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1. Project title and ADF file number.

ADF Project Number 20120015/SPCDB AGR1303/SaskCanola/WGRF AGR1302 "Transformations and Fate of Seed-Placed Sulfur Fertilizers in Saskatchewan Soils" Final Report February 2016

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4. Abstract/ Summary: *This must include project objectives, results, and conclusions for use in publications and in the Ministry database. Maximum of 300 words in lay language.*

The form of sulfur (S) fertilizer can influence its behavior and crop response. Field studies were conducted in 2013 and 2014 along with a growth chamber study to evaluate five sulfur fertilizer forms (ammonium-sulfate, ammonium-thiosulfate, gypsum, potassium-sulfate and elemental-sulfur) applied in the seed-row with wheat, canola and yellow peas, at 20 kg S ha^{-1} alone, and in combination with monammonium fertilizer (MAP) at 20 kg P_2O_5 ha^{-1}, in Brown and Black Chernozem and Gray Luvisol Saskatchewan soils. The fate of fertilizer was evaluated by measuring soil available sulfate and phosphate in the seed-row, crop sulfur and phosphorus uptake and grain yields. The soils used in the study were marginally deficient in sulfur. Canola was most responsive to the sulfur fertilizers, with limited response of wheat and pea to S fertilization in the majority of cases. Sulfate and thiosulfate forms were effective in enhancing short-term soil available sulfate supplies in the seed-row, along with crop sulfur uptake and yield compared to the elemental-sulfur fertilizer form which releases sulfate slowly by oxidation. Gypsum maintained the highest seed-row sulfate concentrations over time, a consequence of its slightly soluble nature which reduced the sulfate leaching. Most of the S uptake occurred over the period from one to four weeks after seeding and fertilizing. Combination of sulfur fertilizer with MAP may provide some enhancement of phosphate availability, but effects were typically small. Using the Canadian Light Source synchrotron, thiols and ester sulfates were identified as short-term products formed from seed-row placed sulfur fertilizers in prairie soils that likely originate from microbial immobilization of fertilizer sulfur. The CLS spectra provided some evidence of elemental S oxidation to sulfate occurring over time. XANES spectroscopy revealed that one week after fertilizer application, P species present in the seed-row included similar proportions of adsorbed and poorly crystalline phosphate forms in both Brown and Black Chernozem Saskatchewan soils. However, fertilization with sulfate was noted to increase the conversion from calcium phosphate to adsorbed P forms in the Brown soil.

5. Introduction: *Brief project background and rationale.*

Sulfur (S) fertilizers have become an important part of the fertilizer mix for Saskatchewan growers. While the use of S fertilizers is a common practice for production of canola and other *Brassicae* crops, it is also becoming more widely recommended for pulse and cereal crops as well (Malhi et al., 2009). There are a wide variety of fertilizer S sources available to growers (Schoenau and Malhi, 2009). Sulfur sources include completely soluble ammonium and potassium sulfate, insoluble elemental S that must be oxidized to sulfate to be plant available, liquid ammonium thiosulfate and gypsum (calcium sulfate) which is slightly soluble. While several studies have looked at the relative plant availability of different sulfur fertilizer sources by examining the end result of application through crop yield response and plant sulfur uptake (e.g., Malhi et al., 2005a), few investigations have been conducted to reveal the specific transformations that different S fertilizers undergo in the soil from the time of application to crop uptake. Understanding the fate of the S fertilizer applied is important when attempting to predict the relative performance of different sulfur fertilizers for different crops under varying application conditions.

Recent research on S fertilization by Qian et al. (2012) has focused on tolerance to various rates and forms of sulfur and phosphorus (P) fertilizer placed in the seed-row of different canola species and varieties. They also suggested species and class specific recommendations for maximum safe-rates of starter fertilizer in seed-row according to the different forms of S and P fertilizer used. Differences in tolerance and plant availability of the P and S fertilizers have been observed in different studies (Malhi et al., 2005a; Malhi et al., 2009; Schoenau and Malhi, 2009). The next step is to examine how different S fertilizer forms affect plant available sulfate and phosphate when applied alone and in combination with monoammonium phosphate (MAP) fertilizer in the seed-row.

The general objective of this study was to evaluate the effectiveness of different fertilizer forms as sources of plant available S to crops. The fate of the fertilizers is assessed by following the supply and content of available sulfate in the seed-row after application of the fertilizer and measuring crop S uptake. Three soils were chosen for the study to provide a contrast in soil properties, and provide representation of the different agricultural regions of Saskatchewan. The specific objectives of the study were to investigate in these soils, under controlled environment conditions and in the field, the effects of five different S fertilizer forms applied alone and in combination with MAP on supply rates and concentrations of plant available sulfate and phosphate in the seed-row following fertilizer application, crop (canola, pea, wheat) uptake of S and P, and yield. Another goal of the study was to develop and employ new techniques for using the Canadian Light Source synchrotron to study the fate of fertilizer in soil. To this end, sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy was used to identify S species in soils from the three sites receiving S fertilizer. Synchrotron-based P K-edge X-ray absorption near-edge structure spectroscopy was used to identify the different P species present in soil samples obtained from the seed-row in the presence and absence of sulfate fertilizer, as little is known about how SO_4^{2-} may influence the P fertilizer reaction products formed in soil.

6. Methodology: *Include approaches, experimental design, methodology, materials, sites, etc.*

Controlled Environment Chamber Study

Soils for the controlled environment chamber experiment were collected in May, 2013 from the surface horizon of farm fields that included an Orthic Brown Chernozem located near Central Butte, SK. (N 50.71 W 106.40), an Orthic Gray Luvisol located near Star City, SK. (N 52.78 W 104.32), and an Orthic Gray-Back Chernozem located near Melfort, SK. (N 52.81 W 104.51). Soil from each site was excavated from the 0-15 cm depth using a shovel, spread and dried at 25 °C for six days, mixed and sieved to remove rocks and large clumps of stubble and roots, and then stored until the controlled environment chamber experiment setup commenced in August 2013.

The controlled environment chamber experiment was set up as a randomized complete block design (4 treatment replicates) in plastic trays measuring 0.73 m in length, 0.16 m in width and 0.16 m in depth. The trays were divided, using plastic section dividers, into 4 equally sized compartments measuring 0.0292 m^2. A weight of air-dried soil of 3.3 kg was added to each compartment. Each compartment was then fertilized with a treatment using the fertilizers and rates listed in Table 1.

Table 1. Fertilizer treatments and rates used in the controlled environment chamber study and 2013 and 2014 field studies.

Treatment	N	P_2O_5	S
		(kg ha^{-1})	
Control	100§		
Control + MAP†	100	20	
Ammonium sulfate (21-0-0-24)	100		20
ATS‡	100		20
Gypsum (0-0-0-16.5; Ca 20%)	100		20
Potassium sulfate (0-0-44-17)	100		20
Elemental sulfur (0-0-0-90)	100		20
AS + MAP	100	20	20
ATS + MAP	100	20	20
Gypsum + MAP	100	20	20
Potassium sulfate + MAP	100	20	20
Elemental sulfur + MAP	100	20	20

†Monammonium phosphate (11-51-0).
‡ATS 12-0-0-26 formulation applied in 2013 field study.
15-0-0-20 formulation applied in 2014 field study.
§N fertilizer applied in wheat and canola crops only in 2013 and 2014 field studies.

Urea fertilizer (46-0-0) was side banded 2.0 cm from the seed for the wheat and canola crops in every compartment at a rate of 100 kg N ha^{-1} of added fertilizer N, including urea plus the nitrogen added in other treatments (e.g. AS, ATS, MAP). The S (and where applicable, P) treatment fertilizer was placed in the seed-row with the seed. No urea fertilizer added to the yellow pea crop as this crop was to fix its own nitrogen, and the pea seed was inoculated with a rhizobium accordingly. Rows measuring 0.18 m in length and 0.015 m in depth were drawn in the center of each compartment using a spoon type opener. Sulfur and where applicable, P fertilizer was spread along the length of each row. In the case of ATS fertilizer, the liquid was dribbled to the side of the seeds to avoid direct contact of the liquid fertilizer with the seed. Seed was spread three-quarters of the row length, leaving the last one-quarter length portion of the row with fertilizer but without seed to allow placement of vertically inserted *in situ* anion resin membrane Plant Root Simulator™ (PRS) probes (Western Ag Innovations, Saskatoon, SK) in an area without plant growth to measure soil supply rates of SO_4-S and PO_4-P.

Hard red spring wheat (*Triticum aestivum* var. Waskeda), canola (*Brassica napus* var Liberty Link 150) and yellow pea (*Pisum sativa* var. CDC Meadow) were each grown separately for 56 days in each of the three soil types. Trays were placed in a controlled environmental chamber and were rotated each week during the four week growth period. Growth chamber conditions were maintained on a 18/6 h day-night length cycle. The day and night temperature of the growth chamber was 23 and 18 °C, respectively. Relative humidity was maintained at 50 % and light intensity was maintained at 615.6 µmol m^{-2} s^{-1}. The plants were watered regularly with distilled water to maintain them at 85 % field capacity throughout the growth period.

Soil samples were collected at one week (7 days), four weeks (28 days) and eight weeks (56 days) of plant growth. Soil micro-cores measuring 1.0 cm in diameter and 4.0 cm in length were obtained from each compartment in the seed-rows where the plants were growing. This size of soil core was used so as to not negatively affect plant development during the 56 day growth period. Soil cores from each replicate of each treatment were frozen at -20 °C until analysis. Soil samples were thawed, ground to pass a 2.0 mm sieve and analyzed for extractable SO_4-S using the 0.01 *M* calcium chloride method (Tabatabi, 1982) and extractable P using the modified Kelowna method (Qian et al., 1994). Anion exchange resin membrane probes (PRS Probes™, Western Ag Innovations, Saskatoon, SK) were removed at the end of the 56 day growth period, washed free of adhering soil, eluted with 0.5 *M* HCl to remove adsorbed ions and analyzed for SO_4-S and PO_4-P (Qian and Schoenau, 2002; Qian et al., 2008). Crops were harvested at eight weeks (56 days) (Fig. 1) after seeding by removing above ground biomass from each treatment, oven drying for 48 hrs at 40 °C, then weighed and ground to ≤ 2.0 mm using a Wiley Mill plant grinder. Plant S concentration in the dried, ground plant material was determined using a LECO™ 1225CR Sulfur Analyzer and P concentration using sulfuric acid digestion (Cresser and Parsons, 1979) followed by automated colorimetry.

