places high concentrations of fertilizer in a restricted soil volume. Broadcasting distributes fertilizer on the soil surface which may be incorporated into the soil. In the latter method, fertilizer-soil contact is maximized (Bailey et al. 1980). The appropriate method of placement depends on the fertilizer source, soil and crop characteristics, as well as agronomic management preferences.

Since P is relatively immobile, placement near roots increases fertilizer P use efficiency, particularly for early crop establishment when roots development is minimal (Bailey et al. 1980). Therefore, banding fertilizer P with or near the seed is more effective than broadcast applications on the Canadian prairies (Bailey and Grant 1990; Bailey et al. 1980; Nyborg and Hennig 1969). The improved fertilizer P use efficiency of banded P fertilizer is due to two factors: 1) reduced soil precipitation and adsorption due to decreased surface area exposed to the soil (Bailey et al. 1980; Soper and Kalra 1969); and, 2) increased root exploitation due to the close proximity of fertilizer to roots (Eghball and Sander 1987; Sleight et al. 1984). For example, fertilizer P use efficiency for banding may be 20%, but only 5% to 10% for broadcasting (Doyle and Cowell 1993a; Peterson et al. 1981). This requires two to four times the amount of broadcast fertilizer P relative to banding. However, Peterson et al. (1981) also reported that banding and broadcasting had similar use efficiencies for winter wheat when Bray soil test P levels exceeded 20 ppm, a very high concentration.

Banding P near or with the seed is most beneficial under cool soil conditions and can cause improved seedling growth and vigor, known as "pop-up effect" (Engelstad and Terman 1980; Zentner et al. 1993). Under these conditions, fertilizer P compensates for the low availability of soil P, low P mineralization rates and limited root growth (Sheppard and Racz 1980; Sutton 1969). The efficiency of P banded, with or near the

seed, decreases as soil temperature increases due to improved soil P availability and increased fertilizer toxicity (Sheppard and Racz 1985). For example, placement of MAP at high rates with or near the seed increases the risk of fertilizer toxicity particularly for crops like canola (Bailey and Grant 1990; Grant et al. 2003b; Nyborg and Hennig 1969; Tisdale et al. 1993).

Placement of AS in close proximity to MAP has increased P availability and uptake in several studies. Beever (1987) observed a 12% and 16% increase in fertilizer P uptake by wheat and canola respectively when MAP and AS were dual banded as compared to MAP alone. Beever also found that the effect of AS on P solubility was greater in neutral soils than in acidic soils. Hammond (1997) reported that the relative increase in P uptake in dual bands of AS and MAP compared to separate bands of each fertilizer was greater for wheat when the band width was increased to 15 cm from 2.5 cm. Hammond also demonstrated that placement of AS in intimate contact with MAP increased fertilizer P uptake as compared to a random placement of the two fertilizers. In field studies by Goos and Johnson (2001), dual banding MAP with liquid ammonium polyphosphate fertilizer improved P uptake by wheat; however, no response in yield was detected. The mechanisms responsible for increased fertilizer P use efficiency will be addressed in Section 2.3.6.

Sulphate is a moderately mobile ion; therefore, the method of placement of AS, as compared to MAP, generally has less affect on fertilizer use efficiency. Broadcasting and banding with or near the seed are both suitable placement methods (Grant et al. 2000). However, broadcast placement is not desirable in dry soil, because a lack of downward water movement may cause the SO_4^{2-} to remain at the soil surface, unavailable for plant uptake (Grant et al. 2000; Nuttall et al. 1990). Band placement may have advantages, as

Hammond (1997) demonstrated that AS may increase root uptake of other nutrients. As well, SO_4^{2-} is more accessible to plant roots as compared to broadcasting, under dry soil conditions. However, seed-placed banding is not suitable when applying high rates of AS, due to the risk of salt or ammonia toxicity, resulting in crop injury and decreased fertilizer use efficiency (Grant et al. 2003b).

Elemental S^0 fertilizer use efficiency is determined by the rate at which it is oxidized to SO_4^{2-} . In addition to particle size, method of placement is one of the most important factors determining the rate of oxidation. Band and seed-row placement of S^0 and S^0 -bentonite fertilizers provide insufficient SO_4^{2-} for optimum crop growth and yield in wheat, canola, rice and maize (Chien et al. 1988; Grant et al. 2003b; Grant et al. 2000; Solberg et al. 1986). Banding minimizes contact between fertilizer particles and microorganisms, thus limiting oxidation to SO_4^{2-} (Germida and Janzen 1993; Solberg et al. 1986). Therefore, to maximize fertilizer-microbial contact, broadcasting followed by soil incorporation is required (Hagstrom 1986; Nuttall et al. 1990). Solberg et al. (1986) found that broadcast applications provided more SO_4^{2-} to the barley crops than banding in both field and incubation studies. However, the difference attributed to method of placement was significant only after the first year of application.

If S^0 fertilizers are applied in a concentrated band, high concentrations of intermediate S oxidation products may accumulate and inhibit complete S^0 oxidation. A portion of the toxicity is related to H^+ release during oxidation, which often decreases S^0 oxidation (Germida and Janzen 1993).

Incorporation of broadcasted fertilizer increases the dispersion and the surface area contact of the fertilizer with the soil. Solberg et al. (1986) and Janzen (1990) reported that two or more tillage passes after broadcasting increased S^0 oxidation and

SO_4^{2-} available for crop uptake. Multiple tillage operations would also increase dispersion of fertilizer banded at planting, but this benefit would only be realized after the cropping season, when the land is tilled for the following crop.

2.3.4 Time of application

Increasing farm size and fertilizer inputs demand that farmers work efficiently within a short growing season. This has led to an increase in fall banding of fertilizer rather than a spring application. However, fertilizers differ in efficiency between spring and fall application.

Fertilizer use efficiency of MAP is generally highest when applied just prior to or at seeding (Harapiak 1980). In the calcareous soils of western Canada, fall application increases the duration of fertilizer P exposure to precipitation and adsorption reactions (Tisdale et al. 1993), decreasing availability to the spring-seeded crop. However, in soils with low P fixing capacity fall and spring applications have approximately equal efficiency and therefore, fall application may be a suitable practice (Hanway and Olson 1980).

The fertilizer use efficiency of AS fertilizer is often highest when applied at or near the time of planting but the timing is less sensitive than for MAP or S^0 fertilizers. In general, SO_4^{2-} volatilization and immobilization losses are not important factors. Nevertheless, significant amounts of SO_4^{2-} may be leached below the rooting zone when applied far in advance of seeding (Hagstrom 1986), decreasing fertilizer use efficiency. Nuttall and Ukrainetz (1991) also reported that spring application resulted in better fertilizer use efficiency than fall application. However, Grant et al. (2003b) found that

broadcasting AS fertilizer in fall and in spring resulted in similar S uptake in canola at two sites; however, fall application was inferior at a third site.

The time of S⁰ fertilizer application is nearly as important as the method of placement used. The short growing season in western Canada not only limits crop production, but microbial oxidation of S⁰ as well. Field studies often indicated that spring applications resulted in minimal S⁰ oxidation for that cropping year (Janzen and Bettany 1986; Karamanos and Janzen 1991; Karamanos et al. 1987; Noellemeyer et al. 1981). Therefore, Hagstrom (1986) suggested that application of S⁰ should occur as far in advance of seeding as possible to encourage oxidation. Similarly, the MB Agriculture Soil Fertility Guide (2001) recommends broadcasting S⁰ fertilizer at least one year prior to the intended crop. The benefit of applying S⁰ well in advance of seeding is also demonstrated by residual S studies. In western Canadian, S⁰ was effective in supplying SO₄²⁻ to the wheat, barley and canola crops two or three years after initial application (Grant et al. 2003b; Grant et al. 2000; Malhi and Johnston 2000). In addition, Grant et al. (2000) noted that minimal oxidation had occurred in the banded S⁰ treatments even after three years. In contrast, Nuttall et al. (1987) reported that spring broadcast S⁰ supplied equal or superior quantities of SO₄²⁻ to canola in field trials in the year of application.

2.3.5 Effect of Environmental Conditions

As alluded to in previous sections, environmental conditions can modify the factors influencing fertilizer use efficiency. For example, increasing soil temperatures often decrease fertilizer P use efficiency (Sheppard and Racz 1985). Rising soil temperatures increase desorption of soil P and increases P concentration in soil solution

(Barrow 1979). Therefore, a greater proportion of soil P may be absorbed by plants, reducing its reliance on fertilizer P and reducing fertilizer P use efficiency.

Root growth and proliferation is greater at higher soil temperatures, increasing soil exploration and contact with P throughout the soil (Sheppard and Racz 1980). Diffusion rates are also dependent on temperature. Nutrient ions diffuse rapidly outward at higher temperatures, increasing the volume of the fertilizer reaction zone. This may increase retention reactions in the soil; however, it may also increase contact with plant roots and stimulate uptake. While fertilizer P use efficiency generally decreases with increasing temperature, the opposite is true for S⁰ fertilizers. The rate of microbial oxidation is dependent on soil temperature, as temperature increases the rate of S⁰ oxidation to SO₄²⁻ increases (Germida and Janzen 1993).

As soil moisture approaches field capacity, diffusion of nutrients increases (Sheppard and Racz 1980), and biological processes, such as microbial S⁰ oxidation, are optimized. Plant uptake of nutrients is also proportional to available soil moisture; as the soil dries, nutrient uptake declines (Boatwright et al. 1964; Clarke et al. 1990). In general, lower soil moisture content decreases fertilizer use efficiency and factors such as appropriate nutrient placement become critical.

2.3.6 Nitrogen Fertilizer Effects on Fertilizer P Utilization

The beneficial effects of combining N and P fertilizers on P fertilizer use efficiency are well established (Dion et al. 1949; Mitchell 1946; Rennie and Soper 1958). Both nitrate and ammonium ions can increase fertilizer P use efficiency (Rennie and Soper 1958). However, the combination of ammonium and P fertilizer is noticeably superior in younger crops and in calcareous soils (Hammond 1997; Olson and Dreier

1956a). The “ammonium ion effect” is attributed to chemical and biological mechanisms, which enhance P uptake (Hammond 1997). Chemical mechanisms include increased size of the fertilizer reaction zone and improved P solubility, while biological mechanisms include root proliferation, increased root-fertilizer contact, cation-anion balance, and ion uptake processes (Beever 1987).

2.3.6.1 Chemical Mechanisms Changes in fertilizer reaction zone pH and ionic strength are the two primary chemical mechanisms by which ammoniacal-N alters plant absorption of fertilizer P (Flaten 1989).

Several ammonium-containing fertilizers, like MAP, AS and AN, dissociate into acidic compounds in the soil (Rader et al. 1943). This decrease in pH associated with N fertilizers may partially explain the increased P solubility and uptake in calcareous soils. For example, the combination of AS fertilizer and superphosphate increased P uptake, but when lime was added to the fertilizer, the beneficial effect of the AS was reduced (Volk 1944). Volk (1944) concluded that the benefit of AS was due to a reduction in fertilizer reaction zone pH. In addition to increased P solubility, pH reduction may allow the P to persist in a soluble form for longer and allow for increased P uptake (Hanson and Westfall 1985).

Rennie and Mitchell (1954) attributed increased P uptake not only to the acidic properties of AN fertilizer, but also to the nitrification of ammonium. Nitrification of ammonium to nitrate releases two protons for each ammonium ion oxidized, acidifying the soil. However, Rennie and Soper (1958) showed that acidification of the P fertilizer reaction zone actually decreased P uptake, disproving nitrification as the mechanism responsible. Researchers hypothesized that acidification of the soil increased calcium

solubility, favoring the formation of calcium-phosphate precipitates which decreased fertilizer P efficiency (Grunes et al. 1958; Olson and Dreier 1956b).

Additional research using nitrification inhibitors confirmed that nitrification is of minimal importance in the ammonium ion effect and increased P uptake. Nitrification inhibitors preserved the N in the ammoniacal-N form, increasing P uptake relative to the treatments where nitrification occurred (Engelstad and Allen 1971; Miller et al. 1970; Nielsen et al. 1967).

In soil with $\text{pH} > 7.2$, HPO_4^{2-} is the dominant form of P, while a reduction in pH causes a greater proportion of the P to exist as H_2PO_4^- . Plant uptake of H_2PO_4^- is greater and more rapid than uptake of HPO_4^{2-} ; therefore, a reduction in fertilizer reaction zone pH may increase P uptake (Havlin et al. 1999; Riley and Barber 1971).

However, reductions in pH within the fertilizer reaction zone only partially account for ammonium ion effect on P uptake. Additions of ammonium salts also increase the ionic strength of the soil solution, and affect exchange reactions in the fertilizer reaction zone. Grunes (1959) found that increases in ionic strength improved the solubility of slightly soluble fertilizer salts. The increase in ionic strength decreased the activity coefficient and increased fertilizer salt solubility. However, Grunes (1959) also noted that at high fertilizer concentrations, activity coefficients eventually increased and P solubility decreased.

Fertilizer bands containing high concentrations of ammonium may also increase the desorption of soil cations, a phenomenon described as the "snow plow effect" (Barry et al. 1983). As the saturated ammonium fertilizer solution moves through the soil, it causes Ca^{2+} to be desorbed from the cation exchange sites. The desorbed Ca^{2+} is pushed ahead of the saturated ammonium fertilizer solution for relatively short distances (Starr

and Parlange 1979). If the increased Ca^{2+} in soil solution is allowed to react with fertilizer P, Ca-P precipitation reactions may increase (Isensee and Walsh 1971). However, it should also be noted that if the desorbed Ca^{2+} is not allowed to move back to the fertilizer application site, exchangeable Ca^{2+} concentrations in the P fertilizer reaction zone may be decreased sharply. For example, Cho (1985) noted that in soils with high cation exchange capacity (CEC) and high concentration of displacing ions, a large portion of the displaced ions would be removed from the affected area.

2.3.6.2 Biological Mechanisms Rennie and Soper (1958) have suggested that the ammonium ion effect may influence biological factors more than chemical mechanisms. Ammoniacal-N fertilizers appear to stimulate both morphological and/or physiological changes in plants that may increase P uptake or P use efficiency.

As mentioned earlier, morphological changes such as root proliferation may increase P utilization by increasing surface contact with the fertilizer band. Researchers have demonstrated that root growth and proliferation may be stimulated by ammonium, nitrate and phosphate ions (Drew 1975; Drew and Saker 1978; Duncan and Ohlrogge 1958). In the fertilizer reaction zone, root proliferation and growth tend to be greatest when ammoniacal-N and P fertilizers were mixed in the same band (Duncan and Ohlrogge 1959; Duncan and Ohlrogge 1958; Miller and Ohlrogge 1958). Plants may respond to localized N and P rich areas by producing more lateral roots or increasing the length of existing lateral roots (Drew and Saker 1978). However, other research does not fully support the root proliferation hypothesis. For example, addition of KNO_3 or KCl increased root proliferation with no increase in P utilization (Blanchar and Caldwell 1966;

Duncan and Ohlrogge 1958). The ammonium ion effect has been observed in the absence of root proliferation as well (Miller 1965; Miller and Vij 1962; Riley and Barber 1971).

