

**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