Fig. 1. Yellow pea plants after eight weeks growth in a controlled environment chamber growing in Brown Chernozem soil from Central Butte along with PRS™ anion resin probes measuring nutrient ion: sulfate-sulfur, phosphate-phosphorus and nitrate-nitrogen supply rates in March, 2014.

2013 and 2014 Field Studies

In 2013 and, again in 2014, three field sites were located in Central Butte, Melfort and Star City areas to represent typical farm fields in the Brown, Gray- Black and Gray soil-climatic zones of Saskatchewan. A farm field near Central Butte SK (N: 50° 43.124; W: 106° 24.552) was selected to represent a typical loamy textured Brown Chernozem, a field research site near Star City SK (N: 52° 47.538; W: 104° 18.171) was selected to represent a typical Gray Luvisol, and a field research site near Melfort SK (N: 52° 48.827; W: 104° 30.738) was selected to represent a typical loamy textured Black Chernozem. The 2013 and 2014 sites were all on farm fields that had been in cereal-legume-oilseed rotations in the past, and were well managed, with fertilizer applications made in previous years that were usual for the areas selected for this study. Soils in 2013 were also considered marginal in soil S. The soil at the Brown Chernozem (Central Butte) site in 2014 was moderately deficient in phosphorus (P) and slightly deficient in sulfur (S) according to soil test. The Gray Luvisol (Star City) site soil was moderately deficient in P and low in S, while the soil at the Black Chernozem (Melfort) site was slightly deficient in P and deficient in S according to soil testing conducted in spring 2014, prior to seeding and fertilizer application treatments (Table 2).

Table 2. Basic soil properties of: Brown Chernozem (Central Butte); Gray Luvisol (Star City) and Black Chernozem (Melfort) sites (0-15cm depth) that were used in the sulfur field studies in 2013 and 2014.

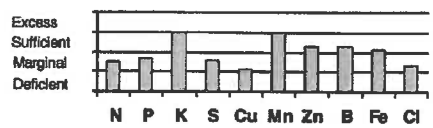
Brown Chernozem, Central Butte, SK
2013 Site

SOIL TEST CHARACTERISTICS

Depth (inches)	Texture	pH 1S:2W	E.C. 1S:2W (mS/cm)	E.C. Calc.Sat.Extr. (mS/cm)	Salinity Rating	Organic Matter %	NH_4-N (lb/ac)	Calculated CEC meq/100g	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Base Saturation Ca (% of CEC)	Mg (% of CEC)	K (% of CEC)	Na (% of CEC)
0-6	Loam	6.8	0.1	0.2	Non Saline											

SOIL TEST NUTRIENT LEVELS

Depth (inches)	NO_3-N	P	K	SO_4-S	Cu	Mn	Zn	B	Fe	Cl
	lb/ac									
0-6	19	48	>600	11	1.3	25.4	5.1	2.6	40	11



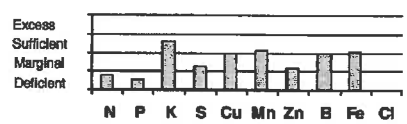
2014 Site

SOIL TEST CHARACTERISTICS

Depth (inches)	Texture	pH 1S:2W	E.C. 1S:2W (mS/cm)	E.C. Calc.Sat.Extr. (mS/cm)	Salinity Rating	Organic Matter %	NH_4-N (lb/ac)	Calculated CEC meq/100g	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Base Saturation Ca (% of CEC)	Mg (% of CEC)	K (% of CEC)	Na (% of CEC)
0-6	Clay Loam	8.1	0.1	0.2	Non Saline											

SOIL TEST NUTRIENT LEVELS

Depth (inches)	NO_3-N	P	K	SO_4-S	Cu	Mn	Zn	B	Fe	Cl
	lb/ac									
0-6	4	11	423	9	1.4	3.5	0.6	1.3	19	



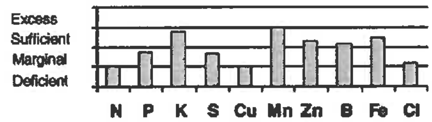
2013 Gray Luvisol, Star City, SK
2013 Site

SOIL TEST CHARACTERISTICS

Depth (inches)	Texture	pH 1S:2W	E.C. 1S:2W (mS/cm)	E.C. Calc.Sat.Extr. (mS/cm)	Salinity Rating	Organic Matter %	NH_4-N (lb/ac)	Calculated CEC meq/100g	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Base Saturation Ca (% of CEC)	Mg (% of CEC)	K (% of CEC)	Na (% of CEC)
0-6	Loam	6.7	0.2	0.5	Non Saline											

SOIL TEST NUTRIENT LEVELS

Depth (inches)	NO_3-N (lb/ac)	P (lb/ac)	K (lb/ac)	SO_4-S (lb/ac)	Cu (lb/ac)	Mn (lb/ac)	Zn (lb/ac)	B (lb/ac)	Fe (lb/ac)	Cl (lb/ac)
0-6	31	50	506	20	1.2	33.3	5.2	1.5	127	9



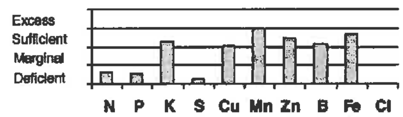
2014 Site

SOIL TEST CHARACTERISTICS

Depth (inches)	Texture	pH 1S:2W	E.C. 1S:2W (mS/cm)	E.C. Calc.Sat.Extr. (mS/cm)	Salinity Rating	Organic Matter %	NH_4-N (lb/ac)	Calculated CEC meq/100g	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Base Saturation Ca (% of CEC)	Mg (% of CEC)	K (% of CEC)	Na (% of CEC)
0-6	Loam	6.5	0.1	0.2	Non Saline											

SOIL TEST NUTRIENT LEVELS

Depth (inches)	NO_3-N (lb/ac)	P (lb/ac)	K (lb/ac)	SO_4-S (lb/ac)	Cu (lb/ac)	Mn (lb/ac)	Zn (lb/ac)	B (lb/ac)	Fe (lb/ac)	Cl (lb/ac)
0-6	20	11	297	4	1.6	20.1	6.7	1.6	203	



Black Chernozem, Melfort, SK

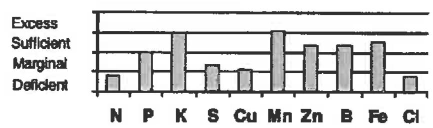
2013 Site

SOIL TEST CHARACTERISTICS

Depth (inches)	Texture	pH 1S:2W	E.C. 1S:2W (mS/cm)	E.C. Calc.Sat.Extr. (mS/cm)	Salinity Rating	Organic Matter %	NH_4-N (lb/ac)	Calculated CEC meq/100g	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Base Saturation Ca (% of CEC)	Mg (% of CEC)	K (% of CEC)	Na (% of CEC)
0-6	Loam	6.4	0.8	1.8	Non Saline											

SOIL TEST NUTRIENT LEVELS

Depth (inches)	NO_3-N (lb/ac)	P (lb/ac)	K (lb/ac)	SO_4-S (lb/ac)	Cu (lb/ac)	Mn (lb/ac)	Zn (lb/ac)	B (lb/ac)	Fe (lb/ac)	Cl (lb/ac)
0-6	24	59	>600	14	1.3	44.7	6.2	2.9	148	6



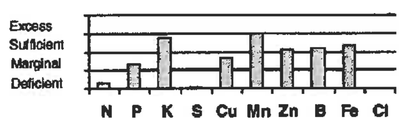
2014 Site

SOIL TEST CHARACTERISTICS

Depth (inches)	Texture	pH 1S:2W	E.C. 1S:2W (mS/cm)	E.C. Calc.Sat.Extr. (mS/cm)	Salinity Rating	Organic Matter %	NH_4-N (lb/ac)	Calculated CEC meq/100g	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)	Base Saturation Ca (% of CEC)	Mg (% of CEC)	K (% of CEC)	Na (% of CEC)
0-6	Clay Loam	6.8	0.1	0.2	Non Saline											

SOIL TEST NUTRIENT LEVELS

Depth (inches)	NO_3-N (lb/ac)	P (lb/ac)	K (lb/ac)	SO_4-S (lb/ac)	Cu (lb/ac)	Mn (lb/ac)	Zn (lb/ac)	B (lb/ac)	Fe (lb/ac)	Cl (lb/ac)
0-6	11	34	500	2	1.0	32.9	2.0	2.1	108	



In the spring of 2013 treatments (Table 1) were applied that were the same forms and rates of fertilizer S and P placed in the seed-row along with same blanket application rate of N as utilized in the controlled environment tray studies described previously. In the spring of 2014 treatments (Table 1) were applied that were the same forms and rates of fertilizer S and P placed in the seed-row along with same blanket application rate of N as utilized in the 2013 field studies (Table 1).

The experimental design for both the 2013 and 2014 seasons was set up as a randomized complete block experimental design with four blocks of replicate treatments for each of the: hard red spring wheat (*Triticum* spp.; Waskeda var.), canola (*Brassica napus*; Liberty link LL 150) and yellow pea (*Pisum sativum*; CDC Meadow var.) crops at each of the Brown Chernozem, Gray Luvisol and Black Chernozem sites. A single row seeder was used to seed and seed-place the S and P fertilizer treatments in plots measuring 3.0 m X 1.0 m in mid-May 2013 and mid-May 2014. Seed-row spacing was set at 25.4 cm for all three crops at all three field research sites in both 2013 and 2014. Wheat and yellow pea seeds were placed at 2.5 cm under the soil surface and canola seeds were placed at 1.0 cm under the soil surface. When applying liquid ATS fertilizer, a separate liquid fertilizer tube was attached to the single row seeder where the ATS was dribble banded into the soil immediately next to the coulter opener. A challenge encountered in the field with the liquid ATS fertilizer was keeping the liquid fertilizer away from the seeds in the seed-row. This was easy to accomplish in the controlled environment tray study but some liquid ATS fertilizer inadvertently splashed and/or coated the seed itself in the field. This was especially a problem in 2014. Furthermore, in 2014, due to availability issues, a different formulation of ATS (15-0-0-20) had to be used which was lower in S analysis and higher in N content than the ATS (12-0-0-26) formulation used in the 2013 field study. This necessitated a higher volume of ATS to be used in 2014 and may explain why some seedling injury to canola and yellow pea was observed in plots amended with this product in 2014.