Nitrogen fertilizers may also affect P utilization by altering the cation/anion balance within the plant. A plant must maintain electroneutrality while absorbing ions from the soil. Therefore, if anion (NO_3^-) uptake exceeds cation uptake, the plant must excrete OH^- or HCO_3^- into the rhizosphere, increasing rhizosphere pH (Riley and Barber 1969). Likewise, if cation (NH_4^+) uptake exceeds anion uptake, the plant must excrete H^+ , decreasing rhizosphere pH (Miller et al. 1970). The biological acidification of the rhizosphere may increase the solubility of P and the proportion of orthophosphate present as $\text{H}_2\text{PO}_4^{2-}$. Riley and Barber (1971) found that the pH in the rhizosphere of ammonium fertilized soybeans was 1.9 units lower than soybeans fertilized with nitrate. Phosphorus uptake was inversely correlated to rhizosphere pH in this experiment. Soon and Miller (1977) also reported that biological reduction in rhizosphere pH increased P utilization. Phosphate absorption was about 50% greater from the rhizosphere amended with ammonium than was calculated from soluble P concentrations in the rhizosphere alone. They attributed this to increased concentrations of total soluble P as well as a larger proportion of P in the H_2PO_4^- form. Blair et al. (1971) compared P uptake in corn seedlings amended with ammonium and nitrate fertilizers in soils with pH 4.2 to 8.2. They postulated that at low soil pH, nearly all the P would exist in the H_2PO_4^- form and that N form would have little influence on P form or uptake. However, they found that ammonium increased P uptake to a similar degree in soils with pH 5.5 to 8.2. This is interesting, because at pH 5.5 nearly all the solution P exists as H_2PO_4^- . Thus, the physiological acidification of the rhizosphere and the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ balance does not fully explain the ammonium ion effect (Soon and Miller 1977).

Newly developed molecular research techniques may provide more insight into the ammonium ion effect. Until recently, root proliferation was thought to be regulated by metabolites in a feedback mechanism. Researchers now hypothesize that metabolically independent signaling may regulate this process (Leyser and Fitter 1998; Zhang and Forde 1998). McCully (1999) has also speculated that similar signaling systems probably exist for ammonium and phosphate, resulting in increased nutrient utilization.

When discussing the benefits of the ammonium ion effect, it is important to remember that many crop species have greatest growth and P uptake when both ammonium and nitrate are available (Yibirin et al. 1996). Yibirin et al. (1996) suggested that the combination of nitrate and ammonium provided electrical charge balance to the root, resulting in improved crop growth.

From the preceding discussion it is clear that no single mechanism is entirely responsible for the ammonium ion effect. Most likely it is a combination of both biological and chemical mechanisms, and is probably modified by numerous environmental conditions.

2.3.7 Nitrogen Fertilizer Effects on Fertilizer S Utilization

Nitrogen fertilizers may have a limited effect on SO_4^{2-} uptake. Blair et al. (1970) found that SO_4^{2-} uptake was increased more by NH_4^+ than by NO_3^- . Mamaril and Miller (1970) reported similar trends, but they also observed that the ammonium ion effect was much less pronounced with SO_4^{2-} uptake as compared to P uptake.

The influence of N fertilizers on SO_4^{2-} fertilizer utilization appears to be primarily related to biological mechanisms. Blair et al. (1970) suggested that cation (NH_4^+) uptake

stimulated anion (SO_4^{2-}) uptake to maintain physiological electroneutrality. Increased root exploration, root proliferation and overall increased growth associated with N fertilization may also increase SO_4^{2-} uptake.

In recent years, molecular techniques have isolated specific uptake and assimilation pathways. A deficiency in S represses the uptake and assimilation of N by repressing transcriptional expression of ion transporters (Kopriva et al. 2002; Koprivova et al. 2000). Conversely, researchers have observed an increased production of enzymes relating to SO_4^{2-} uptake and reduction to S when ammonium was supplied (Brunold and Suter 1984; Suter et al. 1986). Koprivova et al. (2000) observed similar increases when either ammonium or nitrate fertilizer was supplied.

Nitrogen can influence S^0 oxidation in several ways. Microorganisms have a high requirement for N, and moderate concentrations of fertilizer N may stimulate population growth and subsequently oxidation rates (Lettl et al. 1981). However, Lettl et al. (1981) also reported that high N concentrations inhibited S oxidation. In addition, nitrification of ammoniacal-N fertilizer reduces the pH of the surrounding soil. In soils with low pH buffering capacity, the decrease in pH may inhibit S^0 oxidation (Germida and Janzen 1993).

2.3.8 Sulphur Fertilizer Effects on Fertilizer P Utilization

Sulphate and S^0 fertilizers have the potential to modify fertilizer P utilization through biological and chemical mechanisms.

2.3.8.1 Biological Effects The addition of S^0 to P fertilizer may have an indirect stimulus on P uptake. Crops such as canola have a high S requirement and, when

balanced with an optimum amount of N fertilizers, plant growth increases significantly (Grant et al. 2003b; McGrath and Zhao 1996). This increased growth rate also requires that the plant increase P uptake to sustain that overall increase in growth.

2.3.8.2 Chemical Effects Generally, phosphate ions compete more strongly for adsorption sites in soil than sulphate ions (Barrow 1969; Ensminger 1954; Fox et al. 1964). As a result, sulphate fertilizer may have limited effect on P availability (Geelhoed et al. 1997; Pigna and Violante 2003); however, exceptions were found in the literature.

Sulphate fertilizers, such as AS, have been used extensively in P utilization studies (Beever 1987; Goos and Johnson 2001; Hammond 1997). However, the influence of SO_4^{2-} on P availability and uptake is difficult to distinguish from the ammonium ion effect on crops. Soil incubation studies may be useful to isolate the effect of sulphate. Using calcareous soils, Kumaragamage et al. (2004) found that SO_4^{2-} increased the solubility and mobility of P within the soil solution, independent of ammonium influence. They hypothesized that competition between SO_4^{2-} and PO_4^{2-} anions to precipitate with calcium increased the concentration of soluble P that remained in solution. Singh et al. (1998) reported similar trends in acidic to neutral pH soils containing exchangeable Al^{3+} and Fe^{2+} . They reported that competitive adsorption of SO_4^{2-} to Fe and Al oxides increased the concentration of P that remained in soil solution, compared to soils where a competitive anion was not present.

Similarly, increased concentrations of soluble P were observed with the addition of AS fertilizer to soils in Manitoba with high P retention capacities (He et al. 2002). In the same study, soluble P concentrations were highest with the addition of the NPS

fertilizer. The authors did not speculate on the possible mechanisms responsible for increased P solubility, but the observations may have been confounded by pH effects.

Metson and Blakemore (1978) reported that on acidic New Zealand soils with high anion adsorption capacity, SO_4^{2-} competed effectively with P for adsorption sites. However, in soils with low adsorption capacity, SO_4^{2-} had little effect on P adsorption. Geelhoed et al. (1997) also found that SO_4^{2-} fertilizers competed with P fertilizers for adsorption, increasing plant available P. Pigna and Violante (2003) stated that pH determined the ability of sulphate to compete with phosphate for sorption. At $\text{pH} < 4.5$, SO_4^{2-} competed effectively with phosphate, increasing available phosphate in volcanic soils.

Oxidation of S^0 may also increase P solubility and P fertilizer use efficiency (DeLuca et al. 1989; Friesen et al. 1987; Ghani et al. 1994; Lee et al. 1987). The oxidation process lowers the pH of the fertilizer reaction zone, increasing the solubility of fertilizer P (Kashirad 1972). In growth chamber experiments, Mitchell et al. (1952) observed significant increases in P uptake by wheat when S^0 was added to MAP; however, field trials did not produce similar results. Recently, Goos and Johnson (2001) found that P uptake by wheat increased significantly when ammonium polyphosphate liquid fertilizer was combined with S^0 ; although no additional yield response was recorded. The increase in P uptake occurred early (< 4 leaf) but the uptake was lower compared to similar treatments where AS fertilizer was added with ammonium polyphosphate.

2.3.9 Phosphate Fertilizer Effect on S Fertilizer Utilization

Addition of P to SO_4^{2-} or S^0 fertilizers may increase the efficiency of either S source. The direct effect of P on SO_4^{2-} uptake is likely due to the biological influence of P on crop growth. Santoso et al. (1995) found that mixing P and S fertilizers increased S uptake of corn. The increase was attributed to P induced root proliferation (Jackson et al. 1990; Lefroy et al. 1997; Robinson 1994), increasing the potential for S uptake. Santoso et al. (1995) also suggested that total plant growth increased with P fertilization, thereby increasing the uptake of S.

As was stated previously, P competes strongly with SO_4^{2-} for retention in both calcareous and acidic soils, increasing the availability of SO_4^{2-} (Barrow 1969; Ensminger 1954; Fox et al. 1964; Geelhoed et al. 1997).

Microbial oxidation of S^0 is influenced by the presence of other nutrients in the soil. Several studies have reported that the addition of P to S^0 stimulated oxidation rates (Bloomfield 1967; Janzen and Bettany 1987; Lawrence and Germida 1988; Lee et al. 1987). For example, combining P with elemental S increased oxidation rates by 16% to 300% (Santoso et al. 1995; Sholeh et al. 1997). Plant uptake of SO_4^{2-} also reflected the increased oxidation rates (Lefroy et al. 1997; Santoso et al. 1995). The benefit of P fertilizer on S oxidation is probably due to the direct nutritional benefit to the oxidizing microorganisms (Santoso et al. 1995). The additional P would allow population to increase rapidly, given adequate supplies of N and carbon for growth and reproduction.

From a practical perspective, addition of P fertilizer simply for the purpose of increasing SO_4^{2-} utilization is not efficient, due to the relative expense of phosphate fertilizers. However, if both nutrients are required, placement of P fertilizers with S^0

appears to stimulate microbial populations and improve fertilizer use efficiency of S° fertilizers.

2.4. Fertilizer Toxicity

Placement of fertilizers in or near the seed row can delay or reduce germination and emergence of most crops due to the toxic effects of NH_4^+ or the osmotic stresses caused by high concentrations of fertilizer salts. The severity of the injury depends on crop, soil and environmental factors. Generally, wheat is tolerant to moderate concentrations of seed placed fertilizer, while sensitive crops such as canola can only tolerate limited amounts of seed placed fertilizer. Soil and environmental factors such as soil texture, pH, moisture and temperature all influence the severity of fertilizer toxicity. Agronomic practices such as increasing seed bed utilization (SBU) can also decrease the risk of crop injury due seed placed fertilizer.

Placement of phosphate fertilizers with the seed is an effective agronomic practice for providing phosphorus to cereal and oilseed crops (Bailey et al. 1998; Bailey and Grant 1990; Olson and Dreier 1956a). Sulphate fertilizers may also be placed with the seed and the practice is often used in canola production (Grant et al. 2003b). However, placement of one or both of these fertilizers in or near the seed row may cause injury to germinating seeds, delay or reduce emergence and reduce yields of many small seeded crops (Nyborg 1961). In general, this damage occurs as result of two processes; 1) specific compound toxicity, such as ammonia or phosphate toxicity, and, 2) general salt or osmotic injury (Cook and Scott 1987; Deibert 1994; Ward 1987).

2.4.1. Ammonia Toxicity

MAP and AS fertilizers may form free NH_3 and when placed in or near the seed row may be potentially toxic to developing crops. Ammonia toxicity is dependent on numerous crop and soil environment parameters including crop type, soil pH, soil texture, soil moisture, fertilizer type and proximity of the fertilizer to the seed (Bennett and Adams 1970a; Bennett and Adams 1970b; Bremner and Krogmeier 1989; Deibert 1994; Dowling 1998).

Relatively low concentrations of NH_3 (aq) in soil solution, or NH_3 (g) in the soil atmosphere are toxic to seeds and seedlings. Either form of NH_3 can pass freely through the cell walls of the seed, where hygroscopic NH_3 binds to the water within the seed and burns the embryo tissue, reducing germination potential (Deibert 1994; Warren 1962). In addition, Britto et al. (2001) determined that the mechanism for ammonia toxicity to barley seedlings (*Hordeum vulgare*) was at least in part due to futile cycling of ammoniacal-N in the root. Ammonia sensitive species are unable to exclude NH_4^+ from the cytosol and expend large amounts of energy exporting NH_4^+ from the cell resulting in poor growth. There is also evidence that NH_3 can affect metabolic processes such as the Krebs cycle (Vines and Wedding 1960).

The intensity of NH_3 toxicity rises with increasing NH_3 concentrations. Much of the early work in NH_3 toxicity research used more than lethal concentrations of NH_3 (Allred and Ohlrogge 1964; Blanchar 1967). However, Bennett and Adams (1970b) observed incipient NH_3 crop injury when concentrations were at least 76% lower than lethal concentrations; therefore, significant injury is possible at low fertilizer rates.

Recent work in Australia evaluated the susceptibility of different crops to NH_3 toxicity. Dowling (1998) grouped crop tolerance levels into three categories: high -

barley, and wheat; intermediate - sorghum, chickpea and canola; and low - sunflower and cotton. In general, dicot crops are considered to be less tolerant to ammoniacal-N fertilizers than monocot crops (Carter 1967; Dubetz et al. 1959). For example, injury was observed in canola plants with 40% less seed applied NH_3 as compared to wheat (Dowling 1998). Growth cabinet experiments (Nyborg 1961) and field experiments (Nyborg and Hennig 1969) in western Canada also demonstrated that barley and wheat had significantly more tolerance to seed placed fertilizer than rapeseed.

2.4.2. Phosphate and Sulphate Specific Ion Toxicity

Phosphate and sulphate ions contained in MAP and AS fertilizers respectively, may also be toxic to developing crops at high concentrations; however, the risk of specific ion toxicity is much less than that for NH_3 . For example, toxic concentrations of sulphate in the soil solution from AS fertilizer application would be overshadowed by toxic concentrations of ammoniacal-N included in the fertilizer. The risk of phosphate toxicity is less than that of sulphate; however, phosphate toxicity can occur under completely different conditions. Bhatti and Loneragan (1970) observed necrosis in the tips of wheat leaves and poor growth related to excess accumulation of P. They suggested that the P toxicity was due to high rates of P application and excess salt accumulation which disrupted osmoregulation within the cells of the wheat seedlings. In contrast, Green and Warder (1973) demonstrated that P toxicity could occur even at relatively low P concentrations. Wheat seedlings grown in a P deficient environment developed a hyperactive P sink when a P source was introduced. The P deficient seedlings acquired excess P causing toxicity injury. In general, however, the risk of

sulphate and phosphate causing a specific ion toxicity is low because relatively small amounts of AS and MAP fertilizers are applied.

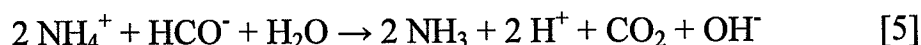
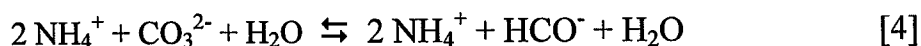
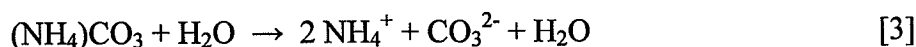
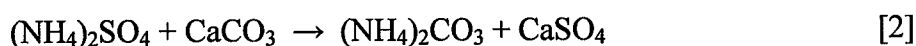
2.4.3. Salt and Osmotic Toxicity

The soluble fraction of most fertilizer products contains salts; as the fertilizer dissolves, these salts are released into the soil solution. As with NH_3 toxicity, confining fertilizer to a small volume, or fertilizer band, increases the fertilizer salt concentration many times higher than the surround bulk soil (Cummins and Parks 1961; Rader et al. 1943). Therefore, seed placement of MAP and AS fertilizers in a confined band may also increase the risk of salt toxicity, or burning of seeds and seedlings (Olson and Dreier 1956a).