As in the controlled environment tray study and in the 2013 and 2014 field seasons, soil sample cores using a micro-coring device 1.0 cm in diameter and to approximately the depth of seeding and fertilizer S and P placement (2.0 cm) was removed from the seed-rows of each treatment in each of the three crops at: 1 week (7 days), 4 weeks (28 days) and 8 weeks (56 days) after seeding was conducted. The micro-soil cores were frozen after field collection, thawed and air-dried, ground with a wooden rolling pin, and analyzed for extractable SO_4^{2-}-S and extractable PO_4^{2-}-P content. Selected soil-micro cores were also collected and were used for XANES synchrotron spectroscopy to identify S and P species in the seed row. The collected soil samples were air-dried, ground with a wooden rolling pin, and analyzed for S forms by S K-edge XANES spectroscopy. The S XANES spectra of selected soil samples was conducted at the Soft X-ray Micro-characterization beamline (SXRMB) at the Canadian Light Source (CLS), Saskatoon, Canada in February, May and October of 2014. At crop maturity at the three Saskatchewan sites in mid-August, using a hand sickle, 1.0 m row length above ground plant samples were harvested from each treatment plot in each of the wheat, canola and yellow pea crops at all three field sites. Plant samples were used for assessment of total plant biomass, grain yield and straw biomass. Plant samples were dried, weighed to obtain a total plant biomass and threshed to separate grain and straw. During the threshing operation, a straw sub-sample from each threshed plant sample was ground to ≤ 2.0 mm using a Wiley Mill for S and P analysis. Threshed grain samples were cleaned, weighed and a sub-sample was ground to a fine powder using a Retsch ZM 200 for S and P analysis. Grain and straw samples were digested for P analysis using a sulfuric acid digest. Both grain and straw samples were analyzed using a LECO™ S-144DR S analyzer.

XANES Synchrotron Spectroscopy

The S XANES spectra of selected soil samples collected in 2013 was conducted at the Soft X-ray Micro-characterization beamline (SXRMB) at the Canadian Light Source (CLS), Saskatoon, Canada in February, May and October of 2014. Selected soil-micro cores were collected and used for XANES synchrotron spectroscopy to identify S and P species in the seed row in spring of 2015. The collected soil samples were air-dried, ground with a wooden rolling pin, and analyzed for S forms by S K-edge XANES spectroscopy. The S XANES spectra of all the soil samples from all three sites and S standards were determined at the Soft X-ray Micro-characterization Beamline (SXRMB) at the Canadian Light Source (CLS), Saskatoon, Canada (Fig. 2). In the procedure used, a small amount of air-dried, ground composite soil sample from each treatment, or ground S standards, was thinly spread over double-sided C tape, mounted on a stainless steel sample holder and placed in the vacuum chamber. Soil sample spectra were collected in partial fluorescence yield (PFY) mode to improve detection limits over total fluorescence or electron yield measurements, and the spectra of S reference standards were collected in total electron yield (TEY) mode to avoid self-absorption effects due to high concentration. Spectra were collected from 2430-2520 eV with a constant dwell time of 4.0 s. Multiple spectra were collected and averaged as required to obtain an adequate signal to noise ratio for analysis. XANES spectra were analyzed using WinXAS 3.1. software. The averaged XANES spectra were background subtracted to the pre-edge region using a first-order polynomial fit. In this report, different S fertilizer treatments for the three different Saskatchewan sites are presented.

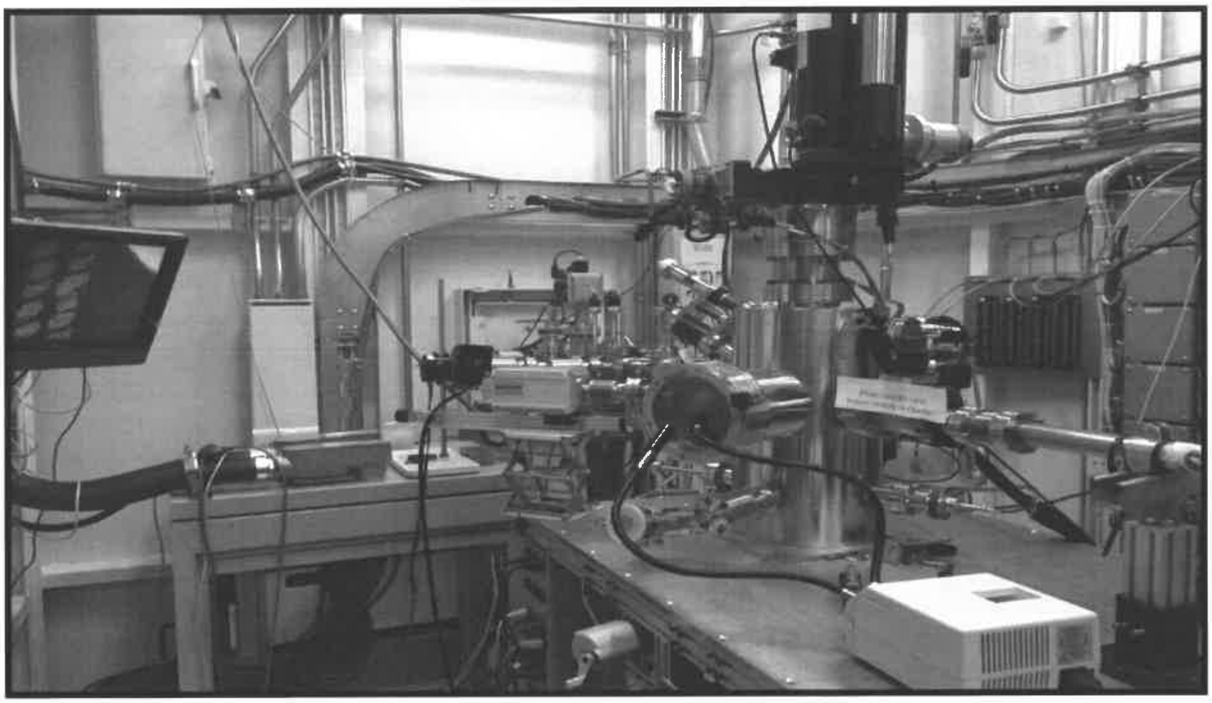


Fig. 2. End station of the SXRMB at Canadian Light Source, Saskatoon, SK used to measure soil S speciation in the collected samples.

The P XANES spectra of all the P fertilized soil samples and P standards were determined at the Soft X-ray Micro-characterization Beamline (SXRMB) at the Canadian Light Source (CLS), Saskatoon, Canada (Fig. 3). In the procedure used, a small amount of air-dried, ground composite soil sample from each treatment, or ground P standards, was thinly spread over double-sided C tape, mounted on a stainless steel sample holder and placed in the vacuum chamber.

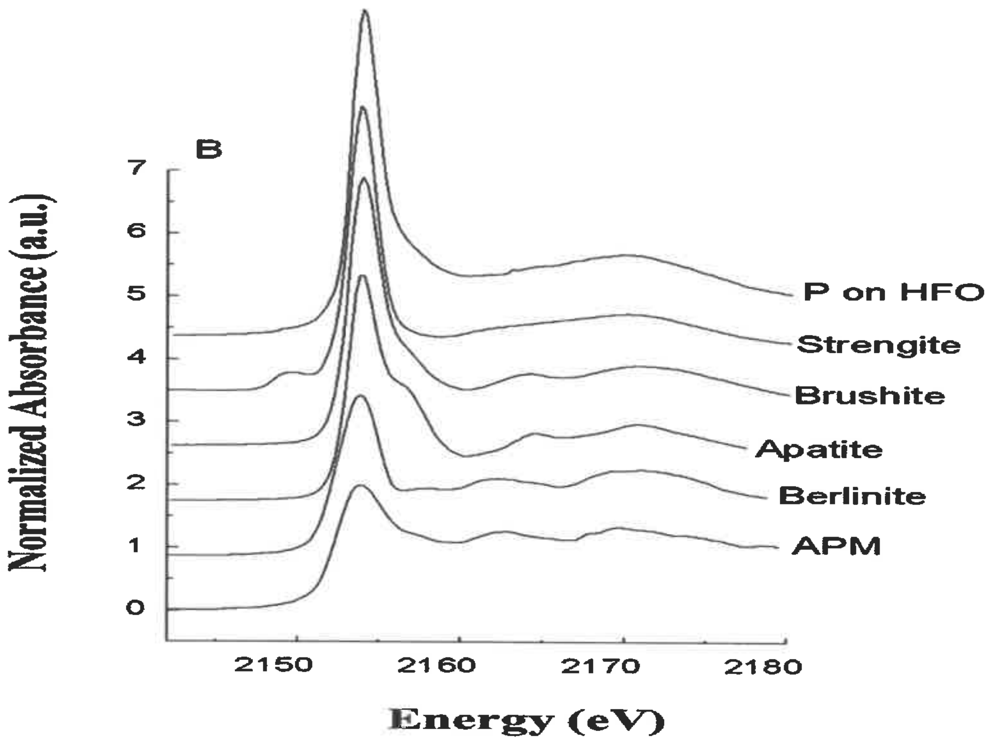


Fig. 3. Normalized P K-edge X-ray absorption near edge structure (XANES) spectra of different P reference compounds: phosphate adsorbed on an Fe oxide (P on HFO), strengite ($FePO_4.2H_2O$), brushite ($CaHPO_4.2H_2O$), apatite [$Ca_5(PO_4)_3(OH,F,Cl)$], berlinite ($AlPO_4$), APM ($NH_4H_2PO_4$) used in linear combination (LC) fitting.

Soil sample spectra were collected in partial fluorescence yield (PFY) mode to improve detection limits over total fluorescence or electron yield measurements, and the spectra of P reference standards were collected in total electron yield (TEY) mode to avoid self-absorption effects due to high concentration. Spectra were collected from 2100-2200 eV with a constant dwell time of 4.0 s. Multiple spectra were collected and averaged as required to obtain an adequate signal to noise ratio for analysis. XANES spectra were analyzed using WinXAS 3.1. software. The averaged XANES spectra were background subtracted to the pre-edge region using a first-order polynomial fit.

7. Research accomplishments: *(Describe progress towards meeting objectives. Please use revised objectives if Ministry-approved revisions have been made to original objectives.)*

Objectives	Progress

1) To determine the forms and plant availability of sulfur formed over a period of weeks to months following application to soils under controlled environment and field conditions.	The controlled environment growth chamber tray studies with the wheat, canola and yellow pea crops on the Brown Chernozem, Gray Luvisol and Black Chernozem soils have been completed and the soil and plant samples analyzed, according to schedule. Data interpretation and analyses of the data from the controlled environment chamber studies is completed. The 2013 and 2014 field experiments with the three crops grown at the three Saskatchewan field research sites: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) have been completed. A 2015 field experiment at the Brown Chernozem (Central Butte) site, not planned in the initial proposal, but included to provide some additional long-term data was completed. Plant and soil sample laboratory analysis for S and P have been completed. Analysis of soil samples collected from the study for S and P speciation has been completed at the Canadian Light Source (CLS) XANES beamline.
2) To assess the interaction of sulfur placed in the soil in a band together with phosphorus fertilizer.	This has been addressed through the successful completion of the controlled environment and two years of field experiments with three crops grown on the three soils and measurements of available S and P in the soil over time and crop S and P uptake. Also this has been assessed through the application of the XANES spectroscopy to reveal S and P forms in the soils with and without added sulfate fertilizer at the Brown and Black Chernozem sites.
3) To develop and employ novel methodology using the new SXRMB beamline at the Canadian Light Source.	We have been successful in developing methodology for using the SXRMB XANES beamline at the CLS for the assessment of soil sulfur and phosphorus forms in samples collected from seed-row fertilizer bands in the field. For example we have been able to trace the oxidation of elemental S over time using this technique, and in 2014 work, we were able to identify different organic and inorganic S fertilizer reaction products produced in the seed-over over 8 weeks in the field. In 2015, we completed the assessment of P forms arising in the soil seed-row with and without S fertilizers added.
add additional lines as required	

8. Discussion: *Provide discussion necessary to the full understanding of the results. Where applicable, results should be discussed in the context of existing knowledge and relevant literature. Detail any major concerns or project setbacks.*

Controlled Environment Chamber Study

Crop biomass yield

The effects of application of seed row placed S and P fertilizer treatments on above-ground biomass yield (g pot^{-1}) of wheat, canola and yellow peas after eight weeks of growth on Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils is shown in Table 3. Application of the S and P forms had variable effects on wheat, canola and yellow pea biomass yield for all three soils. Significant ($P \leq 0.05$) yield enhancement was found in the gypsum plus MAP treatment for wheat and canola in all three soils. The ATS plus MAP treatment also frequently yielded higher than the control.

Table 3. Mean biomass yield (g pot^{-1}) of wheat, canola and pea grown in fertilizer amended Brown Chernozem (Central Butte), Gray Luvisol (Star City), and Black Chernozem (Melfort) soils.

Treatment*	WHEAT (g pot^{-1})			CANOLA (g pot^{-1})			YELLOW PEA (g pot^{-1})		
	Central Butte	Star City	Melfort	Central Butte	Star City	Melfort	CentralButte	Star City	Melfort

Control	16.5 bc#	8.1 ef	12.3 de	9.3 c	10.9 e	10.9 c	21.1 a	15.4 bc	16.8 b
MAP	16.1 bc	14.7 b	12.4 de	11.8 c	16.6 cd	12.2 c	20.2 a	21.8 a	17.1 b
AS	11.8 f	5.6 f	12.0 e	23.5 ab	17.7 bcd	26.6 a	13.6 d	16.9 ab	21.3 a
AS + MAP	12.8 ef	10.3 de	17.0 ab	23 ab	19 abc	26.2 a	15.9 cd	17.8 ab	21.3 a
ATS	17.6 ab	13.1 bcd	12.1 e	23 ab	18.6 abc	20.9 b	20.4 a	19.7 ab	17.0 b
ATS + MAP	18.5 ab	14.2 bc	15.8 abc	24.8 a	16.9 cd	25.2 ab	15.7 cd	17.8 ab	14.3 bc
Gyp	13.9 def	11.1 cde	15.0 bc	20.0 b	16.0 d	23.8 ab	16.2 cd	11.7 c	6.2 d
Gyp + MAP	19.5 a	16.5 ab	17.6 ab	23.7 ab	23.0 a	25.1 ab	17.2 abc	18.3 ab	21.6 a
PS	17 abc	15.1 b	18.0 a	23.1 ab	20.6 abc	25.3 ab	18.9 abc	15.1 bc	12.5 c
PS + MAP	14.1 def	14.4 bc	15.2 bc	24.0 ab	22.1 ab	24.3 ab	19.2 abc	22.3 a	21.6 a
ES	14.2 def	13.8 bcd	13.1 cde	10.1 c	10.9 e	13.2 c	20.3 a	14.1 bc	6.9 d
ES + MAP	15.0 cde	18.8 a	8.5 f	9.7 c	15.2 de	12.1 c	19.9 ab	19.3 ab	22.9 a
P × S fertilizer effect†									
LSD ($p<.05$)	2.68	3.59	2.75	4.40	4.44	4.47	3.90	5.70	4.14
P Value (.05)	0.004	0.041	<.001	0.731	0.076	0.531	0.202	0.156	<.001
F Value	4.32	2.61	7.87	0.56	2.19	0.84	1.54	1.72	16.36
SEM††	0.93	1.25	0.96	1.54	1.55	1.56	1.36	1.99	1.44

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; Gyp = Gypsum; PS = Potassium Sulfate and ES = Elemental sulfur
\# Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, p <0.05)
† ANOVA results relate to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil
†† Standard error of means

Canola biomass yield response to the fertilizer S and P amendments was greater than for wheat and yellow pea. Some negative effects on wheat and yellow pea biomass were observed from seed-placed AS in the Brown Chernozem soil. This likely is a consequence of ammonia toxicity that may be expected from seed-placed AS given the high pH of this soil (Table 4). Gypsum, PS and ES also had a negative effect on biomass yield of pea at the Black Chernozem site and the reason for this is not known. Significant ($P \leq 0.05$) yield enhancement was observed in canola for application of all sources of S except ES. Similar results were found in canola in which S sources were applied in combination with MAP.

Table 4. Properties of the Central Butte (Brown Chernozem), Star City (Gray Luvisol) and Melfort (Gray-Black Chernozem) soils (0-15cm) used in the growth chamber experiment.

Soil properties	Site		
	Central Butte	Star City	Melfort
Soil Classification	Brown Chernozem	Gray Luvisol	Black Chernozem
Texture	Loam	Loam	Loam
pH*	8.1	6.7	6.4

EC (dS m^{-1})#	0.2	0.2	0.8
NO_3-N (kg ha^{-1})†	8	35	27
PO_4-P (kg ha^{-1})†	28	56	66
K^+ (kg ha^{-1})†	626	567	672
SO_4-S (kg ha^{-1})†	13	22	16

* pH of a 1 : 2 (soil : water) extract
# Electrical conductivity of a 1 : 2 (soil : water) extract
† Extractable NO_3-N, PO_4-P, K^+ and SO_4-S.

For the wheat crop, the overall highest biomass yield was found in wheat grown on the Central Butte soil amended with gypsum and MAP. ES plus MAP performed best in wheat grown on the Star City soils whereas PS produced the highest mean yield of wheat when added to the Black Chernozem soil. For the canola crop, the overall highest biomass yield was found in canola grown on the Black Chernozem soils with AS. With the exception of ES, application of all S alone and S + P combinations to canola grown on Brown and Black Chernozem soils resulted in significant ($P \leq 0.05$) yield increases over the control. Yellow peas grown on Brown Chernozem and Gray Luvisol soils did not show any significant positive responses to addition of S alone, but did respond to MAP addition on the Gray Luvisol soil. The addition of Gypsum + MAP and PS + MAP produced a positive yield response in peas on the Black Chernozem soil.

The results obtained in this controlled environment study indicate differences in yield response to added seed placed S forms alone and in combination with MAP among the three soil types. Differences in response of wheat, canola and pea were observed which mainly reflect differences in crop requirements for S, with the high S demand by canola (Malhi et al., 2005a) reflected in greater response, compared to wheat (Malhi et al., 2009) and pea. Indication of yield enhancement was found in the gypsum plus MAP treatments in all soils and crops. Gypsum plus MAP and ATS plus MAP increased yield over the control and was often more effective than other S fertilizer sources. The good performance of gypsum plus MAP in this controlled environment study may be attributed to its slightly soluble nature, reducing leaching. Upon gypsum addition, Ca^{+2} replace adsorbed Al^{+3} that increase solution Al^{+3} and possibly decrease the soil pH at the microsite. This would be especially true with band-applied gypsum where the localized fertilizer zone pH is depressed (Havlin et al., 2005). This may be of benefit in enhancing nutrient availability, especially in a soil of high pH such as the Brown Chernozem soil.

Application of AS and ATS was occasionally less effective in increasing yield and may be explained by some injury created by these fertilizers when placed in close proximity to the seed in the seed-row, especially in the high pH Central Butte soil (Qian et al., 2012). Under conditions of high soil pH, ammonium in these fertilizers will convert to ammonia gas which will accentuate injury potential.

In most cases, application of S sources alone did not increase yield for wheat and yellow pea, largely reflecting their lower requirements for S compared to canola, which responded the greatest to addition of S in this study. Malhi et al. (2009) examined wheat yield response to S fertilizer on a S deficient Gray Luvisol loam soil in northern Saskatchewan that had 15 kg S ha^{-1} added as SO_4-S and ES and reported a significant seed and straw yield increase of spring wheat over no-S and ES in the first year of application. Sulfur application has also increased yield of field pea when soil available S levels were inadequate (Haderlein and Dowbenko, 2002). In the silt loam textured soils of Minnesota, ATS was found to contribute significant yield increase over ES (McKay, 1996), and AS was found to contribute significant yield increase compared to ES in a study at three sites in Western Canada (Haderlein and Dowbenko, 2002).