High osmotic pressure, or low water potential, in a fertilizer band can drastically reduce or delay germination. High osmotic pressures may affect seed germination in several ways; the difference in water potential between the seed and soil solution may cause water in the embryo to move into the soil solution, burning the seed, thus reducing germination (Deibert 1994). Williams and Shaykewich (1971) determined that potential of imbibing seeds was -100 MPa; therefore, imbibition was not inhibited, but as enzymatic activity and radical elongation began, the osmotic potential of the seed was insufficient to absorb additional water from the soil solution and as a result germination ceased (Bewley and Black 1982; Dowling 1998). High osmotic pressure can restrict the ability of the developing roots to absorb water against a steep solute concentration gradient. Under very high osmotic pressure, root cells may lose cellular water to the soil environment; in these conditions plant growth is limited and under prolonged stress, plant death occurs.

2.4.4. Soil Factors and Fertilizer Toxicity

Soil factors such as soil texture, SOM, CEC, environmental conditions and pH can moderate the injury caused by specific ion toxicities and osmotic effects (Dowling 1998). Clay minerals adsorb ammonium onto the surfaces and interlayer spaces, reducing the harmful concentrations in soil solution. Conversely, other soil minerals like CaCO_3 may increase the risk of NH_3 toxicity. For example, addition of AS fertilizer to soils containing CaCO_3 , results in the rapid formation of free ammoniacal-N and CaSO_4 through the following reaction (Fenn and Hossner 1985):



Increasing soil moisture contents associated with finer textured soils and increasing SOM can decrease damaged to germinating seeds caused by fertilizer NH_3 toxicity and osmotic affects. Ammonia has a high affinity for water; when the NH_3 combines with H_2O , the damaging effect on the seed or seedling is reduced (Deibert 1994). Higher soil water content also decreases the diffusion potential of NH_3 as well as favouring the formation of less toxic NH_4^+ ions. Increased soil water also dilute ammoniacal-N and fertilizer salts concentrations in soil solution, decreasing the potential for crop injury (Nyborg 1961; Nyborg and Hennig 1969). Rader et al. (1943) suggested that soil moisture was also one of the most important factors determining osmotic pressure and the salt effect in crop production.

Soil temperature can be an important factor in determining the extent of injury caused by seed row placed fertilizer. Increased soil temperature can increase germination and growth rates; as the metabolic activity of the crop increases, the effects of NH_3 toxicity and/or osmotic stress may also increase. For example, Helms et al. (1996) showed that ammonium toxicity decreased soybean germination with increasing temperature and increased moisture stress. Woodstock and Tsoa (1986) also observed increased injury to soybeans and corn from ammoniacal-N as temperatures increased from 5°C to 25°C . Conversely, Cummins and Parks (1961) observed no significant fertilizer related toxicity injury to wheat seedlings as temperature increased from 10°C to 29°C . In general, as temperature increases, metabolic activity of the plant increases and so does the severity of injury associated with ammoniacal-N toxicity and osmotic stress.

Toxic concentrations of ammoniacal-N are further lowered by biological nitrification. Nitrification converts ammoniacal-N to nitrate, a less toxic ion. Therefore, over time, the toxic effects of ammoniacal-N and excess fertilizer salts to the crops will diminish.

Soil pH influences the ammoniacal-N species balance as well as pH dependent CEC in the soil. As the pH decreases, the less toxic NH_4^+ ions concentrations increase while NH_3 concentrations decrease in soil solution (Warren 1962). Soil pH also influences the CEC associated with edges of minerals and SOM, also known as pH dependent CEC. As the pH increases, protons dissociate from the edge of clays, oxides or SOM particles, exposing negatively charged functional groups, increasing the negative charge of the particles. Therefore, as the negative charge increases with increasing soil pH, NH_4^+ adsorption lowers the concentration of NH_4^+ in soil solution. For example, Stevenson and Bates (1968) observed greater fertilizer toxicity at low soil CEC than at

high soil CEC. Bennett and Adams (1970a) concluded that soils with pH below 7 and high CEC would have the least damage due to NH_3 toxicity, presumably due to NH_4^+ adsorption. In addition they found that Ca^{2+} deficiency caused by competition with NH_4^+ for plant uptake was the primary cause of injury at low pH and low CEC; under these conditions the toxicity was not caused directly by NH_3 .

2.4.5. Fertilizer Characteristics

The ammonia toxicity and the osmotic effect of a fertilizer is related to the concentration of the salts as well as the chemical characteristics of the salts (Dowling 1998). Often fertilizers with high nutrient concentrations have less risk of salt toxicity because a lower rate of fertilizer is needed (Cummins and Parks 1961); however, NH_3 toxicity may still be a concern (Dowling 1998). For example, the salt index, pH and the ammonium concentration of MAP are relatively low (Table 2.1). From this table, it is apparent that the addition of AS to MAP increases both the salt and ammoniacal-N concentration added to the soil.

Fertilizer Property	Fertilizer Product			
	urea	diammonium phosphate	monoammonium phosphate	ammonium sulphate
Nutrient analysis	46-0-0	18-46-0	11-52-0	21-0-0-24
Salt index	75	35	30	70
pH (sat. sol.)	10.7	7.4	4.7	4.5

In incubation studies by He et al. (2002), electrical conductivity values for the NPS fertilizer were intermediate to MAP only and MAP + AS treatments, indicating that the salt toxicity of NPS may be greater than MAP and less than MAP + AS. Water

extractable NH_4^+ concentrations were also intermediate for the NPS fertilizer relative to MAP and MAP + AS. Canola and wheat emergence was also tested with the NPS fertilizer. With wheat, emergence counts in the NPS fertilizer treatments were higher than the AS treatment, but lower than the MAP treatments; however, the differences were not significant. Given that the NPS fertilizer contains more ammonium and salts than MAP, but less than MAP + AS, these results are logical. With canola, the results were not consistent and differences were not significant.

Seed row placement of a combination of NH_4^+ fertilizers would increase the risk of fertilizer related injury (Rader et al. 1943). In canola production, MAP and AS are often placed with or near the seed; this practice increases both the NH_4^+ and soluble salts near the seed. As a result, it may be necessary to limit the amount of MAP and AS placed with the seed to rates that are less than if either fertilization was applied alone. The risk of fertilizer injury can also be decreased by increasing the volume of the soil-fertilizer reaction zone, or SBU. Increasing the SBU or distribution of seed row placed fertilizer with wider seed row openers will decrease the risk of injury (Roberts and Harapiak 1997).

3. EMERGENCE, MACRONUTRIENT UPTAKE AND CROP YIELD WHEN FERTILIZED WITH HOMOGENEOUS GRANULAR NITROGEN-PHOSPHORUS-SULPHUR FERTILIZER

Key Words: Elemental S, sulphate, phosphate, seed-placed fertilizer, airseeder, spring wheat (*Triticum aestivum*) spring canola (*Brassica napus* L.)

3.1 Abstract

Field studies in southern Manitoba conducted over two years evaluated the effect of a homogeneous nitrogen-phosphorus-sulphur (NPS) fertilizer on emergence and crop uptake of phosphorus (P) and sulphur (S). Fertilizer treatments consisted of NPS, monoammonium phosphate (MAP) + ammonium sulphate (AS), MAP + elemental S-bentonite (S^o), MAP only and a control (no P or S). In a second study conducted with canola alone, S was applied at 0, 5, 10, 15 and 20 kg ha⁻¹ as MAP + S^o, MAP + AS and NPS. None of the P and S fertilizer sources or S rates affected wheat or canola emergence. At midseason, the NPS and other P fertilizer sources increased dry matter yield of wheat 6- 10%, but not of canola; all of the phosphate fertilizers increased P uptake 8 – 10% in wheat and 23 – 45% in canola, while only NPS and AS increased S uptake 7 – 9% in wheat and 25 – 70% in canola. At physiological maturity, the differences in yield and P and S uptake had largely disappeared; however, all of the P fertilizers increased total P uptake in wheat by 9 – 12%. There were no beneficial or detrimental effects on P uptake by combining N, P and S into a homogeneous granule. The oxidation of seed-placed S^o appeared to be negligible in most cases. Overall,

homogeneous NPS appears to be an excellent source of fertilizer P, but the majority of the elemental S in this fertilizer does not generally become available during the first growing season.

3.2 Introduction

Soil concentrations of phosphorus (P) and sulphur (S) in western Canada are often below that required by crops to produce economically optimal yields; therefore, commercial P and S fertilizers are frequently required. Phosphorus is essential for vigorous early season growth and promotes uniform maturation of the crop. Sulphur is essential for the formation of proteins, especially in high protein oilseed crops such as canola (Bailey and Grant 1990; Jackson 2000).

Monoammonium phosphate (MAP) and ammonium sulphate (AS) are the most common P and S fertilizers used in crop production in western Canada (Korol 2002). Bentonite-elemental S fertilizers are also applied, but require biological oxidation to sulphate to become available to the plant. Transformation of elemental S to sulphate is dependent on environmental conditions, such as soil moisture and temperature; management practices, such as placement and timing of application; and fertilizer characteristics, such as particle size and degree of dispersion (Bettany and Janzen 1984; Grant et al. 2003b; Lupwayi et al. 2001).

Recently, Cargill developed a unique granular fertilizer that combines N, P and S into a single homogeneous granule. Another unique characteristic of the granule is that 50% of the S is in the sulphate (SO_4^{2-}) form, while the remaining 50% is in the elemental S (S^0) form. Combining N, P, SO_4^{2-} , and S^0 into a single granule may have several benefits. Ammonium ions may improve P availability and utilization by modifying the

chemical characteristics of the fertilizer reaction zone and by modifying the biological responses of a crop (Beever 1987). The addition of AS to a MAP band may further increase P availability and uptake by wheat and canola (Beever 1987; Rennie and Soper 1958). Hammond (1997) demonstrated that the benefits of AS on P availability could be increased by placing the AS granule in physical contact with the MAP granule as compared to a random distribution of the two granules. The intimate contact between the AS and MAP granules was most beneficial when the fertilizer was distributed over a 15 cm wide band, similar to the fertilizer band produced with an airseeder with sweep type openers.

In calcareous soils, such as those found in western Canada, sulphate ions may compete with phosphate ions to precipitate with Ca, increasing the concentration of soluble P available for crop uptake (Kumaragamage et al. 2004). Singh et al. (1998) observed similar results in acidic soils, where SO_4^{2-} was retained by exchangeable Al and Fe, leaving P in soil solution. In addition, Mitchell et al. (1952) found that the oxidation of S^0 acidified the fertilizer reaction zone, increasing the solubility of calcium phosphates in greenhouse studies; however, the results could not be duplicated in the field.

Banding higher concentrations of ammonium based phosphate and sulphate fertilizers to improve P fertilizer efficiency may injure the emerging crop when the fertilizer is placed near or with the seed. The ammonium concentration and salt index of monoammonium phosphate (MAP) is relatively low; however, the addition of AS dramatically increases the risk of toxicity compared to MAP alone (Dowling 1998; Rader et al. 1943). This type of risk is especially large for sensitive crops such as canola (Grant et al. 2003b).

The objective of this study was to evaluate the agronomic performance of the NPS fertilizer under field conditions in Manitoba. The agronomic performance was assessed on the basis of seed-row toxicity in both wheat and canola and the plant availability of the P and S fertilizer components of the NPS fertilizer relative to commercial MAP, S^o and AS fertilizers.

3.3 Methods and Materials

3.3.1 Site Selection and Description

Small-plot experiments were conducted at five sites across southern Manitoba in 2002 and 2003. In 2002, one field site was located near Elm Creek, MB and one site north of Brandon, MB. In 2003, field sites were located at Elm Creek, MB; Rivers, MB; and Rosenort, MB. Composite soil samples containing 15 cores were taken at the 0- to 15-cm and 15- to 60-cm depth at each site. Site characteristics and nutrient levels are shown in Table 3.1. All sites except the Rosenort site were selected based on deficient to marginal soil test P and S levels.

Table 3.1 Physical and chemical characteristics of soils in the field experiments

Characteristics	Depth (cm)	Site				
		Brandon (2002)	Elm Creek		Rivers (2003)	Rosenort (2003)
			(2002)	(2003)		
Soil Texture		clay loam	loamy sand	loam	clay loam	clay
pH	0-15	7.4	6.9	6.9	7.5	8.1
EC (2:1 saturated paste)	0-15	0.9	0.6	0.6	0.3	1.9
OM (%)	0-15	4.7	2.3	2.3	2.9	6.4
NO ₃ ⁻ -N (kg ha ⁻¹)	0-15	13.4	84.2	76.2	28.0	58.3
	15-60	13.4	103.6	94.2	15.7	77.4
Extractable P (Olsen mg kg ⁻¹)	0-15	18.0	9.0	7.0	9.0	18.0
S (kg ha ⁻¹)	0-15	13.4	15.7	15.8	11.2	56.1
	15-60	53.8	26.9	22.4	17.9	403.6

3.3.2 Experimental Design and Treatments

The field experiments were divided into two studies: 1) a P and S fertilizer source study; and 2) a S-fertilizer source by rate study. The first study was conducted on two crops, Canada Western Red Spring wheat (*Triticum aestivum* L. cv. AC Barrie) and spring canola (*Brassica napus* L. cv. DKL 34-55 Helix[®]). The experimental design for each crop was a randomized complete block. Each block in each crop contained five, 1.7 m by 5 m fertilization treatment plots, with all five treatments assigned randomly within the block and replicated four times. The P and S granular fertilizer treatments were applied with the seed at 15.85 kg P ha⁻¹ and 16.5 kg S ha⁻¹ (see Section 3.33). The treatments included a control, with no P or S fertilizer; MAP, no S; MAP + Tiger 90[®] bentonite – elemental S (MAP + S[°]); MAP + AS; and the homogeneous NPS fertilizer with 50% SO₄-S and 50% S[°]-S.

In the second study, the experimental design was a factorial design, with three sources of S-fertilizer and four S rates. Spring canola, DKL 34-55, was the only crop grown in this study. Fertilizer sources and S-rates were assigned at random across 13 plots in each block; plot size was 1.7 m by 5 m; each block was replicated four times. The treatments included a control (MAP, 0 kg S ha⁻¹); MAP + S[°]; MAP + AS; and NPS. Phosphorus was applied at 19.2 kg ha⁻¹; while in treatments containing S-fertilizer, S was applied at 5, 10, 15 and 20 kg ha⁻¹. The fertilizer treatments were placed with the seed (see Section 3.33). When NPS fertilizer S-rates were below 20 kg ha⁻¹, MAP was added to make P rates equivalent across all treatments. To compensate for N applied at the highest rate of AS (17.5 kg N ha⁻¹), ammonium nitrate was surface applied to equalize N fertilizer application in all treatments.

Nitrogen was applied as urea at a rate adjusted for the N applied in the MAP fertilizer to provide a total of 100 and 140 kg N-fertilizer ha⁻¹ in wheat and canola respectively. Potassium was applied as KCl at a rate of 46.3 kg K ha⁻¹. The N and K were applied in bands 10 cm away from the seed row during the planting operation using mid-row banders. Liquid copper-chelate and boron were applied to the plots at Rivers 2003 and Elm Creek 2002 based on soil test results.

3.3.3 Crop Establishment and Measurements

The wheat and canola were planted at a rate of 140 kg and 6.15 kg ha⁻¹, respectively, with a 1.65-m-wide plot airseeder and at a depth of 2 to 2.5 cm. Sweep-type openers were used and seed and P and S fertilizer treatments were spread over a 10 cm band on 20 cm spacing, or 50% seedbed utilization to simulate typical airseeder planting practices in western Canada. Sites were planted between May 9 and May 29 in both years. Wheat and canola were seeded in the border areas as well as the alleys between the plots to reduce edge effects. Pesticides applied to plots included a preseeding glyphosate application, site-specific in-crop herbicide applications, and fungicide application with Folicur[®] in wheat and Ronalin[®] in canola. Insecticides were also applied at all Elm Creek sites and Rosenort due to high grasshopper infestations. The herbicides were applied with a 4 m bicycle sprayer, while the fungicides were applied with a 1.6 m- boom backpack sprayer. All pesticides were applied at the rates recommended by the Manitoba Crop Protection Guide (2002).