Application of ES to soil is followed by oxidation to SO_4-S by S oxidizing microorganisms. The effectiveness of ES in supplying S to crops depends largely on time and method of application as this influences the rate of oxidation to plant available SO_4. To assure adequate S availability, ES should be incorporated into the soil as far ahead of planting as possible to give time for the ES to be oxidized to SO_4-S (Chien et al., 1988, Janzen and Bettany 1984; Wen et al., 2001; Solberg et al., 2003). The oxidization process may take several weeks to months depending upon environmental conditions (Wainwright et al., 1986), population size of oxidizing microorganisms (Lee et al., 1988) and application of ES, with broadcast incorporation found superior to banding (Havlin et al., 2005). However, oxidation rates of ES are slow in cold, dry soils. There are many reports of inadequate supplies of SO_4 from ES in the year of application in western Canada (Karamanos and Poisson, 2004; Malhi et al., 2005a). In this experiment, the crop was grown for 8 weeks and this appears to be insufficient time for significant oxidation of ES to available S. In a three year field experiment, seed yields of canola improved considerably when ES was surface broadcast or broadcast and incorporated into the soil as finely ground powder or as a suspension in water (Malhi et al., 2005b).

Sulfur and phosphorus uptake

Total S and P concentrations were determined in all plant samples collected after 8 weeks of growth and multiplied by biomass dry matter yield to calculate total S and P uptake (mg pot^{-1}) for wheat, canola and pea as shown in Tables 5, 6 and 7 respectively. Application of P and S sources and their interactions significantly ($P \leq 0.05$) affected wheat and canola S uptake from all three soils, except ES and ES + MAP treatments (Tables 5 and 6). However, variable treatment effects were observed for pea S uptake (Table 7). Sulfur uptake by pea in fertilized treatments in the Brown Chernozem were all similar and not significantly different from the unfertilized control. Peas grown on Gray Luvisol and Black Chernozem soils were found to have significant response in increased S uptake when treated with AS, AS + MAP and ATS. Application of S forms alone and in combination with P generally increased S uptake over the unfertilized control, with the exception of the ES treatment. Lack of significant enhancement of S uptake with ES is attributed to low oxidation in the soils over the 8 week period. Comparing S alone to S + P combination, the addition of MAP tended to increase S uptake by wheat in Gray Luvisol and Black Chernozemt soils, but not in Brown Chernozem soil. This reflects overall greater responsiveness of wheat yield to P application in the Gray Luvisol and Black Chernozem soils. Similar to wheat S uptake, the canola S uptake responded positively to application of S fertilizer with the exception of ES.

Table 5. Sulfur and phosphorus uptake (mg pot^{-1}) by wheat grown in fertilizer amended Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils.

Treatments*	WHEAT					
	Total S uptake (mg pot^{-1})			Total P uptake (mg pot^{-1})		
	Brown Chernozem	**Gray Luvisol**	**Black Chernozem**	**Brown Chernozem**	**Gray Luvisol**	**Black Chernozem**
Control	15.4 b[#]	16.7 e	14.4 d	50.9 a	29.6 bcd	33.1 ab
MAP	16.0 b	20.3 de	11.7 d	41.7 ab	34.1 ab	37.4 ab
AS	25.2 a	16.6 e	25.8 bc	29.9 c	19.4 d	34.4 ab
AS + MAP	27.0 a	24.0 bcd	31.8 a	35.2 bc	23.6 cd	38.5 a
ATS	29.0 a	28.2 ab	24.6 c	37.9 bc	33.0 abc	37.6 a
ATS + MAP	25.2 a	26.8 bc	33.4 a	42.3 ab	36.4 ab	39.1 a
Gyp	29.2 a	25.4 bcd	31.1 ab	33.4 bc	31.3 abc	30.4 b
Gyp + MAP	24.6 a	32.6 a	30.5 ab	36.9 bc	34.8 ab	37.3 ab
PS	27.3 a	27.9 ab	34.6 a	36.6 bc	29.3 bcd	34.4 ab
PS + MAP	25.8 a	24.9 bcd	33.3 a	37.3 bc	31.0 bc	35.1 ab
ES	16.7 b	17.7 e	10.2 d	38.1 bc	37.8 ab	36.4 ab
ES + MAP	16.3 b	21.3 cde	13.9 d	39.6 bc	41.7 a	38.9 a
P × S fertilizer effect†						
LSD ($p < 0.05$))	5.81	5.64	5.78	10.04	10.51	7.09
P Value (0.05)	0.590	0.057	0.040	0.351	0.999	0.839
F Value	0.75	2.36	2.63	1.15	0.04	0.41
SEM††	2.03	1.97	2.02	3.50	3.67	2.47

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; Gyp = Gypsum, PS = Potassium Sulfate and ES = Elemental sulfur
\# Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, p <0.05)
† ANOVA results relate to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil
†† Standard error of mean

Table 6. Sulfur and phosphorus uptake (mg pot^{-1}) by canola grown in fertilizer amended Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils.

Treatments*	CANOLA					
	Total S uptake (mg pot^{-1})			Total P uptake (mg pot^{-1})		
	Brown Chernozem	**Gray Luvisol**	**Black Chernozem**	**Brown Chernozem**	**Gray Luvisol**	**Black Chernozem**
Control	15.4 d[#]	13.8 ef	11.3 e	21.3 c	32.0 cd	43.3 de
MAP	16 d	9.2 f	10.3 e	34.5 bc	45.2 ab	59.1 c
AS	25.2 b	18.6 def	24.3 cd	45.4 ab	37.4 bcd	70.6 ab
AS + MAP	27.0 bc	35.2 a	35.3 ab	58.9 a	43.0 ab	79.4 a
ATS	29.0 c	22.5 cde	34 abc	51.5 a	40.1 abc	56.9 c
ATS + MAP	25.2 ab	36.8 a	23.7 d	58.7 a	45.9 ab	62.9 bc
Gyp	29.2 bc	25.2 bcd	25.2 cd	45.5 ab	37.8 bcd	53.0 cd
Gyp + MAP	24.6 a	28.6 abc	27 bcd	57.4 a	46.3 ab	60.2 c
PS	27.3 bc	29.5 abc	39.1 a	47.4 ab	45.2 ab	55.3 c
PS + MAP	25.8 bc	32.9 ab	25.9 bcd	60.3 a	48.1 a	62.3 bc
ES	16.7 d	10.8 f	10.3 e	35.9 bc	29.8 d	35.9 e
ES + MAP	16.3 d	16.2 def	11.8 e	33.9 bc	37.0 bcd	40.3 e
P × S fertilizer effect†						
LSD (*p*< *0.05)*)	7.62	9.86	9.68	14.97	9.56	10.00
P Value (0.05)	0.042	0.044	0.012	0.645	0.742	0.653
F Value	2.59	2.57	3.45	0.67	0.54	0.66
SEM††	2.66	3.44	3.37	5.22	3.33	3.49

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; Gyp = Gypsum, PS = Potassium Sulfate and ES = Elemental sulfur

Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, p <0.05)

† ANOVA results relate to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil

†† Standard error of mean

Table 7. Sulfur and phosphorus uptake (mg pot^{-1}) by pea grown in fertilizer amended Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils.

Treatments*	YELLOW PEA					
	Total S Uptake (mg pot^{-1})			Total P Uptake (mg pot-1)		
	Brown Chernozem	Gray Luvisol	Black Chernozem	Brown Chernozem	Gray Luvisol	Black Chernozem
Control	22.0 a#	12.8 b	11.0 de	36.8 abcd	33.8 ab	26.9 abc
MAP	20.9 a	16.0 ab	7.3 e	44.1 a	43.2 a	22.1 cd
AS	25.9 a	20.0 a	22.2 a	31.2 cd	39.1 ab	30.8 ab
AS + MAP	21.6 a	20.2 a	16.3 bc	42.0 ab	44.3 a	32.6 a
ATS	26.4 a	20.2 a	20.6 ab	35.4 bcd	34.8 ab	23.8 bcd
ATS + MAP	21.3 a	21.2 a	13.0 cd	44.7 a	39.0 ab	24 bcd
Gyp	23.7 a	18.2 ab	11.7 cde	29.1 d	30.5 b	9.0 ef
Gyp + MAP	23.1 a	16.0 ab	14.7 cd	35.1 bcd	40.9 ab	27.7 abc
PS	23.8 a	20.5 a	11.4 de	36.6 abcd	38.0 ab	17.0 de
PS + MAP	23.5 a	17.6 ab	14.8 cd	39.5 abc	41.7 ab	31.5 ab
ES	22.8 a	13.6 b	12.2 cd	44.3 a	33.9 ab	8.4 f
ES + MAP	22.4 a	18.1 ab	16.6 bc	44.7 a	37.1 ab	33.0 a
P × S fertilizer effect†						
LSD (*p*< *0.05)*)	9.17	6.18	4.88	8.63	12.07	12.05
P Value (0.05)	0.946	0.483	0.002	0.524	0.923	<.001
F Value	0.23	0.91	4.77	0.85	0.28	8.60
SEM††	3.20	2.15	1.70	3.01	4.21	2.83

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; Gyp = Gypsum, PS = Potassium Sulfate and ES = Elemental sulfur

Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, *p* <0.05)

† ANOVA results relate to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil

†† Standard error of mean

Application of different S fertilizers without and with MAP had limited effect on wheat and pea P uptake in the three soils evaluated (Tables 5 and 7), and effects were similar among treatments and often not significant. However for canola (Table 6), the addition of S fertilizer, with the exception of ES, resulted in significant increases in P uptake as the S limitation was overcome. The highest uptake of P was observed in treatments where MAP was added along with the S fertilizer.

The increased S uptake by wheat and canola observed in response to fertilizer S amendment was associated with an increase in S concentration in the biomass. Sulfate and thiosulfate S fertilizer forms were more effective in increasing S uptake than ES. The effect of ES and ES plus MAP on S uptake was mostly non-significant. The physical dispersion of the ES and oxidation of elemental S to SO_4-S under the conditions of this study were not rapid enough to supply a sufficient amount of available S to the crops over the time period evaluated. Karamanos and Janzen (1991) reported that the application of ES fertilizers at rates of 30-120 kg S ha^{-1} produced a response equivalent to that of SO_4-S fertilizer at 5 kg S ha^{-1} for yield and 10 kg S ha^{-1} for S uptake of canola.

The addition of MAP was effective in increasing canola P uptake, and the addition of S fertilizer alone also increased uptake of P by the canola over the 8 week growth period. There was no significant ($P \leq 0.05$) effect on wheat and pea P uptake. Overall, these soils had relatively high contents of extractable available P such that large responses of P uptake to added P fertilizer would not be anticipated. In some cases, significant increases in

P uptake over control and MAP alone were found in canola grown in AS, AS + MAP, ATS and ATS + MAP. This may be associated with an effect of ammonium, since ammonium is known to stimulate P uptake from fertilizer bands (Miller and Ohlrogge, 1977). In a greenhouse study, Morden et al. (1986) measured the response of barley (*Hordeum vulgare* L.) and rapeseed (*Brassica napus* L.) to banded ATS plus MAP, and P uptake was noticeably increased compared to the control.

Soil sulfate and phosphate supply rates and concentrations in the seed-row

The supply rates of SO_4-S and PO_4-P (µg cm^{-2}) over the 8 week period that the anion resin PRS™ probes were in the row containing fertilizer amendment treatments are shown in Figs 5 and 6.. Overall, there was a significant interaction of S and P sources for supply of SO_4-S. A trend in increase of PO_4-P supply was noted through the interaction of S and P source effects but was not significant ($P \leq 0.05$) (Fig. 6). As expected, SO_4 and thiosulfate sources had significantly higher supply rates of SO_4-S than the control receiving no fertilizer S or the MAP alone treatment. For the Brown Chernozem soil, gypsum had the highest supply rate of SO_4-S in the row, that may be explained by the slightly soluble nature of gypsum restricting the leaching of SO_4 away from the zone of placement over the 8 weeks of the study. The PS at the Gray Luvisol and Black Chernozem produced the highest supply rates of SO_4. The supply rates are consistent with the good yield responses found in canola to these S forms. Of the S fertilizer forms, the ES treatment had the least effect on enhancing soil SO_4 supply rate, and it was only significantly enhanced in the ES+MAP treatment versus MAP alone in the Brown and Black Chernozem soils. The addition of MAP did not usually significantly affect the SO_4 supply rate except for the ES treatment in the Brown and Black Chernozem soils where the SO_4 supply rate was increased. In a couple of cases (ATS at Brown Chernozem and PS at Gray Luvisol), addition of MAP resulted in lower supply rates of SO_4. This may be a consequence of anion competition for resin membrane adsorption sites.

The addition of S fertilizer alone generally had little influence on soil supply rates of PO_4 for the three soils over eight weeks (Figure 6). The addition of MAP fertilizer alone produced higher mean PO_4-P supply rates than the unfertilized control. Treatments with MAP plus S fertilizer sometimes had higher PO_4-P supply rates than the control and MAP alone treatments, especially in Brown and Black Chernozem soils, suggesting that S fertilizers, especially when combined with MAP, are enhancing availability of P in some instances.

Soil sampling for analysis of residual nutrient concentration in the seed-row where plants were growing was completed one, four and eight weeks after seeding. Soil samples were analyzed for extractable available soil SO_4-S and PO_4-P concentrations (Tables 8, 9 and 10). Repeated measurements analysis was performed to statistically evaluate the day effect and day plus treatment effect interactions (Day × P sources × S sources) and it was found that day effect was significant and day plus treatment effect interactions were not significant ($P \leq 0.05$) (Table 8).

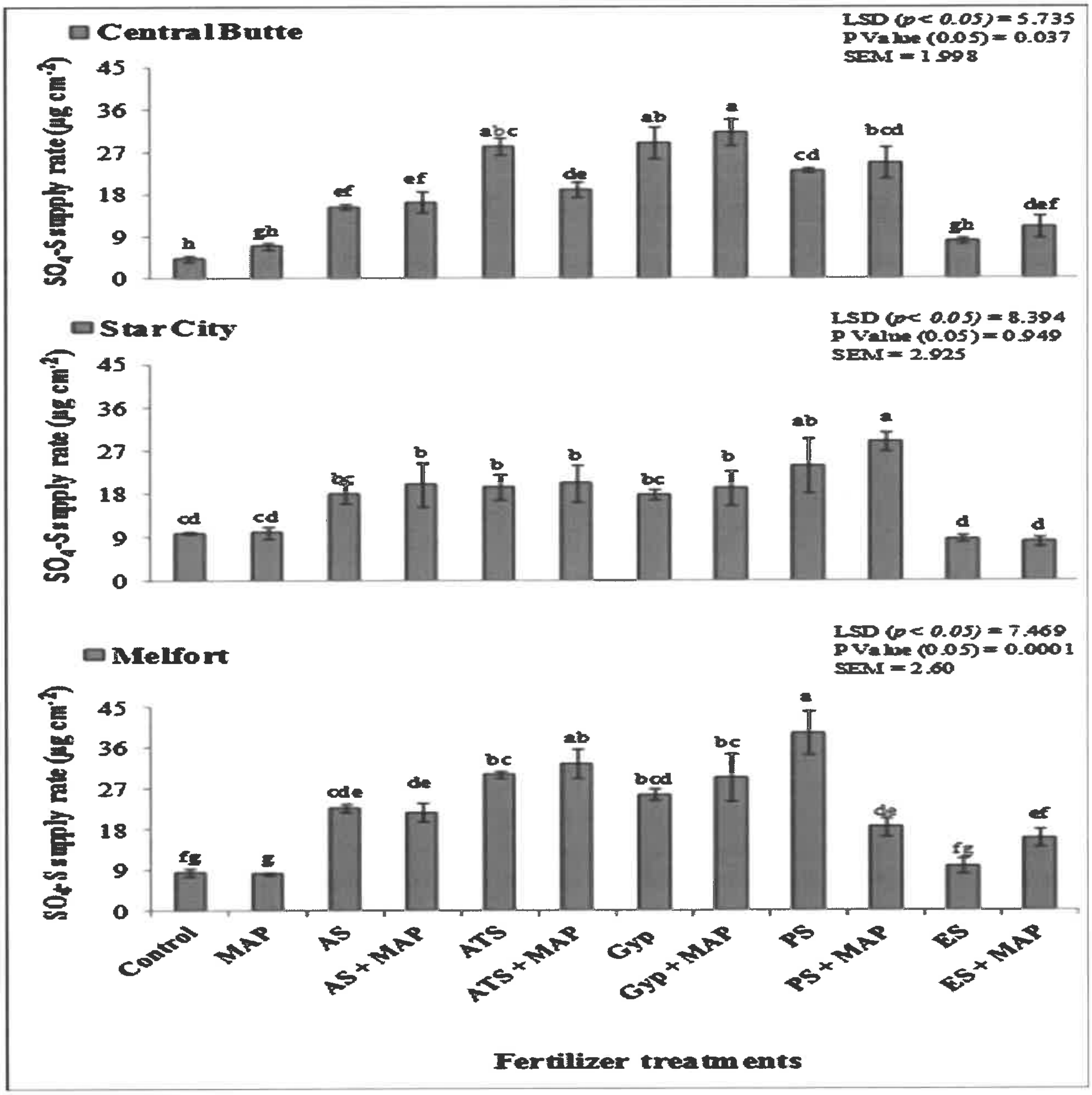


Fig. 5. Mean (N = 48 and n = 4) SO_4-S supply rate (µg cm^{-2}) in Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils over 8 weeks (56 days). Error bars are standard error of mean. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; Gyp = Gypsum, PS = Potassium Sulfate; ES = Elemental sulfur). For a soil (graph), means with different letters are significantly different (LSD, $P \leq 0.05$).

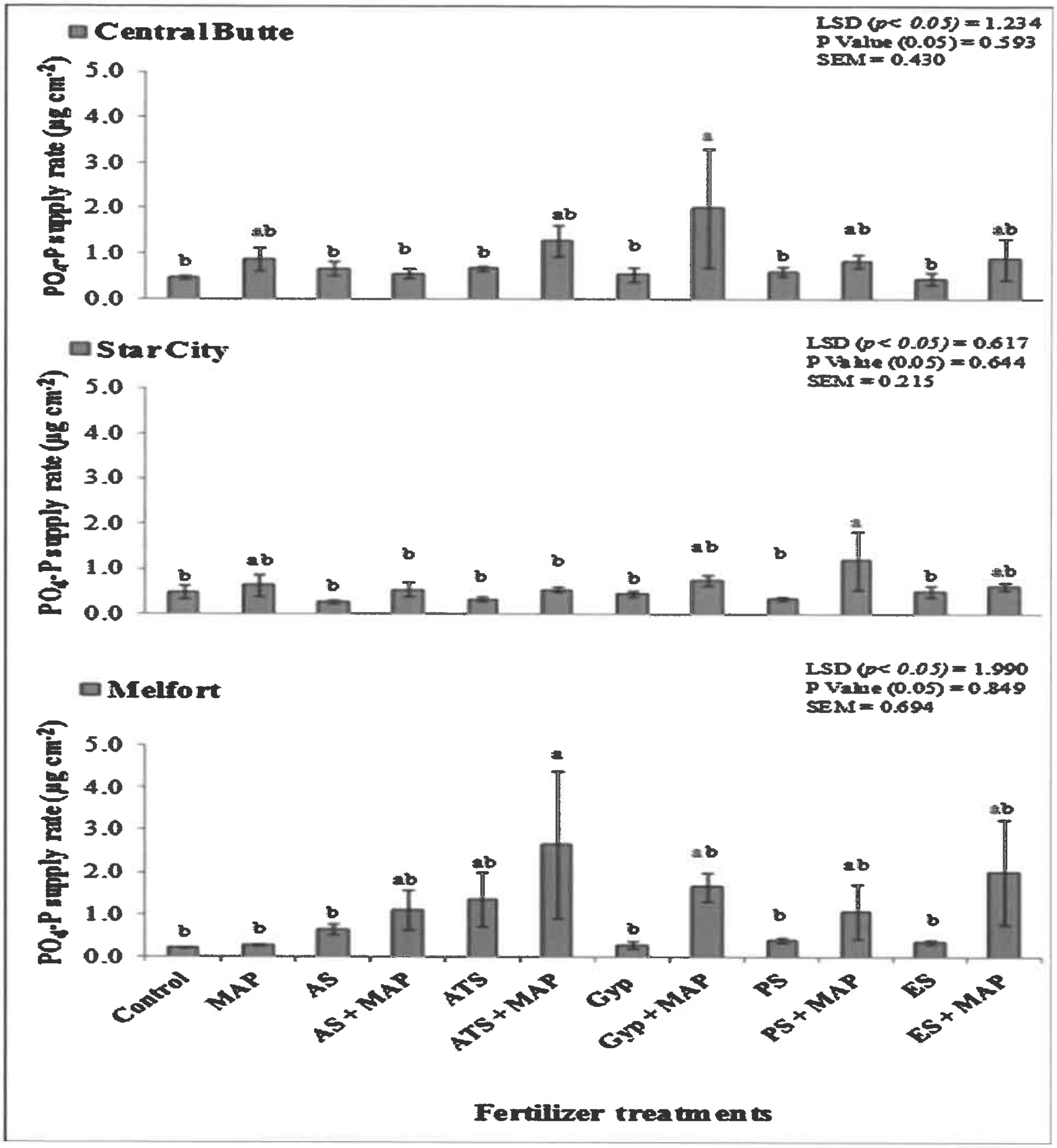


Fig. 6. Mean (N = 48 and n = 4) PO_4-P supply rate (µg cm^{-2}) of Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils over eight weeks (56 days). Error bars are standard error of mean. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; Gyp = Gypsum; PS = Potassium Sulfate; ES = Elemental sulfur). For a soil (graph), means with different letters are significantly different (LSD, $P \leq 0.05$).