To determine the toxicity of the P and S fertilizer to wheat and canola, emergence counts were conducted in two-row by two-metre quadrats, 0.4 by 2.0 m. Plant counts

were taken 5, 12 and 19 days after seeding and the same location in each plot was used for all counts.

At midseason in 2002, 50% heading in wheat or 40% flowering on the main stem of canola, a two-row by two-metre sample of above ground plant tissue was hand harvested from each plot. In 2003, the sample size was increased to four-rows by two-metres in an attempt to decrease in-treatment variation. The midseason samples were dried at 35 to 40°C to approximately five percent moisture and dry matter biomass was calculated. Both crops were also harvested at physiological maturity. The sample size area was two-rows by three-metres in 2002 and was doubled to four-rows by three-metres in 2003. The above ground plant tissue was dried, threshed and weighed for both seed and straw yield. Canola straw, wheat straw and wheat seed collected at midseason and harvest were ground with a Wiley mill to pass a 2 mm sieve. The ground plant tissue, wheat seed and whole canola seeds were analyzed for total N and S using a Leco CNS Analyzer (Leco CNS 2000 Elemental Analyzer Instructional Manual 1998). Total P in the ground tissue and whole canola seed was analyzed using the wet oxidation method (Parkinson and Allen, 1975), a spectrophotometer and the molybdenum blue method (Murphy and Riley, 1962). One standard sample and one blank were analyzed with every 15 to 18 tissue or seed samples for quality assurance.

The percent green seed in the canola samples was determined as a measure of seed quality. The quantity of green seeds was estimated by transferring 100 seeds to strips of masking tape using a plastic strip with 100 small dimples that are each approximately the size of a seed. The seeds on the masking tape were crushed with a roller, exposing the internal contents of the seed (Canadian Grain Commission 2004; Daun and Symons

2000). Crushed seeds that had a distinctly green color were counted as damaged. Three sub-samples were taken from each seed sample.

3.3.4 Data Analyses

Statistical analyses of the field studies were conducted using the Mixed Model procedure of the Statistical Analysis System (SAS) package (SAS 1999). Site years were treated as fixed effects because available soil P and S concentrations differed considerably with location. Descriptive statistics were used to test the error variance and the skewness (γ) of the data (Webster 2001) using SAS Proc Univariate. Most of the crop data had approximately normal distributions and skewness less than 0.5 (data not presented). Statistical analyses of transformed data did not produce results that were different from the non-transformed data; therefore, the untransformed data was used in all analyses.

The P and S fertilizer source study was analyzed using the ANOVA model. LSMEANS was used to compare the different P and S fertilizer treatments, and a SAS macro was used to convert mean separation to letter groupings (Saxton 1998). A probability level (α) of 0.05 was used as the significance threshold for crop measurements across the fertilizer treatment means. The wheat and canola crops were analyzed separately.

The ANOVA model and LSMEANS were also used for the S-fertilizer source by rate study. These data were analyzed as an incomplete factorial, comparing the different sources (averaged across rates), different rates (averaged across fertilizer sources) and the interaction of fertilizer source and S rate (note: in the source by rate interaction, it is only appropriate to compare within a specific rate, not across rates). In the S-fertilizer source

by rate study, only one control was used (MAP, no S); therefore, to compare the three S fertilizer sources, the control was artificially duplicated so that each of the three fertilizer treatments contained a control to represent 0 kg S ha⁻¹.

3.4 Results and Discussion

3.4.1 Weather Conditions

Environmental conditions at Elm Creek 2002, Brandon 2002 and Elm Creek 2003 were generally favourable for crop production. However, in 2003 all of the sites showed signs of heat stress during flowering and seed development stages, resulting in pod abortion in canola. At Rivers 2003, soil conditions were dry during planting, and cumulative precipitation was less than 10 cm by crop maturity, while at the Rosenort 2003 site, nearly 40 cm of precipitation accumulated in the first six weeks after planting (data not presented).

3.4.2 P and S Fertilizer Source Study

3.4.2.1 Wheat and Canola Emergence We did not observe a decrease in seedling emergence with the NPS fertilizer or the other fertilizer sources in wheat or canola relative to the control (data not presented). He et al. (2002) also observed no significant differences in either wheat or canola emergence when similar combinations of fertilizers were placed with the seed in a growth chamber study. The fertilizer rates and/ or concentration of fertilizer in the seed-row band appeared to be below toxic levels with the seedbed utilization and environmental conditions in our study.

3.4.2.2 Midseason At 50% anthesis, P fertilization increased total above ground wheat biomass by 6 to 10% relative to the control when the data from all sites were combined (Table 3.2). The NPS treatment produced the highest the mean dry matter yield values, though it was not statistically different from the other P fertilizers treatments.

Phosphate uptake by wheat followed a similar trend as biomass yield at anthesis. The MAP, MAP + AS and NPS treatments increased P uptake by 10, 8 and 13% relative to the control (Table 3.3). Though the NPS treatment had the highest numerical tissue P concentration (data not presented), the highest above ground biomass yield (Table 3.2) and the highest apparent P fertilizer use efficiency (8.2%, calculated as P uptake in treatment minus the control, divided by fertilizer P applied), the P uptake was not significantly greater than for the other P fertilizer treatments.

When all the site years were combined, S uptake by wheat at anthesis was greatest in treatments containing sulphate fertilizer (Table 3.4). The AS and NPS treatments produced similar results with 7.4 and 8.8% greater S uptake than MAP alone. To

Table 3.2 Effect of P and S fertilizer source on wheat dry matter accumulation at anthesis

Fertilizer Treatment	Site					Mean	
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
	(kg ha ⁻¹)						
Control	3428	5374	5244 ^b	3459	5397	4580 ^b	
MAP	3909	5230	6387 ^a	3622	5605	4943 ^a	
MAP + S°	3879	5459	6064 ^a	3681	5243	4859 ^a	
MAP + AS	4046	5052	5244 ^b	3772	5672	4945 ^a	
Homogeneous NPS	3883	5419	6102 ^a	3723	5966	5025 ^a	
ANOVA	<i>df</i>	<i>P > F</i>					
Fertilizer Treatment	4	0.2081	0.5976	0.0027*	0.7376	0.0786	0.0015*
Site x Treatment	16						0.0552
Residual C.V. (%)		9.30	7.32	5.30	9.38	5.98	7.30

^{a-b} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

* Significant at $P < 0.05$

Fertilizer Treatment	Site					Mean	
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
	(kg ha ⁻¹)						
Control	9.30	12.91	10.22 ^b	6.76	10.24 ^{ab}	9.89 ^b	
MAP	11.69	12.83	12.89 ^a	7.52	9.97 ^b	10.91 ^a	
MAP + S ^o	10.83	12.13	12.79 ^a	7.52	9.78 ^b	10.62 ^{ab}	
MAP + AS	11.15	11.56	12.96 ^a	7.62	10.32 ^{ab}	10.72 ^a	
Homogeneous NPS	11.69	13.09	12.52 ^a	7.55	10.97 ^a	11.19 ^a	
ANOVA	<i>df</i>	<i>P > F</i>					
Fertilizer Treatment	4	0.4563	0.5217	0.0019*	0.5522	0.0418*	0.0185*
Site x Treatment	16						0.2817
Residual C.V. (%)		18.42	11.32	6.58	10.79	4.76	12.03

^{a-b} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

* Significant at $P < 0.05$.

estimate the availability of S^o oxidation from the NPS fertilizer, S uptake from the MAP + S^o treatment was compared to S uptake MAP only. Sulphur uptake from the MAP treatment was nearly identical to the MAP + S^o treatment, indicating that little or no S^o was oxidized from the latter fertilizer. Populations of S^o oxidizing microorganisms were assumed to be ubiquitous and non-limiting to the oxidation process (Lawrence and Germida 1991b). Therefore, the main limitation of S^o oxidation was probably due to the nature of the S^o fertilizer or fertilizer management practices (i.e. banding).

In the P and S fertilizer source experiment with canola, three of the four replicates of the MAP + AS treatment at the Elm Creek 2002 site were unusable due to planting problems. Therefore, the mean for the AS treatment is not reported for this site, and Elm Creek 2002 is not included in the mean of all site years.

At midseason (~40% flowering on the main stem), the different fertilizer sources resulted in few significant increases in canola dry matter yields at individual sites and none when all site years were combined (Table 3.5). Phosphate fertilization increased P

uptake by 26 to 45% in canola at flowering when all of the sites were combined with the exception of data from Elm Creek in 2002 (Table 3.6). The apparent P fertilizer use efficiency value was the highest for NPS fertilizer, 18.9%, though it was not statistically different from the other P and S fertilizer combinations.

Table 3.4 Effect of P and S fertilizer source on S accumulation in wheat tissue at anthesis

Fertilizer Treatment	Site					Mean	
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
	(kg ha ⁻¹)						
Control	4.91	9.46	6.16 ^b	5.10	11.56 ^{bc}	7.44 ^b	
MAP	5.84	9.13	7.33 ^a	5.15	12.36 ^{abc}	7.95 ^b	
MAP + S ^o	5.87	9.93	7.11 ^a	5.42	11.15 ^c	7.90 ^b	
MAP + AS	6.94	9.23	7.93 ^a	5.83	12.77 ^{ab}	8.54 ^a	
Homogeneous NPS	6.53	9.51	7.74 ^a	5.85	13.60 ^a	8.65 ^a	
ANOVA	<i>df</i>	<i>P > F</i>					
Fertilizer Treatment	4	0.0549	0.8891	0.0053*	0.4548	0.0207*	<0.0001*
Site x Treatment	16						0.1659
Residual C.V. (%)		14.58	10.81	7.53	13.21	7.56	10.52

^{a-c} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

* Significant at $P < 0.05$.

Table 3.5 Effect of P and S fertilizer source on canola dry matter accumulation at 40% flowering

Fertilizer Treatment	Site					Mean ^x	
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
	(kg ha ⁻¹)						
Control	2023	2757 ^{bc}	2664 ^c	2026	2536	2312	
MAP	2504	3079 ^{ab}	2998 ^{ab}	2061	2332	2471	
MAP + S ^o	2502	2527 ^c	3083 ^a	2132	2304	2506	
MAP + AS	2603	- ^z	2764 ^{bc}	1878	2407	2413	
Homogeneous NPS	2309	3502 ^a	3031 ^{ab}	2174	2583	2526	
ANOVA	<i>df</i>	<i>P > F</i>					
Fertilizer Treatment	4	0.2233	0.0250*	0.0381*	0.4610	0.4630	0.3161
Site x Treatment	16						0.0986
Residual C.V. (%)		14.89	11.78	6.65	11.30	10.26	11.17

^{a-c} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

^x Mean across sites does not include Elm Creek 2002 because of insufficient replication in one treatment.

^z Insufficient replication.

* Significant at $P < 0.05$.

Fertilizer Treatment	Site						
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)	Mean ^x	
	(kg ha ⁻¹)						
Control	7.27 ^b	7.50 ^b	7.36 ^b	5.74	5.76	6.53 ^b	
MAP	10.06 ^a	10.37 ^a	9.98 ^a	6.20	6.96	8.30 ^a	
MAP + S ^o	10.28 ^a	8.33 ^b	10.23 ^a	6.25	6.80	8.39 ^a	
MAP + AS	10.43 ^a	- ^z	9.21 ^a	5.48	6.99	8.03 ^a	
Homogeneous NPS	10.13 ^a	11.85 ^a	9.98 ^a	6.58	7.38	9.52 ^a	
ANOVA	<i>df</i>	<i>P > F</i>					
Fertilizer Treatment	4	0.0381*	0.0060*	0.0086*	0.2197	0.0748	0.0014*
Site x Treatment	16						0.1389
Residual C.V. (%)		14.56	13.73	10.60	11.16	10.77	12.73

^{a-b} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

^x Mean across sites does not include Elm Creek 2002 because of insufficient replication in one treatment.

^z Insufficient replication.

* Significant at $P < 0.05$.

Sulphate fertilization increased midseason S uptake at two individual sites; however, a site by treatment interaction occurred when all of the sites were combined and therefore the mean was not reported (Table 3.7). Fertilization with NPS and MAP + AS increased S uptake by canola at Brandon 2002 and Elm Creek 2003 by 41 to 123% relative to MAP alone (Table 3.7). At Brandon 2002, S uptake reflected the amount of SO₄²⁻ added in each fertilizer treatment (i.e. AS > NPS > S^o = MAP). The NPS and MAP + AS treatments also produced greater S uptake at Elm Creek 2003 relative to the MAP + S^o or MAP alone. Sulphur uptake from NPS was numerically higher but statistically equivalent to AS at this site (Table 3.5). At midseason, both of these sites appeared to be mildly S deficient because tissue S concentrations in treatments with MAP alone were less than the marginal concentration of 0.25% (data not presented) established by Bailey (1986). Therefore, under conditions of mild midseason deficiency, the performance of NPS as a sulphur fertilizer was inconsistent relative to AS. At the remaining three sites,

tissue S concentrations appeared sufficient for all treatments, accounting for the minimal differences in S uptake between the different S fertilizer sources.

Fertilizer Treatment	Site					
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)	
	(kg ha ⁻¹)					
Control	4.23 ^c	10.52	7.57 ^b	7.70	19.39	
MAP	5.02 ^c	10.95	6.69 ^b	8.14	18.78	
MAP + S ^o	4.39 ^c	10.08	6.96 ^b	7.60	19.35	
MAP + AS	11.17 ^a	- ^z	9.46 ^a	8.73	21.83	
Homogeneous NPS	7.15 ^b	14.62	11.15 ^a	8.67	22.40	
ANOVA	<i>df</i>	<i>P</i> > <i>F</i>				
Fertilizer Treatment	4	<0.0001*	0.1019	0.0006*	0.6489	0.0905
Residual C.V. (%)		19.34	19.24	13.73	16.30	10.01

^{a-c} Mean values followed by the same letter (within columns) are not significantly different $P > 0.05$.

^z insufficient replication.

* Significant at $P < 0.05$.

There was no evidence of oxidation of the S^o fertilizer at mid-season in either wheat or canola. The tissue S concentration and S uptake in the MAP and MAP + S^o treatments were not statistically different at any of the sites, indicating that the SO₄²⁻ was not produced in any significant quantity.

3.4.2.3 Harvest Yields, Nutrient Uptake and Seed Quality

At physiological maturity, P and S fertilization did not significantly increase wheat grain yields (Table 3.8) or total above ground biomass yields at any site (data not presented). The only significant effect of fertilizer source on yield was an apparent decrease in grain yield for the MAP + S^o treatment at Rosenort 2003. The reasons for this apparent decrease are not known.

Excess heat during anthesis and grain filling, especially in 2003, may have limited grain yield to a greater extent than differences due to the fertilizer treatments.

Fertilizer Treatment	Site					Mean	
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
	(kg ha ⁻¹)						
Control	2528	3496	3418	1481	2038 ^a	2592	
MAP	2545	3565	3418	1645	2148 ^a	2680	
MAP + S ^o	2713	3393	3649	1721	1761 ^b	2640	
MAP + AS	2503	3430	3292	1782	2138 ^a	2629	
Homogeneous NPS	2402	3532	3339	1898	2129 ^a	2658	
ANOVA	<i>df</i>	<i>P > F</i>					
Fertilizer Treatment	4	0.8472	0.9881	0.3153	0.2359	0.0170*	0.9353
Site x Treatment	16						0.6089
Residual C.V. (%)		14.65	13.37	6.97	14.42	7.42	12.00

^{a-b} Mean values followed by the same letter (within columns) are not significantly different.