Table 8. P values for the treatment effects in fertilizer amended Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils.

Treatment effetcs*	SO_4-S			PO_4-P		
	Brown Chernozem (Central Butte)	Gray Luvisol (Star City)	Black Chernozem (Melfort)	Brown Chernozem (Central Butte)	Gray Luvisol (Star City)	Black Chernozem (Melfort)
Day	<.001	<.001	<.001	<.001	<.001	<.001
P sources[#]	0.488	0.630	0.841	<.001	<.0001	<.001
S sources[#]	<.0001	<.0001	0.007	0.858	0.417	0.571
(P × S) sources	0.820	0.999	0.915	0.918	0.653	0.675
Day × (P × S)	0.985	0.999	0.995	0.990	0.585	0.947

*ANOVA results relate to the day effects (repeated measurements) independently for each soil
** Phosphorus (P) and Sulfur (S) sources

All soils generally had higher SO_4-S and PO_4-P concentrations in the seed-row 7 days after seeding and fertilizer application, followed by a large decrease in concentrations from day 7 to day 28, especially for sulfate, reflecting high plant uptake and sulfate depletion over this time period (Tables 9 and 10). The lowest extractable concentrations in the seed-row were found at eight weeks (day 56). Gypsum and gypsum plus MAP treatments had higher content of SO_4-S for all days in all soils, similar to the observation for supply rate of SO_4-S, and is attributed to reduced movement of SO_4 away from the zone of placement with this slightly soluble form. Elemental S had the lowest extractable SO_4 concentrations, as oxidation is required to produce SO_4.

Table 9. Mean soil extractable sulfate concentrations (mg SO_4-S kg^{-1}) in fertilizer amended Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils over time.

Treatments*	SO$_4$-S (mg kg^{-1})								
	Brown Chernozem (Central Butte)			Gray Luvisol (Star City)			Black Chernozem (Melfort)		
	Day 7	Day 28	Day 56	Day 7	Day 28	Day 56	Day 7	Day 28	Day 56
Control	4.9 c#	4.3 b	2.9 a	5.4 c	2.6 b	4.1 ab	7.6 b	3.6 e	3.2 c
MAP	5.3 c	5 b	4.0 a	6.9 c	3.8 b	3.4 b	15.5 b	6.0 cde	5.1 bc
AS	37.3 bc	7.7 ab	5.4 a	33.6 c	19.2 b	4.2 ab	176.2 a	11.9 bcd	6.9 abc
AS + MAP	37.6 bc	5.8 b	4.4 a	46.2 c	18.1 b	6 ab	114.1 ab	10.8 cde	5.4 bc
ATS	21.1 bc	9.2 ab	4.8 a	18.8 c	10.8 b	5 ab	46 ab	21.4 abc	8.7 ab
ATS + MAP	15.3 bc	14.8 ab	5.6 a	34.1 c	8.7 b	5.3 ab	38.5 b	15.5 bcd	8.7 ab
Gyp	160.4 a	17 ab	4.4 a	165.1 ab	71.4 a	16.8 a	115.0 ab	27.3 ab	11.9 a
Gyp + MAP	166.6 a	22.8 a	4.4 a	168.6 a	109.8 a	16.2 a	100.8 ab	32.3 a	11.7 a
PS	110.5 ab	19.8 ab	3.5 a	55.2 bc	9.9 b	4.6 ab	81.2 ab	14.0 bcd	6.3 bc
PS + MAP	40.5 bc	9.9 ab	3.7 a	47.5 c	12.3 b	4.9 ab	113.8 ab	23.5 abc	8.3 ab
ES	30.2 bc	7.6 ab	4.7 a	5.7 c	5.7 b	5.7 ab	7.4 b	6.1 de	5.9 bc
ES + MAP	11.3 bc	8.2 ab	3.8 a	10.1 c	6.5 b	15.5 ab	11.9 b	4.5 e	6.1 bc
P × S fertilizer effect†									
LSD (*P<.05*)	103.26	16.53	3.04	112.25	47.04	13.15	135.03	16.41	4.97
P Value (.05)	0.019	0.361	0.849	0.049	0.001	0.499	0.218	0.015	0.134
F Value	2.74	1.16	0.55	2.23	4.17	0.97	1.44	2.90	1.70
SEM††	35.38	5.67	1.04	38.46	16.12	4.51	46.26	5.50	1.70

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; Gyp = Gypsum; PS = Potassium Sulfate and ES = Elemental sulfur

Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, p <0.05)

† ANOVA results relate to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil

†† Standard error of mean

Sulfur treatments had limited influence on PO$_4$-P concentrations compared to the unfertilized control (Table 9). but MAP and MAP + S fertilizer treatments had significantly higher extractable PO$_4$-P than treatments without MAP. All soils generally had higher PO$_4$-P concentration at the beginning of the experiment at Day 7, consistent with differences observed at the day 28 and 56 of the experiment (Table 10). The concentration of PO$_4$-P at day 56 in the Brown Chernozem and Gray Luvisol soil were significantly ($P \leq 0.05$) increased over control by the application of MAP only.

Table 10. Mean soil extractable sulfate concentrations (mg PO$_4$-P kg^{-1}) in fertilizer amended Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) soils over time.

Treatments*	PO_4-P (mg kg^{-1})								
	Brown Chernozem (Central Butte)			Gray Luvisol (Star City)			Black Chernozem (Melfort)		
	Day 7	Day 28	Day 56	Day 7	Day 28	Day 56	Day 7	Day 28	Day 56
Control	25.2 b#	21.4 cd	14.8 b	20.2 c	20.1 de	17.3 cd	33.7 bc	31.0 bc	24.9 b
MAP	68.2 ab	38.4 abc	29.5 a	78.2 a	43.5 bc	25.0 ab	91.4 ab	49.6 a	58.2 a
AS	27.0 b	20.0 d	14.8 b	29.9 bc	16.8 e	14.2 d	32.6 c	26.3 c	22.8 b
AS + MAP	95.3 a	40.3 a	29.8 a	69.1 a	52.0 ab	30.6 a	77.9 abc	51.5 a	29.8 b
ATS	26.9 b	19.5 d	16.1 b	22.6 c	17.9 e	13.3 d	31.8 c	28.2 c	23.4 b
ATS + MAP	73.8 ab	48.6 a	28.9 a	47.8 abc	35.3 cd	26.1 ab	71.6 abc	48.8 a	37.9 b
Gyp	24.1 b	22.1 bcd	15.4 b	19.8 c	19.1 de	17.3 cd	31.9 c	29.3 c	25.9 b
Gyp + MAP	79.3 ab	39.6 ab	31.3 a	48.2 abc	62.3 a	27.9 ab	73.1 abc	51.6 a	33.4 b
PS	26.2 b	20.3 d	15.5 b	24.3 c	18.7 e	14.3 d	33.6 bc	26.6 c	24.8 b
PS + MAP	75.0 ab	44.4 a	24.9 a	69.6 a	46.8 abc	24.7 abc	123.3 a	56.4 a	39.2 ab
ES	24.0 b	20.0 d	14.8 b	22.3 c	19.8 de	16.2 d	32.6 c	28.1 c	21.8 b
ES + MAP	45.6 ab	41.7 a	24.1 a	59.7 ab	41.8 bc	20.9 bcd	83.3 abc	47.5 ab	35.5 b
P × S Fertlizer effect†									
LSD (*p*<.05)	62.12	17.95	8.03	31.92	16.33	7.67	58.66	17.10	20.15
P Value (0.05)	0.161	0.005	<0.001	0.002	<0.001	<0.001	0.0359	0.002	0.0449
F Value	1.61	3.55	6.48	4.09	8.23	5.22	2.39	4.25	2.27
SEM††	21.28	6.15	2.75	10.94	5.59	2.62	20.10	5.86	6.90

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; Gyp = Gypsum; PS = Potassium Sulfate and ES = Elemental sulfur

Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, p <0.05)

† ANOVA results relate to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil

†† Standard error of mean

The addition of SO_4 and thiosulfate fertilizers increased the supply rates of SO_4-S over the 8 week period compared to the control and MAP only treatments, while elemental S had less effect and only when combined with MAP. Oxidation of the ES fertilizer to SO_4 was only partial over the 8 weeks of the study. Higher supply rates of PO_4-P when combined with S fertilizers may be explained by the acidifying effect of the S fertilizers on enhancing solubility of P fertilizer reaction products in these neutral-calcareous soils.

Fertilizer treatment effects on extractable SO_4-S and PO_4-P concentrations in the seed row were similar to that observed for supply rates, with SO_4 and thiosulfate forms resulting in significantly higher SO_4-S concentrations and the addition of MAP significantly increasing seed-row extractable PO_4-P content. Time significantly affected both SO_4-S and PO_4-P concentrations in the seed-row. With the exception of ES, fertilizer S treatments generally had highest SO_4-S concentration at the beginning of the experiment at day 7, that greatly decreased coinciding with plant uptake from day 7 to day 28, indicating a period of rapid soil S uptake for all crops. By the end of the growth period at day 56, soil SO_4 contents were low in all treatments, indicating effective utilization of the seed-placed fertilizer by the crop.