* Significant at $P < 0.05$.

All of the P fertilizers significantly increased total combined P uptake in the biomass compared to the control when averaged over all site years (Table 3.9). However, there were no differences among the different fertilizer P sources. The apparent fertilizer P use efficiency in the wheat trials was low, only 8 to 10% of applied P.

Fertilizer Treatment	Site					Mean	
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
	(kg ha ⁻¹)						
Control	14.1	19.4	13.0	7.3	11.5	13.1 ^b	
MAP	16.0	20.8	16.1	8.1	12.3	14.7 ^a	
MAP + S ^o	15.9	19.7	16.6	8.6	10.8	14.3 ^a	
MAP + AS	15.2	21.5	15.3	8.3	12.7	14.6 ^a	
Homogeneous NPS	13.7	21.4	15.2	9.0	12.3	14.3 ^a	
ANOVA	<i>df</i>	<i>P > F</i>					
Fertilizer Treatment	4	0.2519	0.7659	0.1412	0.4793	0.1154	0.0465*
Site x Treatment	16						0.6020
Residual C.V. (%)		11.12	13.27	12.43	16.17	8.31	12.88

^{a-b} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

* Significant at $P < 0.05$.

Application of P fertilizers also appears to have increased total S uptake in the wheat seed and straw compared to the control (Table 3.10) yet dry matter yield was unaffected. Nearly significant increases in crop growth ($P = 0.052$) due to P fertilization appear to have increased uptake of S. Differences among the S fertilizer sources were small, inconsistent and generally not significant.

Table 3.10 Effect of P and S fertilizer source on total S accumulation in wheat seed and straw

Fertilizer Treatment	Site					Mean	
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
	(kg ha ⁻¹)						
Control	6.31	10.75	9.98 ^c	5.56	10.34	8.57 ^b	
MAP	7.21	12.26	10.56 ^{bc}	5.69	10.54	9.26 ^{ab}	
MAP + S ^o	7.80	12.42	11.23 ^{ab}	6.21	10.52	9.61 ^a	
MAP + AS	7.85	12.31	11.51 ^a	6.27	11.21	9.83 ^a	
Homogeneous NPS	7.06	11.74	10.68 ^{abc}	6.84	11.23	9.53 ^a	
ANOVA	<i>df</i>	<i>P > F</i>					
Fertilizer Treatment	4	0.0838	0.6329	0.0190 [*]	0.1210	0.2046	0.0191 [*]
Site x Treatment	16						0.9140
Residual C.V. (%)		10.38	13.94	5.26	11.73	5.92	9.97

^{a-b} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

^{*} Significant at $P < 0.05$.

At physiological maturity, canola seed yield and total above ground biomass were not significantly increased by the P and S fertilizer treatments relative to the control at any of the individual sites or when all site years were combined (data not presented). Total uptake of P and S was also not significantly increased by the different combinations of P and S fertilizers as compared to the control within site years or averaged across sites (data not presented). The N to S ratio of the total above ground biomass was significantly lower in the MAP + AS treatment than MAP + S^o and the NPS fertilizer had an intermediate N to S ratio (Table 3.11). This corresponds to the proportion of S found as

plant available SO_4^{2-} in each fertilizer, $\text{AS} > \text{NPS} \gg \text{S}^\circ$. The MAP and MAP + S° treatments had statistically similar S concentrations (%), S uptake and N to S ratios, indicating that little or no S° oxidation occurred when the fertilizer was restricted to the seed row placed band. Grant et al. (2000) also observed that band or seed-placed S° did not increase canola yields even three years after application. Solberg and Nyborg (1986) attributed low rates of S° oxidation and SO_4^{2-} recovery from banded S° to minimal contact between the fertilizer and sulphur oxidizing microbes.

Table 3.11 Effect of P and S fertilizer source on the N to S ratio of canola straw and seed

Fertilizer Treatment	Site					Mean ^x	
	Brandon (2002)	Elm Creek (2002)	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
	(N:S ratio)						
Control	9.12	6.56	7.55	10.28	5.38	8.09 ^a	
MAP	10.49	7.01	6.26	10.72	5.39	8.21 ^a	
MAP + S°	8.61	6.17	6.34	10.67	5.36	7.76 ^a	
MAP + AS	5.62	- ^z	6.51	9.10	5.06	6.57 ^b	
Homogeneous NPS	8.03	7.60	6.83	9.84	5.04	7.45 ^{ab}	
ANOVA	df	<i>P</i> > <i>F</i>					
Fertilizer Treatment	4	0.0992	0.5590	0.5683	0.4497	0.2811	0.0227 [*]
Site x Treatment	16						0.1983
Residual C.V. (%)		38.95	19.43	12.52	16.72	9.73	22.26

^{a-b} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

^x Mean across sites does not include Elm Creek 2002 because of insufficient replication in one treatment.

^z insufficient replication.

^{*} Significant at $P < 0.05$.

When all of the 2003 sites were combined, the canola green seed counts in the NPS treatment were 43, 44 and 38% lower than the control, MAP and MAP + S° treatments respectively (Table 3.12). Fertilizers containing SO_4^{2-} (NPS and MAP + AS) generally decreased green seed in canola relative to MAP alone. The SO_4^{2-} may enhance uniform maturity, decreasing green seed (Duke and Reisenauer 1986). Grant et al. (2003a) also reported that AS decreased chlorophyll content, or green seed, relative to S°

on S deficient soils. However, in our experiment, green seed counts in AS treatments were not significantly less than those treated with S^o.

Table 3.12 Effect of P and S fertilizer source on the canola seed quality: green seed					
Fertilizer Treatment	Site				Mean
	Elm Creek (2003)	Rivers (2003)	Rosenort (2003)		
(% green seed)					
Control	3.42 ^a	11.17 ^a	3.58		6.06 ^a
MAP	2.42 ^{ab}	11.83 ^a	4.00		6.08 ^a
MAP + S ^o	2.00 ^{bc}	10.17 ^{ab}	4.50		5.56 ^{ab}
MAP + AS	1.58 ^{bc}	7.46 ^{bc}	2.83		3.94 ^{bc}
Homogeneous NPS	1.17 ^c	6.33 ^c	2.75		3.42 ^c
ANOVA	df	P > F			
Fertilizer Treatment	4	0.0118*	0.0225*	0.5276	0.0204*
Site x Treatment	16				0.0643
Residual C.V. (%)		35.88	24.74	46.50	33.91

^{a-c} Mean values followed by the same letter (within columns) are not significantly different at $P < 0.05$.

* Significant at $P < 0.05$.

3.4.3 S-Fertilizer Source by Rate Study

3.4.3.1 Canola Emergence Differences in emergence counts due to S-fertilizer source or rate were small, inconsistent and generally not significant. The addition of sulphur fertilizer significantly decreased emergence in four of thirteen measurements. Three of these four cases showed no difference among the S sources. In the remaining case where S sources differed in their effect on emergence, S^o produced significantly lower emergence than NPS or AS; the reason for this unexpected observation is not known. The effect of increasing S rate on canola emergence was not significant in any measurement except in one of thirteen cases where there was a significant S-fertilizer source by rate interaction (data not presented), but no obvious trends were observed.

3.4.3.2 Midseason When the canola was at 40% flowering (on the main stem), there were no significant differences in total above ground biomass, tissue P concentration or P uptake with the various fertilizer sources or S rates and no interactions between fertilizer source and S rate (data not presented). However, S uptake generally increased with the proportion of S present as SO_4^{2-} in each fertilizer. As a result, the apparent fertilizer S use efficiency was 15 to 38% for AS, 6 to 22% for NPS and < 3% for S° . Sulphur uptake from the AS treatment was significantly higher than from the NPS treatment at 10 and 15 kg S ha^{-1} (Figure 3.1). The S° treatment produced lower S uptake than the NPS treatment, but only significantly lower at 10 and 20 kg S ha^{-1} . There were no statistical differences in S uptake between the control and $\text{MAP} + \text{S}^\circ$ at any rate, indicating that no significant

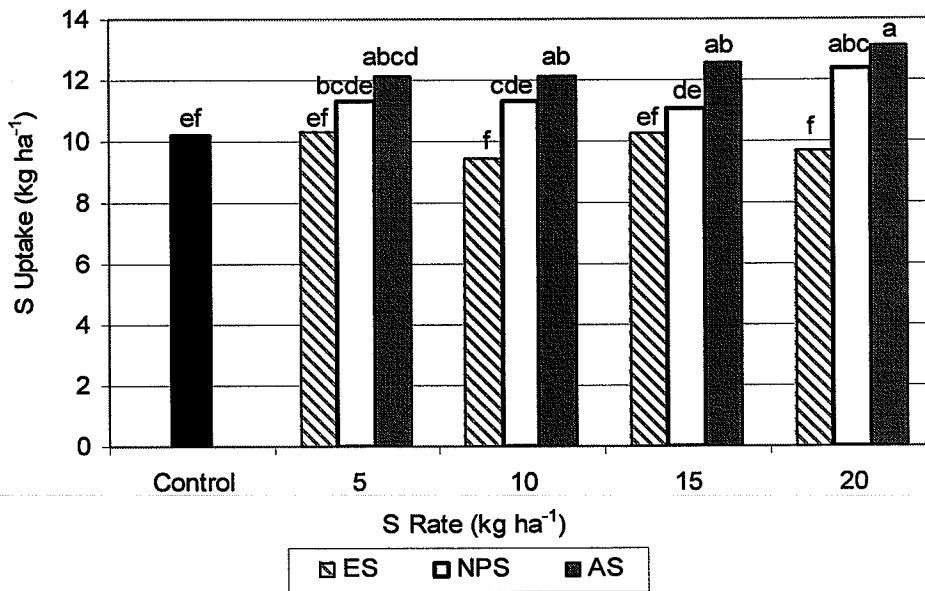


Figure 3.1 S uptake by canola at 40% flowering at different rates and sources of S fertilizer averaged across five site years ($P > 0.0188$).
 ES = Elemental Sulphur AS = Ammonium Sulphate

amount of S^o oxidized at this stage. Also, the intermediate values for S uptake from the NPS treatment (MAP + S^o < NPS < MAP + AS) appear to indicate that the S^o portion of the NPS fertilizer was not oxidized by midseason, either.

3.4.3.3 Harvest Seed Yields, Straw Yields, Nutrient Uptake and Seed Quality

At physiological maturity, canola seed yield, total above ground biomass, and total P and S fertilizer uptake were not significantly affected by the different fertilizer sources, S rates or interactions between S sources and rates (data not presented). The disappearance of differences observed in S uptake at midseason is not uncommon in western Canada. Moisture may become more limiting to S uptake than S supply by mid to late summer. In addition, sub-surface soils may have considerable reserves of SO₄²⁻ salts, and as S-deficient crops access the SO₄²⁻ at depth, differences due to S fertilizer source or rate may disappear (Anderson 1966; Bole and Pittman 1984; Grant 1991). Evidence that the canola in our experiment was not S deficient at maturity is provided by the seed S concentrations (%) for the control treatment (MAP only), which were generally above the critical seed S concentration of 0.35% (data not presented) established for double low rape seed by Pinkerton (1998). Hot, dry weather during flowering and pod filling in 2003 may have also minimized differences at maturity; as pod abortion was evident at all sites.

In contrast to the P and S fertilizer source study, (Section 3.4.2.3), S fertilizer source and rate had no consistent effect on green seed count (data not presented).

3.5 Summary and Conclusion

The objective of this study was to assess the agronomic performance of the NPS fertilizer in wheat and canola production in western Canada. The main agronomic research questions that we attempted to answer were compared to other commercial granular P and S fertilizers: 1) what is the risk of seed row toxicity of the NPS fertilizer; and 2) how plant available are the P and S from the NPS fertilizer?

The different sources and rates of P and S fertilizer, including the NPS fertilizer, had little or no effect on the emergence of wheat and canola with the fertilizer rates and the 50% seedbed utilization in our study. This confirms the results from a preceding growth chamber study where He et al. (2002) observed no difference in wheat and canola emergence between the NPS fertilizer and other granular fertilizers with similar P and S rates used in our experiment.

For both field studies at midseason, the wheat dry matter yield increase was similar for the NPS fertilizer and conventional MAP and S fertilizer sources while canola dry matter yield was not consistently increased by any of the P and S fertilizer sources or S rates. At physiological maturity, wheat seed and biomass yields were not increased by P and S fertilization. Similarly, canola seed and biomass yields were not increased by any of the other P and S fertilizer sources or S rates at maturity.

In the P and S fertilizer source study at midseason, the NPS fertilizer treatment increased P uptake by 10% in wheat and 46% in canola, relative to the control although neither was significantly greater than conventional MAP fertilizer, with or without S fertilizer. Apparent P fertilizer use efficiency was low in our experiment, up to 8% for

wheat, and up to 19% for canola. At maturity, the mean P uptake for the NPS treatment was similar to the other P fertilizer sources, 8 to 10% greater than the control. The apparent P fertilizer use efficiency in wheat was 8% for the NPS fertilizer. While with canola at maturity, we did not observe any differences between the P fertilizer sources. Furthermore, in the S fertilizer source by rate study there was no apparent benefit to P utilization in canola at either midseason or maturity as a result of increasing the S rate from 5 to 20 kg S ha⁻¹ for any of the P and S sources.

Theoretically, increasing the concentration or rate of SO₄²⁻ placed with the P fertilizer could increase P availability. The SO₄²⁻ may combine with Ca to form gypsum, leaving less Ca available to retain P; however, there was no evidence that the inclusion of AS and S^o in the NPS granule increased P availability in our experiments.

The efficiency of the S fertilizers appeared to be related to the proportion of SO₄²⁻ present in each of the S fertilizers. The MAP + AS and NPS fertilizer treatments both contain plant available SO₄²⁻ and produced greater S uptake than MAP + S^o in wheat and canola at midseason. The S fertilizer use efficiency for NPS fertilizer was approximately 4% in wheat, and 13 to 27% in canola. However, midseason S uptake by canola was not consistent in the P and S fertilizer source study; at one site, NPS was equivalent to MAP + AS, while at a second site, MAP + AS was significantly superior to NPS. When canola was fertilized at 10 kg S ha⁻¹, S uptake produced by the NPS treatments was intermediate to MAP + AS and MAP + S^o, while S uptake was similar to MAP + AS at 20 kg S ha⁻¹. At 20 kg S ha⁻¹, the rates of SO₄-S applied as NPS (10 kg SO₄-S ha⁻¹) may have been sufficient to meet the crop requirement for S without any contribution from S^o portion of the NPS fertilizer. There was no consistent S uptake response to NPS fertilizer or the

other S fertilizer treatments in wheat or canola at maturity and increasing the rate of fertilizer S had little to no effect on S uptake by canola in our experiment.

Throughout all the field experiments, there was no difference in S uptake between MAP and MAP + S^o treatments in either wheat or canola, irrespective of S rate. Given the lack of apparent oxidation from the MAP + S^o fertilizer, we speculate that the S^o portion of the NPS fertilizer did not oxidize to any significant extent. One of the reasons for the poor performance of S^o in these experiments may be the fundamental contradiction between the optimum placement of P and S^o fertilizers. Soil contact must be minimized with P fertilizers to limit P retention by Ca, Al and Fe; while conversely, S^o must have maximum soil-fertilizer contact to increase microbial oxidation (Grant et al. 2003b). Therefore, banding NPS fertilizer favours P fertilizer use efficiency, but reduces the potential for S^o oxidation.

Canola seed quality was improved with sulphate fertilizers in the P and S fertilizer source study. The percent green seed was lower with the NPS treatment than the control, MAP or S^o treatments but similar to AS treatments when the data from 2003 fertilizer source study were combined.

Overall, the NPS fertilizer appears to be an excellent source of P, equivalent to conventional MAP fertilizers. However, given the lack of S^o oxidation in our field study, the plant-available S supplied from the NPS fertilizer will probably be less than AS, but better than S^o fertilizers. In situations where soil supplies of S are not extremely low, the NPS fertilizer should provide adequate S for most crops and may possibly supply a slow-release form of S for long term improvements in S fertility. However, short term S fertilization rates may need to be higher than for pure sulphate fertilizers on soils that have low subsoil sulphate concentrations.

4. PHOSPHORUS AND SULPHUR AVAILABILITY OF HOMOGENEOUS NPS FERTILIZER IN TWO SUCCESSIVE CROPS GROWN IN A GROWTH CHAMBER

Key Words: spring canola (*Brassica napus*), P, S, homogeneous fertilizer, elemental S, S oxidation

4.1 Abstract

A controlled environment study was conducted to determine the capacity of a single application of granular homogeneous nitrogen (N), phosphorus (P) and sulphur (S) fertilizer to supply P and S to two successive canola crops. Fertilizer treatments consisted of NPS, monoammonium phosphate (MAP) + ammonium sulphate (AS), MAP + elemental S-bentonite (S^o), MAP only, AS only and a control (no P or S). The P and S uptake were measured for each crop 45 d after emergence. The soil was physically mixed and then incubated between crops to stimulate S^o oxidation. In the first crop, dry matter yield, apparent P fertilizer use efficiency and the apparent S fertilizer use efficiency of NPS fertilizer was 75%, 81% and 35% of that for MAP + AS, respectively. When the second canola crop was grown, the dry matter yield, and residual P and S uptake were highest with the NPS fertilizer, which was attributed to a nutrient carry-over effect. There was no evidence of S^o oxidation from the NPS fertilizer, though small amounts of oxidation occurred in the MAP + S^o treatment. When both harvests were combined, the apparent P fertilizer use efficiency was 56%, equivalent to MAP + AS even though the cumulative dry matter yield for NPS was only 83% of that for MAP + AS. In contrast to the high P fertilizer use efficiency, the apparent S fertilizer use efficiency for NPS was 46% of that for MAP + AS. This may indicate that all of the S supplied by NPS

originated from the SO₄-S portion of the fertilizer and that little or no oxidation occurred from the S^o-S portion of the NPS fertilizer, even after two simulated cropping seasons and favourable environmental conditions.

4.2 Introduction

Soil phosphorus (P) and sulphur (S) concentrations are often insufficient for optimal crop production in western Canada (Doyle and Cowell 1993a; Doyle and Cowell 1993b; Grant et al. 2001; Nyborg et al. 1999). The availability of P is particularly important for a crop early in the growing season. Severe P deficiency early in the cropping season may limit crop development and yield, even when sufficient P is supplied later in the season (Barry and Miller 1989). Therefore, P fertilizers, such as monoammonium phosphate (MAP), are often applied with or near the seed when the crop is planted. Confining the P fertilizer to a band, with or near the seed, also reduces the contact between the fertilizer and the soil and reduces P fixation. Furthermore, placement in or near the seed row positions the fertilizer in a zone with high root density. However, the efficiency of P fertilizer use by the crop is often low in the first crop after application. For example, in the year of application, a maximum of 20 and 50% of P may be utilized by wheat and canola respectively. The remaining fertilizer P may be moderately available to subsequent crops, increasing the utilization of the initial P fertilizer application (Selles 1993; Wagar et al. 1986).

Sulphur requirements are often less than P, though this varies with crop type. For example, Manitoba Agriculture recommends application of approximately 17.5 kg P ha⁻¹ and 20 kg S ha⁻¹ for canola production. The S is essential for amino acid and protein synthesis, which is especially important in high protein crops such as canola. Sulphur

deficiency can limit plant growth as well as decrease seed yield. Several S fertilization strategies may be used to correct soil S deficiencies; including: 1) application of ammonium sulphate (AS), which is readily plant available and is commonly used in canola production; and 2) application of elemental S (S°), which must be biologically oxidized to sulphate (SO_4^{2-}) before being absorbed by the crop.

Biological processes such as S° oxidation are sensitive to environmental conditions as well as fertilizer characteristics and management practices. Abundant soil moisture, adequate soil aeration, a neutral to alkaline soil pH and warm soil temperatures are favourable for biological S° oxidation (Germida and Janzen 1993). Also, any fertilizer characteristic or management practice that increases contact between S° and soil microorganisms increases the potential for oxidation. For example, reducing the fertilizer particle size increases the effective surface area of the particle exposed to the soil. However, method of S° application may also determine the degree of soil-fertilizer contact. For example, broadcast application followed by incorporation maximizes contact with oxidizing microbes, increasing SO_4^{2-} production. In contrast, confining S° fertilizer to a band generally restricts short-term oxidation due to minimal contact with the soil, cooler soil temperature at depth, and possible accumulation of toxic intermediate oxidation products (Germida and Janzen 1993). Oxidation of banded S° may be improved in the years following application if the soil is tilled (Lupwayi et al. 2001). Tillage disperses the fertilizer band, mixing the S° in a larger volume of soil and increasing contact with oxidizing bacteria (Janzen 1990). Overall though, SO_4 production from S° is slow compared to SO_4^{2-} release from ammonium sulphate fertilizer.

Cargill recently introduced a homogeneous granular NPS fertilizer comprised of monoammonium phosphate, ammonium sulphate and elemental S (13% N, 33% P_2O_5 ,

7.5% SO₄-S, 7.5% S^o-S). In a previous field experiment, we did not observe a release of plant available S from the S^o-S portion of the NPS fertilizer in the year of application. Therefore, the primary objective of this experiment was to determine the availability of the S^o-S portion of the NPS fertilizer to the initial and to the subsequent crop in a controlled environment. In addition, we wanted to determine the capacity of the NPS fertilizer to supply P over two cropping periods.

4.3 Materials and Methods

4.3.1 Growth Cabinet Procedures and Soil Description

A growth cabinet experiment was conducted in 2004 using Almassippi loamy sand (LS) and Pigeon Lake sandy loam (SL) soils from Elm Creek, MB, and Carman, MB respectively. The soil characteristics and soil nutrient levels are shown in Table 4.1.

Table 4.1 Physical and chemical characteristics of soils used in the growth cabinet experiment		
Characteristic	Soil	
Soil Series	Almassippi	Pigeon Lake
Taxonomic classification	Gleyed Rego Black	Gleyed Cumulic Regosol
Texture	Loamy sand	Sandy loam
Depth of soil layer (cm)	0-15	0-15
pH	8.1	6.3
EC (2:1 saturated paste)	0.4	1.0
OM (%)	2.2	3.7
Carbonates	None detected	None detected
NO ₃ ⁻ -N (mg kg ⁻¹)	12	5
Extractable P (Olsen P mg kg ⁻¹)	8	14
SO ₄ ²⁻ -S (mg kg ⁻¹)	4	4
Exchangeable Ca (mg kg ⁻¹)	3800	2300
Exchangeable Mg (mg kg ⁻¹)	450	470
Container Moisture Capacity ^z (%)	25	29

^z Estimate of field moisture capacity

In this study, NPS fertilizer was applied at a rate of 39.4 mg P and 41.0 mg S pot⁻¹, equivalent to 100 kg product ha⁻¹ (14.4 kg P ha⁻¹ and 15 kg S ha⁻¹). All other P and S treatments were applied at equivalent rates to the P and S in the NPS fertilizer. The

modest rate of S was below the 20 kg S ha⁻¹ recommended by Manitoba Agriculture, to keep each S treatment within the crop's responsive range. The six fertilizer treatments included: Control (no P or S); MAP (no S); AS (no P); MAP + S^o; MAP + AS; and NPS. The MAP + S^o treatment was compared to MAP alone as an estimate of potential S^o oxidation in the NPS treatment.

The top 15 cm of soil was collected from the respective sites, air-dried and passed through a 4.75 mm sieve. In total, 4.6 kg of air-dried soil (4.1 L) was added to 5 L cylindrical plastic pots with sealed bottoms, with a soil depth of 15 cm. The bottom layer of soil (2.3 kg) was placed into the pot; ammonium nitrate was added at a rate equivalent to 120 kg N ha⁻¹, plus additional ammonium nitrate was added to treatments that did not contain AS so that equal amounts of N were applied to each treatment. Potassium, equivalent to 51.5 kg K ha⁻¹; CuCl₂ · 2H₂O, equivalent to 10 ppm Cu ha⁻¹; and ZnCl₂, equivalent to 10 ppm Zn ha⁻¹ were also added onto the bottom layer soil. The second layer of soil (1.1 kg) covered the basal fertilizer treatments. The granular P and S fertilizer treatments were applied at random in a 10 cm wide band on top of the second layer of soil. The third layer of soil (800 g) was added and 15 canola seeds (*Brassica napus* L. cv. DKL 34-55 Helix[®]) were placed on the surface and covered with the fourth layer of soil (400 g).

The experimental design was a randomized complete block and all treatments were replicated three times in each of two growth chambers, for a total of six replicate. The temperature of the growth chambers was 20°C for 16 hours during the day, with a light intensity of 600 lum ft⁻², and 10°C for 8 hours at night. The pots were weighed on a daily basis and water was added to maintain the soil moisture content at 70% to 90% of container-soil moisture capacity (Klute 1986). After emergence, six seedlings were

selected and the remaining plants were removed. The above ground plant material was harvested 45 days after half of the successful canola seedlings emerged (He et al. 2002). Plant samples were dried at 65°C and ground to pass a 2 mm sieve. The N and S concentration of the ground plant tissue was determined by AGVISE Laboratories, Northwood, ND. Total N concentration was determined by dry combustion with a Perkin Elmer N Analyzer, while total S was determined by wet digestion and analyzed with an ICP (Jones 2001). Tissue P concentration was determined using the wet oxidation digestion (Parkinson and Allen, 1975) and the molybdenum blue method of measurement on a spectrophotometer (Murphy and Riley, 1962). One standard sample and one blank were analyzed with every 14 tissue samples for quality assurance.

After the first crop was harvested, the effect of intensive tillage was simulated on all treatments by passing the soil through a 2.54 cm mesh screen and the soil was returned to each respective pot. The soil moisture was maintained at 75% to 95% of container moisture capacity and the soils were incubated in the growth chamber at 20°C for 27 days, to simulate the heat units, base 10°C, which accumulate in southern Manitoba between mid-August and early May. After 14 days, intensive tillage was simulated a second time, and then incubated for another 13 days. A third intensive tillage operation simulated soil disturbance at planting.

A second crop of canola was seeded without additional P and S fertilization to test the availability of residual P and S fertilizer and the potential S^o oxidation from the S^o fertilizer sources applied to the first crop. Fifteen canola seeds were placed into four slits, 2 cm deep by 10 cm long and the soil was packed lightly to close the slits and increase seed-soil contact. Potassium nitrate, at a rate of 100 kg N ha⁻¹, was applied to the soil surface and watered in; no additional P or S was applied. Growth chamber conditions

were identical to the first portion of the experiment. Above ground plant material was harvested 45 days after emergence, dried, ground and analyzed as before. A final intensive tillage treatment was applied to all pots, to thoroughly mix the soil prior to final soil sampling.

4.3.2 Soil Sampling and Analysis

To measure S^o oxidation and total SO₄-S availability, soil samples were taken from each pot after the first, third and final simulated tillage treatments. A 2 cm diameter soil core, containing approximately 20 g of soil, was taken from each pot. Sulphate was extracted with 0.001M CaCl₂ with a 1:2 soil to water ratio (McKreague 1981). A Technicon Autoanalyzer II Single-Channel Colorimeter was used to determine the SO₄-S concentration in the extract using the automated methylthymol blue method (Ellis 2004; Greenberg et al. 1998).

4.3.3 Data Analyses

Statistical analyses of the growth chamber experiment were conducted using the General Linear Model procedure of the Statistical Analysis System (SAS) package (SAS 1999). Descriptive statistics were used to test the error variance and the skewness (γ) of the data (Webster 2001) using SAS Proc Univariate. Most of the crop data had approximately normal distributions and skewness less than 0.5 (data not presented). Statistical analyses of transformed data did not produce results that were different from the non-transformed data; therefore, the untransformed data was used in all analyses.

A simple RCB ANOVA model and a Fisher's protected least significant difference test were used to test the effect of the fertilizer sources in the two soils. A

probability level (α) of 0.05 was used as the significance threshold for crop and soil $\text{SO}_4\text{-S}$ measurements across the fertilizer treatment means. Single degree of freedom contrasts were used to analyze $\text{SO}_4\text{-S}$ concentrations at different sampling times.

4.4 Results and Discussion

4.4.1 Dry Matter Yield

First Crop

Phosphate and sulphur fertilization significantly increased dry matter yield of the initial crop of canola at flowering (Table 4.2); however, the response to S fertilization was much greater than the response to P. In both soils, MAP + AS fertilizer increased dry matter accumulation by 253 to 282% relative to the control (no P or S). The AS only and NPS treatments produced equivalent yields in both soils; however, the dry matter yield for both treatments were 21 to 25% lower than for the MAP + AS treatment. Phosphate fertilization significantly increased dry matter yield relative to the control in the Almassippi LS but not in the Pigeon Lake SL soil because the latter soil had high initial concentrations of available P (Table 4.1). In a growth chamber study, He et al. (2002) found that NPS produced canola dry matter yields equivalent to MAP + AS; however, their P and S rates were 300% higher than rates used in this study and may have masked the limited availability of S^0 in NPS fertilizer. In our experiment, S^0 in either the MAP + S^0 or NPS did not increase yields compared to the MAP treatment in either soil, which is similar to results reported by Noellemeyer et al. (1981) and He et al. (2002). Therefore, it appears that the majority of the yield response to S may be attributed to SO_4^{2-} fertilization in both soils.

Table 4.2 Effect of granular P and S fertilization on dry matter yield in two successive crops of canola harvested 45 d after emergence (dry matter basis)

Fertilizer Treatment	Dry Matter Yield								
	First Crop			Second Crop			First + Second Crop		
	Almassippi LS	Pigeon Lake SL	Mean	Almassippi LS	Pigeon Lake SL	Mean	Almassippi LS	Pigeon Lake SL	Mean
	(g pot ⁻¹)								
Control	5.70 ^d	5.02 ^c	5.36	3.01 ^d	3.99 ^b	3.50	8.71 ^e	9.01 ^d	8.86 ^c
MAP	7.13 ^c	5.97 ^c	6.55	3.74 ^{cd}	4.44 ^b	4.09	10.87 ^d	10.42 ^{cd}	10.64 ^d
AS only	16.75 ^b	13.93 ^b	15.34	4.13 ^c	8.03 ^a	6.08	20.89 ^c	21.96 ^b	21.42 ^c
MAP & S ^o	7.21 ^c	6.25 ^c	6.73	4.21 ^c	5.31 ^b	4.76	11.41 ^d	11.49 ^c	11.49 ^d
MAP & AS	21.79 ^a	17.72 ^a	20.75	5.71 ^b	7.92 ^a	6.81	27.49 ^a	27.57 ^a	27.57 ^a
NPS	16.27 ^b	13.46 ^b	14.86	6.67 ^a	9.18 ^a	7.93	22.93 ^b	22.79 ^b	22.79 ^b
LSD ($\alpha = 0.05$)	1.20	1.28	^y	0.96	1.35	^y	1.42	1.90	1.21
ANOVA	<i>df</i>					<i>P > F</i>			
Fertilizer	5	<0.0001*	<0.0001*	<0.0001*	<0.0001*		<0.0001*	<0.0001*	
Block(Chamber)	5	0.0645	<0.0001*	0.3496	0.0104*		0.0892	<0.0001*	
Residual C.V. (%)		8.12	10.07	17.56	17.58		7.01	9.29	
Fertilizer	5		<0.0001			<0.0001			<0.0001*
Block(Chamber)	5		<0.0001*			0.7289			<0.0001*
Soil	1		<0.0001			<0.0001			0.6605
Soil x Fertilizer	5		0.0422*			0.0054*			0.8504
Residual C.V. (%)			8.99			19.69			8.65

^{a-c} Mean values followed by the same letter (within columns) are not significantly different at $P > 0.05$.

^y LSD is not reported because there was a Soil x Fertilizer interaction.

* Significant at $P < 0.05$.

Second Crop

In the second crop after P and S fertilization, the residual effect of the SO₄-S fertilizer increased dry matter yield of canola at flowering, but residual P fertilizer produced little to no increase (Table 4.2). The NPS fertilization treatment produced the greatest dry matter yield in the Almassippi LS. In the Pigeon Lake SL, the NPS treatment also appeared to increase dry matter more than the other treatments, but the difference was not significant. The greater yield of the second crop in the residual NPS treatment may have been due to higher concentrations of residual fertilizer P and SO₄ nutrients remaining in the soil after the first crop was harvested (this will be discussed in more detail in the S utilization section).

Cumulative Dry Matter Yield for Both Crops

When both harvests were combined, the trend in total dry matter yield for each treatment was similar in each soil (Table 4.2). The NPS fertilizer increased cumulative yield by 157% relative to the control when averaged across both soils, which was significantly less than MAP + AS but significantly greater than MAP + S^o and AS only treatments. The total dry matter yield produced by MAP + S^o was numerically, but not significantly, higher than MAP, indicating that little or no S^o oxidation occurred but was not sufficient to increase yield over the course of the two cropping periods.

4.4.2 S Utilization

First Crop

The tissue S concentrations (%) for all the treatments were well below the critical concentration of 0.25% established by Bailey (1986) when the canola was harvested 45 d

after emergence (data not presented). However, the NPS treatment did not exhibit visual S deficiency symptoms until 40 d after emergence, when purpling of the leaf margins and reduced flowering were noted.

Sulphate fertilization increased S uptake by flowering canola in both Almassippi LS and Pigeon Lake SL soils (Table 4.3). The fertilizer treatments produced similar S uptake trends in both soils. Sulphur uptake from the NPS treatment was lower than from MAP + AS but higher than from MAP or MAP + S°. However, S uptake from the NPS treatment was lower than hypothesized. We had hypothesized that the S fertilizer use efficiency (S uptake for treatment minus the S control, divided by fertilizer S applied) of the NPS fertilizer would be approximately 50% lower than MAP + AS because only 50% of the S is in the immediately available SO_4^{2-} form, similar to results reported by He et al. (2002). However, fertilizer S uptake for the NPS fertilizer was only 35% of that for MAP + AS in our study (Table 4.4). The lower than expected S utilization in the NPS treatment may be attributed to a higher proportion of SO_4 -S reacting with soil Ca to form less soluble products. For example, the reactive Ca^{2+} in the soil might precipitate a larger proportion of SO_4 -S from the NPS fertilizer than from MAP + AS simply because the rate of SO_4 -S application is 50% lower for the NPS fertilizer and the degree of soil contact with the fertilizer granules is much greater. In addition, the NPS fertilizer contains small quantities of CaSO_4 in addition to the $(\text{NH}_4)_2\text{SO}_4$ (AS); when two sources of a common anion are added to the soil, common ion interference may have suppressed the solubility of CaSO_4 . However, according to the manufacturers, the concentration of CaSO_4 in the NPS fertilizer is low (< 0.1%) and therefore does not explain the lower than expected S uptake in the first crop.

Table 4.3 Effect of P and S fertilization on S accumulation in two successive crops of canola harvested 45 d after emergence

Fertilizer Treatment	S Uptake								
	First Crop			Second Crop			First + Second Crop		
	Almassippi LS	Pigeon Lake SL	Mean	Almassippi LS	Pigeon Lake SL	Mean	Almassippi LS	Pigeon Lake SL	Mean
	(mg pot ⁻¹)								
Control	4.09 ^c	4.06 ^d	4.08 ^d	2.36 ^b	2.57 ^c	2.47 ^d	6.45 ^c	6.63 ^c	6.54 ^d
MAP	5.03 ^c	4.38 ^d	4.70 ^d	2.75 ^b	2.73 ^c	2.74 ^{cd}	7.78 ^c	7.11 ^{de}	7.44 ^d
AS only	18.14 ^a	16.08 ^b	17.47 ^b	4.65 ^a	5.12 ^a	4.89 ^{ab}	22.79 ^a	21.92 ^b	22.36 ^b
MAP & S ^o	5.04 ^c	4.43 ^d	4.74 ^d	2.99 ^b	3.62 ^b	3.30 ^c	8.03 ^c	8.05 ^d	8.04 ^d
MAP & AS	19.17 ^a	20.91 ^a	20.04 ^a	4.40 ^a	5.12 ^a	4.76 ^b	23.57 ^a	26.03 ^a	24.80 ^a
NPS	10.44 ^b	9.48 ^c	9.96 ^c	5.09 ^a	5.90 ^a	5.50 ^a	15.54 ^b	15.38 ^c	15.46 ^c
LSD ($\alpha = 0.05$)	2.28	0.79	1.24	0.93	0.85	0.65	2.51	1.26	1.52
ANOVA	<i>df</i>		<i>P > F</i>						
Fertilizer	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*	
Block(Chamber)	0.3423	0.0051*	0.1109	0.3856	0.1817	0.0109*			
Residual C.V. (%)	18.59	6.61	21.10	17.09	2.51	7.48			
Fertilizer			<0.0001*			<0.0001*			<0.0001*
Block(Chamber)			0.5980			0.7055			0.7341
Soil			0.3921			0.0156			0.7118
Soil x Fertilizer			0.1854			0.7977			0.2979
Residual C.V. (%)			14.89			20.27			13.13

^{a-c} Mean values followed by the same letter (within columns) are not significantly different at $P > 0.05$.

^y LSD is not reported because there was a Soil x Fertilizer interaction.

* Significant at $P < 0.05$.

Table 4.4 The apparent S fertilizer uptake from a single application of S^x added as commercial granular fertilizers for to successive crops of canola harvested 45 d after emergence

Fertilizer Treatment	Apparent Fertilizer S Uptake						
	First Crop			First + Second Crop			
	Almassippi LS	Pigeon Lake SL	Mean	Almassippi LS	Pigeon Lake SL	Mean	
	(mg pot ⁻¹)						
AS only	14.05 ^a	12.74 ^b	13.40 ^b	16.34 ^a	15.29 ^b	15.81 ^a	
MAP + S ^o	0.01 ^c	0.05 ^d	0.03 ^d	0.25 ^c	0.94 ^d	0.60 ^c	
MAP + AS	14.14 ^a	16.54 ^a	15.34 ^a	15.79 ^a	18.92 ^a	17.36 ^a	
NPS	5.41 ^b	5.11 ^c	5.26 ^c	7.76 ^b	8.26 ^c	8.01 ^b	
LSD ($\alpha = 0.05$)	2.59	0.86	1.52	2.69	1.17	1.80	
ANOVA	<i>df</i>	<i>P > F</i>					
Treatment	3	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Block(Chamber)	5	0.0314	0.0331	0.0665	0.0242	0.0038	0.2637
Soil	1			0.6990			0.2000
Soil x Treatment	3			0.1069			0.1488
Residual C.V. (%)		25.09	8.14	21.58	21.78	8.75	20.80

^{a-d} Mean values followed by the same letter (within columns) are not significantly different at $P > 0.05$.

^x 41 mg S pot⁻¹.

* Significant at $P < 0.05$.

Sulphur uptake was similar for MAP and MAP + S^o treatments, indicating that little or no S^o oxidation occurred in the first canola; therefore, we speculate that little or no oxidation occurred in the NPS treatment. He et al. (2002) also concluded that the S^o in NPS fertilizer did not oxidize during the duration of an incubation study. They observed no significant changes in water extractable sulphate, pH or electrical conductivity during a 9 week soil incubation study. Minimal S^o oxidation is frequently observed in the first crop after application, especially when S^o fertilizer is restricted to a seed-placed band (Chien et al. 1988; Janzen and Bettany 1986; Janzen and Karamanos 1991; Malhi and Johnston 2000). Reducing the contact between microorganisms and fertilizer granules decreases potential S^o oxidation (Germida and Janzen 1993).

Second Crop

The soil in each treatment was mixed and incubated between the first and second crop to simulate the effect of intensive tillage as well as heat accumulation in southern Manitoba between mid-August and early May. The accumulated heat, soil disturbance and adequate moisture should have provided conditions favourable for biological oxidation of S^0 . However, all of the residual S treatments exhibited S deficiency symptoms. The control, MAP and MAP + S^0 treatments had severe chlorosis, stunted growth, purpling and cupping of leaves, petioles and stems, and little or no flower production. The treatments containing NPS, MAP + AS and AS only exhibited less severe symptoms, although flowering was decreased and no pods formed.

The mean S uptake by the second crop from NPS for both soils was 27% higher than from MAP + AS (Table 4.3). However, the amount of weak $CaCl_2$ extractable soil-S from the NPS treatment was similar, if not slightly lower, than from the MAP + AS treatment (Table 4.5). Therefore, the higher S uptake produced by the NPS treatment may be a result of a gradual release of SO_4^{2-} from the NPS fertilizer carried-over from the first crop and not S^0 oxidation during the incubation period. In the first crop, S uptake in the NPS treatment was 35% of that from MAP + AS, 15% lower than expected, potentially leaving that portion of SO_4 -S in a slowly available form. The availability of S^0 from the MAP + S^0 was generally non-existent or very small.

The MAP + S^0 treatment produced consistently lower residual S uptake than the treatments containing AS only, and S uptake values were similar to MAP alone. The addition of S^0 increased S uptake in the Pigeon Lake SL soil but only in the second crop, and not when both crops and/or both soils were combined (Table 4.3, Table 4.5). In this

Table 4.5 0.001 M CaCl₂ extractable soil SO₄-S after 28 days of incubation as a measure of crop available SO₄-S

Fertilizer Treatment	Incubation Time After First Crop						
	Almassippi LS		Pigeon Lake SL		Mean		
	Day 1	Day 28	Day 1	Day 28	Day 1	Day 28	
	(mg pot ⁻¹)						
Control	7.68 ^c	6.44 ^b	7.13	6.53 ^d	7.41 ^c	6.49 ^b	
MAP	7.91 ^{bc}	6.58 ^b	7.36	6.58	7.64 ^c	6.58 ^b	
AS only	9.43 ^a	8.19 ^a	8.42	7.50 ^{ab}	8.93 ^a	7.87 ^a	
MAP + S ^o	7.50 ^c	6.58 ^b	7.91	7.22 ^{bc}	7.73 ^{bc}	6.90 ^b	
MAP + AS	8.83 ^{ab}	8.14 ^a	9.52	8.05 ^a	9.15 ^a	8.10 ^a	
NPS	8.42 ^{abc}	7.59 ^a	8.51	7.73 ^{ab}	8.46 ^{ab}	7.68 ^a	
LSD ($\alpha = 0.05$)	1.06	0.69	ns	0.65	0.83	0.49	
ANOVA	<i>df</i>	<i>P > F</i>					
Treatment	5	0.0098*	<0.0001*	0.0024*	0.0003*	0.0001*	<0.0001*
Chamber	2	0.1604	0.7945	0.9335	0.0138*	0.3376	0.1266
Trt x Chamber	5	0.1536	0.4262	0.7453	0.1219	0.5139	0.1687
Block(Chamber)	4	0.0004*	0.3140	0.9673	0.6103	0.0124*	0.7951
Site	1					0.5216	0.9275
Trt x Site	5					0.3159	0.2030
Residual C.V. (%)		10.78	8.00	11.15	7.43	12.27	8.17

^{a-c} Mean values followed by the same letter (within columns) are not significantly different at $P > 0.05$.

^y LSD is not reported because there was a Soil x Fertilizer interaction.

* Significant at $P < 0.05$.

soil, S uptake in the MAP + S⁰ was 0.89 mg pot⁻¹ higher than for MAP alone (equivalent to only 2.2% of applied S⁰), indicating that only a small amount of S⁰ may have oxidized (Table 4.3). The three intensive soil mixing operations during the incubation period should have increased S⁰ dispersion by increasing the contact with oxidizing microbes as compared to the first crop of canola where the fertilizer was placed in a 10 cm wide band. Janzen (1990) reported that soil mixing, or disturbance, increased S⁰ oxidation in a growth chamber study; however, in our experiment, S uptake from the well-mixed S⁰ treatments was very low. Even though small amounts of S⁰ may have oxidized subsequent to the first crop, the rate of oxidation appears to have been too slow to provide the crop with sufficient S to support canola growth in the second crop following application.

Cumulative S Uptake for Both Crops

The cumulative S uptake for each fertilizer treatment was calculated by combining the S uptake from the first and second crops (Table 4.3). The total S uptake for the NPS treatment was 46% of that for MAP + AS treatment when averaged across the two crops and the two soils. The S uptake in the NPS treatment was still slightly less than expected, but approximately 50% that of the MAP + AS treatment. We had hypothesized that the cumulative S uptake from NPS fertilizer would include the 50% SO₄²⁻ portion plus some oxidized S from the S⁰ fraction, and, therefore, should have been at least 50% of the S uptake from the MAP + AS treatment. However, the S⁰ portion of the NPS fertilizer did not appear to contribute plant available S, probably due to lack of oxidation. We speculated that S⁰ oxidation in the NPS was low due to restricted S⁰ oxidation observed in the MAP + S⁰ treatment. Total S uptake from MAP + S⁰ was not significantly higher

than that from MAP alone. He et al. (2002) also reported that little or no S° oxidation occurred in the NPS fertilizer in similar studies. In our controlled environment experiment, adequate moisture, heat and soil disturbance should have favoured S° oxidation; however, oxidation was minimal and not sufficient to provide either crop with substantial quantities of S. We assumed that populations of S° oxidizing microorganisms were non-limiting in both soils used in the experiment (Lawrence and Germida 1991b) and that the availability of S° would be determined by the characteristics and management of the NPS fertilizer. However, we did not measure the number of S° oxidizing organisms in these soils.

4.4.3 P Utilization

First Crop

Initially, treatments without P fertilization displayed P deficiency symptoms, including dark green, small leaves and stunted growth; however, the symptoms had largely disappeared by the sixth true leaf stage in the AS only treatment. Canola is very efficient at acquiring P from the soil and as the root size increased, the AS only treatment plants may have absorbed sufficient P for the visual deficiency symptoms to disappear (Soper and Kalra 1969).

Phosphate uptake increased significantly when P and SO_4 fertilizers were added to both the Almassippi LS and Pigeon Lake SL soils. The MAP + AS and NPS treatments produced significantly greater P uptake than the other P and/or S fertilizer combinations (Table 4.6) presumably due, in part, to the dry matter yield response to applied SO_4 -S. The fertilizer P uptake values (treatment minus the control) for NPS were slightly lower than MAP + AS, though only significantly lower in the Pigeon Lake SL soil (Table 4.7).

The apparent P fertilizer use efficiency for the NPS and MAP + AS treatments were statistically similar, at 36% and 44% respectively, averaged over both soils. This was more than twice as high as for MAP only or MAP + S°. The high P fertilizer use efficiency for the MAP + AS and NPS treatments was probably a response to SO₄ fertilization. Sulphate fertilization increased canola growth and increased uptake of both fertilizer P (MAP compared to MAP + AS in both soils) and soil P (control compared to AS only in the Pigeon Lake SL soil) (Table 4.6).

Second Crop

In the second crop, the visual P deficiency symptoms were more difficult to identify due to S deficiency symptoms that were also present. The residual fertilizer P uptake in the NPS treatment was 197 to 263% greater than the MAP + AS treatment in the Pigeon Lake SL and Almassippi LS, respectively (P uptake for NPS minus control, divided by MAP + AS) (Table 4.6). In both soils, MAP, AS only, and MAP + S° also produced equivalent or greater P uptake than MAP + AS. The improved P uptake of all of these treatments relative to MAP + AS may have been due to greater fertilizer P carry-over from the first to second crop. Sulphur deficiency was the main limitation to plant growth in these soils. Since the MAP + AS treatment produced the highest dry matter yield and P uptake in the first crop, less residual fertilizer was available for the second crop from this treatment.

Cumulative P Uptake for Both Crops

When both crops were combined, the total P uptake for both crops was the highest for the NPS fertilizer; though it was not statistically greater than for MAP + AS in either soil (Table 4.6, Table 4.7). He et al. (2002) reported similar P uptake responses in canola

Table 4.6 Effect of P and S fertilization on P accumulation in two successive crops of canola harvested 45 d after emergence

Fertilizer Treatment	P Uptake								
	First Crop			Second Crop			First + Second Crop		
	Almassippi LS	Pigeon Lake SL	Mean	Almassippi LS	Pigeon Lake SL	Mean	Almassippi LS	Pigeon Lake SL	Mean
	(mg pot ⁻¹)								
Control	12.97 ^c	14.33 ^e	13.65	4.87 ^c	11.10 ^c	7.99	17.84 ^d	25.42 ^d	21.63
MAP	21.07 ^b	18.69 ^d	19.88	8.27 ^a	15.70 ^b	11.99	29.34 ^b	34.40 ^c	31.87
AS only	18.64 ^b	24.29 ^c	21.46	4.03 ^c	15.81 ^b	9.92	22.67 ^c	40.09 ^b	31.38
MAP & S ^o	20.94 ^b	20.27 ^d	20.60	8.59 ^a	16.58 ^b	12.58	29.53 ^b	36.85 ^{bc}	33.19
MAP & AS	30.36 ^a	31.73 ^a	31.04	6.64 ^b	16.56 ^b	11.60	37.00 ^a	48.29 ^a	42.64
NPS	28.48 ^a	27.41 ^b	27.94	9.53 ^a	21.88 ^a	15.71	38.01 ^a	49.29 ^a	43.65
LSD ($\alpha = 0.05$)	2.63	1.95	^y	1.41	4.06	^y	3.09	4.25	^y
ANOVA	<i>df</i>			<i>P > F</i>					
Fertilizer	5	<0.0001*	<0.0001*	<0.0001*	0.0008*		<0.0001*	<0.0001*	
Block(Chamber)	5	0.0158*	<0.0001*	0.0028*	0.7719		0.6887	0.1013	
Residual C.V. (%)		10.03	7.21	16.94	20.99		8.94	9.16	
Fertilizer	5			<0.0001		<0.0001			<0.0001
Block(Chamber)	5			<0.0001*		0.5796			0.0328*
Soil	1			0.1245		<0.0001			<0.0001
Soil x Fertilizer	5			<0.0001*		0.0270*			0.0001*
Residual C.V. (%)				8.16		22.15			9.01

^{a-d} Mean values followed by the same letter (within columns) are not significantly different at $P > 0.05$.

^y LSD is not reported because there was a Soil x Fertilizer interaction.

* Significant at $P < 0.05$.

Table 4.7 The apparent P fertilizer uptake from a single application of P^x added as commercial granular fertilizers for two successive crops of canola harvested 45 d after emergence

Fertilizer Treatment	Apparent Fertilizer P Uptake						
	First Crop			First + Second			
	Almassippi LS	Pigeon Lake SL	Mean	Almassippi LS	Pigeon Lake SL	Mean	
	(mg pot ⁻¹)						
MAP	8.11 ^b	4.37 ^c	6.24 ^c	11.50 ^b	8.97 ^b	10.24 ^b	
MAP + S ^o	7.97 ^b	5.95 ^c	6.96 ^c	11.69 ^b	11.42 ^b	11.56 ^b	
MAP + AS	17.40 ^a	17.40 ^a	17.40 ^a	19.16 ^a	22.86 ^a	21.01 ^a	
NPS	15.52 ^a	13.08 ^b	14.30 ^b	20.17 ^a	23.87 ^a	22.02 ^a	
LSD ($\alpha = 0.05$)	3.04	1.69	2.01	3.68	4.85	3.12	
ANOVA	<i>df</i>	<i>P > F</i>					
Treatment	3	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*	<0.0001*
Block(Chamber)	5	0.0960	0.0271*	0.7468	0.8899	0.0758	0.3424
Soil	1			0.0061*			0.2969
Soil x Treatment	3			0.3166			0.1295
Residual C.V. (%)		20.15	13.43	21.66	19.15	23.50	23.21

^{a-c} Mean values followed by the same letter (within columns) are not significantly different at $P > 0.05$.

^x 39.4 mg P pot⁻¹.

* Significant at $P < 0.05$.

fertilized with NPS and MAP + AS. The AS contained in both fertilizers may have increased growth and total P uptake by providing improved SO₄²⁻ nutrition (He et al. 2002) and/or may have increased the availability of P by competitively binding with soil Ca to form gypsum (Kumaragamage et al. 2004). As a result, the apparent P fertilizer use efficiency was high, at 54 and 56% for MAP + AS and NPS fertilizers respectively, when both soils were combined (Table 4.7). The remaining P and S fertilizers did not respond similarly between sites, apparently due to differences in soil P reserves. In the very P deficient Almassippi LS, MAP fertilization increased P uptake relative to the control and AS only treatments. There was a P uptake response to P fertilization in the less P deficient Pigeon Lake SL soil, but there was a larger P uptake response when AS only was added to this soil compared to the more P deficient Almassippi LS soil. At both

sites, P uptake was improved by addition of SO₄ fertilizer, probably due in large part to the dry matter yield response to S.

4.5 Summary and Conclusions

The primary objective of the growth chamber study was to evaluate the availability of P and S from a single application of NPS fertilizer to two successive canola crops.

When NPS fertilizer was applied to S deficient soils, dry matter yields were 25% lower than those produced by MAP + AS fertilizer. The uptake of P in the NPS treatment was similar to slightly lower than that of the MAP + AS treatment. However, the apparent S fertilizer use efficiency for the NPS treatment was approximately 35% of that for MAP + AS, indicating that the initial availability of the SO₄-S portion of the NPS fertilizer was less than that of AS. The reasons for the relatively low availability of SO₄-S portion of the NPS fertilizer are not known.

When a second crop of canola was planted in soil where the previous crop was fertilized with P and S, the residual NPS fertilizer produced the largest dry matter yield, P uptake and S uptake at the flowering stage. The greater uptake of residual P and S is likely due to a nutrient carry-over effect due to a lack of uptake by the first crop. The NPS treatment removed less P and S than the MAP + AS treatment in the first crop; therefore, more P and S may have been carried-over to the second crop resulting in greater dry matter accumulation. In spite of intensive soil disturbance, adequate moisture and warm temperatures, S⁰ oxidation and S uptake from the MAP + S⁰ was minimal in

the second crop; therefore, we speculate that S^0 oxidation in the banded NPS fertilizer may also be minimal after the two cropping periods in this experiment.

The cumulative canola dry matter yield (first plus second crop) produced by the NPS fertilizer was 17% lower than for the MAP + AS treatment. Phosphate fertilizer use efficiency of the NPS fertilizer was the highest among treatments at 56%, though this was not statistically higher than MAP + AS. Therefore, the lower yield was attributed to less SO_4 -S in the NPS fertilizer. Total S fertilizer use efficiency (crop 1 + 2) from the NPS fertilizer was only 46% of that of MAP + AS, nearly equivalent to the proportion of SO_4 -S present in the NPS fertilizer.

Overall, the findings of the growth chamber study were similar to the 2 year field study. The NPS fertilizer is an excellent source of P with the availability of P at least equivalent to MAP; however, there was no apparent benefit to P fertilizer utilization with the addition of N and S to the granule. He et al. (2002) also reported that NPS was equivalent to MAP in supplying P for crop uptake. Overall, S uptake in our growth chamber study was approximately half that of AS when uptake for both crops was combined, and given the minimal oxidation from the MAP + S^0 fertilizer, we speculate that only the SO_4^{2-} portion of the NPS fertilizer was available for crop uptake. Reasons for the unexpectedly low efficiency of SO_4 -S uptake from the NPS fertilizer in the initial crop are not known. Therefore, in soils with very low S concentrations and/or when crops with high S requirements are grown, NPS fertilizer applied at normal rates of P and S may not supply sufficient plant available S for optimum yields.

5. GENERAL DISCUSSION

Crop production in western Canada often requires the addition of P and S fertilizer to correct nutrient deficiencies or imbalances. Deficiencies of P and S may be a result of the inherent lack of fertility of the parent material from which the soil developed; removal of nutrients with agricultural crops; land management; short-term deficiencies caused by unfavorable environmental conditions; or a combination of these factors. Conventional P and S fertilizer are often mixed together and applied with or near the seed at planting to maximize the efficiency of the fertilizer and the planting operation. In contrast with the NPS fertilizer, N, P and S are supplied within a single homogeneous granule, and the combination of these nutrients may have beneficial effects on nutrient availability as compared to conventional fertilizers.

The first objective of the study was to determine the potential fertilizer toxicity risk associated with seed-placed NPS fertilizer. In the two-year field study, seed-placed NPS fertilizer did not decrease emergence of wheat or canola relative to the other fertilizer sources when applied at rates equivalent to 19.2 kg P and 20 kg S ha⁻¹. In the growth chamber study, the effect of fertilizer toxicity on canola was not studied because the fertilizer and seed were separated from each other.

The second objective of the study was to determine the availability of P from the NPS fertilizer. In other studies, the chemical and biological availability of fertilizer P has been improved by placing SO₄²⁻ and/or NH₄⁺ in intimate contact with P (Hammond 1997; He et al. 2002; Kumaragamage et al. 2004; Singh et al. 1998). However, no such

improvements were observed in our field study. In general, crops grown in the field trials were responsive to P fertilization early in the growing season, but largely unresponsive by physiological maturity. In the growth chamber, crops responded to P fertilization; however, crops in the growth chamber were harvested prior to maturation. In field trials, fertilization with NPS increased dry matter yield and P uptake in wheat at anthesis compared to the control treatment; however, the increase in yield and P uptake was not significantly greater than with MAP fertilizer only. There were no increases in yield or P uptake observed in canola with any of the P fertilizers regardless of fertilizer S rate or growth stage. Most differences due to fertilizer treatment had disappeared in both wheat and canola by physiological maturity. As at midseason, the total P uptake by wheat was often highest with the NPS fertilizer, but the uptake was not statistically greater than that from MAP fertilizer alone. In canola, there were no differences in total P uptake at maturity, but canola is extremely efficient at utilizing both soil and fertilizer P (Strong and Soper 1974b).

The ready availability of P from the NPS fertilizer in the growth chamber study confirmed the results of the field studies. Due to inadequate supplies of plant available S, dry matter yields in the NPS fertilizer treatment were lower than for MAP + AS. However, P uptake and apparent fertilizer use efficiency were at least as great as for MAP +AS. This suggests that NPS is at least equivalent to MAP as a granular source of P. However, the growth chamber study did not demonstrate a statistically significant benefit of combining N and S with P within a homogeneous granule compared to separate granules of MAP +AS.

The third objective of the study was to determine the availability of S from the $\text{SO}_4\text{-S}$ and $\text{S}^\circ\text{-S}$ portions of NPS fertilizer. Generally, all sources of S fertilizer had little

or no effect on dry matter yields of wheat and canola grown in the field experiments.

Sulphur uptake in wheat and canola from the NPS fertilizer was usually similar to MAP + AS in our field trials. On average, S uptake from the NPS fertilizer was equivalent to S uptake from MAP + AS during flowering in wheat and canola. However, any differences between the NPS fertilizer and the other MAP and S combinations disappeared by physiological maturity.

The S deficient soils used in the growth chamber study more clearly defined the availability of the $\text{SO}_4\text{-S}$ and $\text{S}^\circ\text{-S}$ portions of the NPS fertilizer. For the first crop, dry matter yields with the NPS fertilizer were lower than with MAP + AS but greater than with MAP or MAP + S° . When NPS fertilizer was applied to the soil, crop uptake of S was only 35% of that for MAP + AS. We had hypothesized that the uptake of S from the NPS fertilizer could be as low as 50% of that for MAP + AS, which may indicate that only the $\text{SO}_4\text{-S}$ portion of the NPS fertilizer is immediately available to the crop. The reasons for the unexpectedly low availability of $\text{SO}_4\text{-S}$ from NPS for the first crop are not known. After a second crop was grown with only residual P and S fertilizer, S uptake from the NPS fertilizer improved and was only slightly lower than 50% of S uptake from MAP + AS. As with the field study, there was no indication from the growth chamber study that $\text{S}^\circ\text{-S}$ portion of the NPS fertilizer was oxidizing, even after two canola crops were grown. Numerous other studies have also reported that subsurface placed or banded S° fertilizers have little or no oxidation in the year of application (Chien et al. 1988; Grant et al. 2000; Grant et al. 2003b; Solberg and Nyborg 1986). Tillage and soil mixing often improves dispersion of banded S° (Hagstrom 1986; Nuttall et al. 1990); however, soil mixing between cropping periods in our experiment did not result in significant oxidation

of S⁰-S in the MAP + S⁰ treatment, and may indicate that oxidation was not significant in the NPS treatment.

Overall, the NPS fertilizer is relatively safe to emerging wheat and canola seedlings at rates up to 20 kg S ha⁻¹ and 50% seed bed utilization. Although the availability of P from the NPS fertilizer appears to be at least equivalent to MAP, we speculate that the availability of S may be restricted to the SO₄-S portion of the fertilizer. Considering the lack of oxidation in the MAP + S⁰ fertilizer, the 50% of the S that is in the S⁰ form in the NPS fertilizer, may not be available for at least the first two crops after application. Furthermore, the SO₄-S portion of the NPS fertilizer does not appear to be as quickly available as hypothesized. Therefore, additional AS fertilizer may need to be added to the NPS fertilizer when the soils are very S deficient and crops have high S requirements. Repeated application of the NPS fertilizer may improve long-term S fertility of the soil when the S⁰ portion of the fertilizer eventually oxidizes (Janzen and Bettany 1984a; Lettl et al. 1981), although the exact timing of this release was not determined.

Part of the challenge in maximizing the agronomic effectiveness of the NPS fertilizer is that fundamentally there is an inherent contradiction in fertilizer placement strategies when attempting to maximize both fertilizer P and S⁰ efficiency in the NPS granule. Soil contact with S⁰ must be maximized to ensure adequate contact with oxidizing organisms (Hagstrom 1986; Nuttall et al. 1990). In contrast, P fertilizer-soil contact must be minimized to limit soil retention reactions and to ensure early and efficient uptake; therefore, P should be placed with the seed (Bailey et al. 1980; Bailey and Grant 1990; Grant et al. 2001; Nyborg and Hennig 1969).