The SO_4-S containing fertilizers were effective in improving yield, crop S uptake, soil supply and concentration of SO_4 in the seed row compared to the control and MAP only treatments. Application of S fertilizer has been reported to increase crop yield especially when forms of fertilizer S are added that contain or rapidly produce sulfate, such as AS, ATS, or gypsum (Karamanos and Janzen, 1991; Halley and Deibert. 1996; Johnston et al., 1998; Deibert and Lukah, 2000; Grant et al., 2003 and 2004; Solberg et al., 2007; Malhi et al., 2009). In the initial year of application, SO_4-S sources are more effective in increasing yield than ES (Solberg et al., 2007). However, residual S from ES may become available over time and effectively increase crop yields in subsequent crops (Janzen and Bettany, 1987; Wen et al., 2003; Solberg et al., 2007). Slightly soluble forms of S like gypsum may have an advantage under conditions of high leaching.

2013 Field Study

Canola, wheat and peas growing in the field plots are shown in Fig. 8. Overall, growing conditions at the three field research sites were good in 2013. One issue that was encountered was a severe cleavers weed infestation in the pea plots at the Black Chernozem (Melfort) site. Otherwise the three crops grown at the three field research sites received adequate growing season moisture for the Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem climate zones.

Fig. 8. From top to bottom: canola at Brown Chernozem (Central Butte) site, wheat at Black Chernozem (Melfort) site, and yellow peas at Gray Luvisol (Star City) site in 2013.

For the wheat crop grown at the three field sites in 2013, there was no significant wheat grain yield response to addition of P fertilizer as MAP (Fig. 9). This is consistent with relatively high available P contents of the three soils (Table 1), in which soil P is considered nearly sufficient according to soil test assessment. At the Brown Chernozem (Central Butte) site, there was no yield response to application of sulfur (Fig. 9).

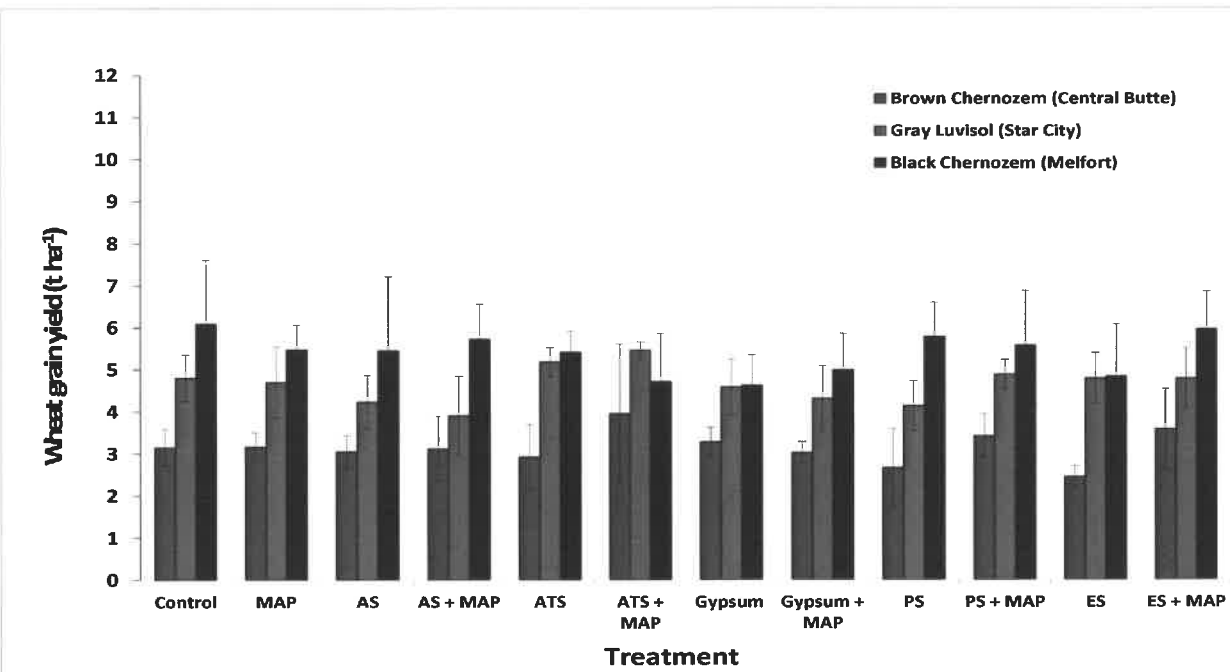


Fig. 9. Wheat grain yield (t ha^{-1}) harvested at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) at the field research trials in fall 2013. Error bars denote standard error of the treatment means with N=48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental Sulfur).

This is attributed to a high measured content of sulfate in the subsoil rooting zone at this site, which became available for plant uptake later in the season. Overall at this site, the liquid ATS plus MAP had the highest mean wheat yield and the elemental S treatment had the lowest. Similar to the Brown Chernozem, wheat on the Gray

Luvisol (Star City) showed limited response to application of S. The AS plus MAP treatment had a lower wheat yield at this site than the urea only control treatment and the reason for this is not known. It is noteworthy that in the controlled environment tray study, wheat biomass yield was lower than the unfertilized control from the addition of ammonium sulfate in the seed-row of wheat. At the Black Chernozem (Melfort) site, there was also no positive yield response of the wheat to added sulfur fertilizer and the ammonium thiosulfate plus MAP treatment had a lower wheat yield than the urea only treatment. The lack of a positive response of the wheat yield to application of sulfur fertilizer reflects the relatively low requirement of this crop for sulfur.

Response of canola to P fertilization with MAP was greater than observed with wheat, with all sites trending towards higher mean grain and straw yields with P fertilization compared to the urea treatment alone (Fig. 7).. However, the differences were not statistically significant. Reflecting the greater soil available sulfur status at the Brown Chernozem site, compared to urea there was no significant response to added S fertilizer and yields were all quite similar. These findings support the conclusion that crops, including canola, grown on soils in the Brown soil zone with large amounts of sulfate salts present in the sub-soil are not responsive to added S fertilizer under normal conditions. However as discussed later there was a response to S by canola on the Brown Chernozem under the unusually wet growing season conditions of 2014, that may be attributed to extensive leaching and lack of upward movement of the subsoil sulfates to the canola roots. The ammonium thiosulfate treatment plus MAP had the lowest mean yield and this is likely a consequence of some delay in germination and emergence as a result of the liquid ammonium thiosulfate fertilizer ending up right on the seed during application. At the Gray Luvisol soil, as would be expected, there was significant ($P \leq 0.05$) response of canola yield to application of S fertilizers (Fig. 10). For example, 20 kg S ha^{-1} as AS seed-row placed yielded 4376 kg canola seed ha^{-1} versus 2937 kg ha^{-1} in the urea only treatment (Fig. 10). Canola yields were also significantly ($P \leq 0.05$) higher with added gypsum and PS S sources. The potassium sulfate produced the highest yield on the Gray Luvisol. The elemental S had higher mean yield but was not statistically significantly different from the urea only treatment. These results demonstrate the importance of adding S fertilizer for canola grown on Gray Luvisol soils, even those that have been well managed in the past with previous additions of S fertilizer and relatively high sulfate levels in the surface soil horizon. There were no significant ($P \leq 0.05$) yield responses to the added S fertilizers at the Black Chernozem site. This may be attributed to a higher supply of available S from mineralization of organic matter in this soil. It is interesting that at this site, the potassium sulfate had a lower yield than the other treatments when applied alone.

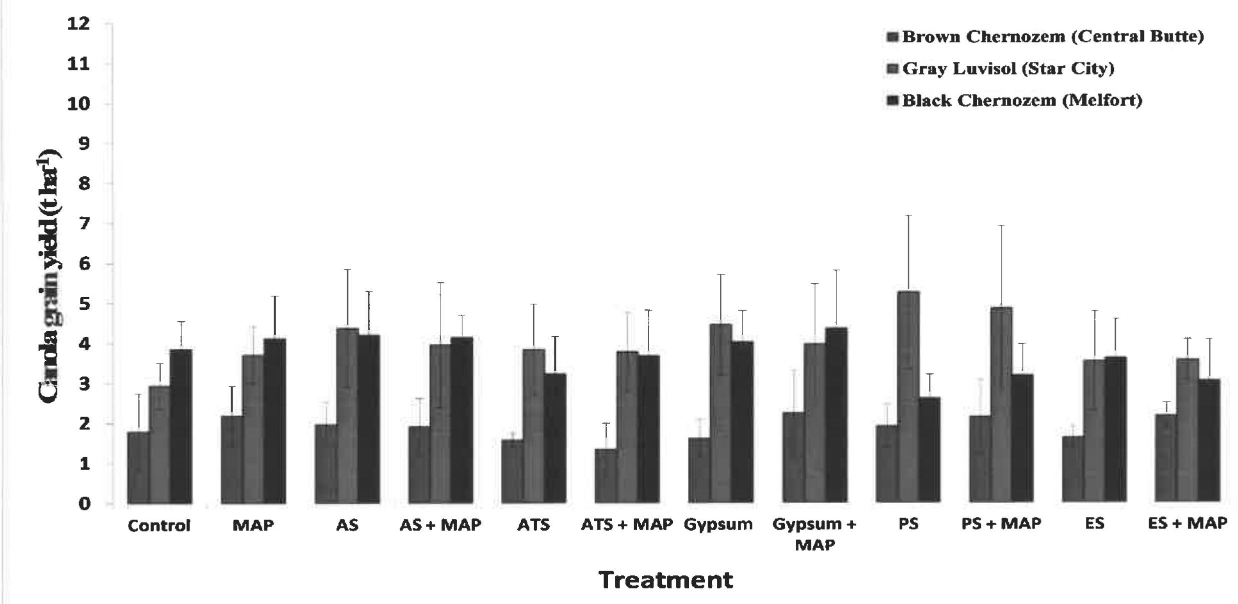


Fig. 10. Canola grain yield (t ha^{-1}) harvested at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) at the field research trials in fall 2013. Error bars denote standard error of the treatment means with N=48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental Sulfur).

For the yellow pea crop grown at the three sites in 2013, there was no yield benefit observed from the addition of the P fertilizer at 20 kg P_2O_5 ha^{-1} in the seed row (Fig. 11). In fact, some negative effects were observed, particularly at the Gray Luvisol site and when the MAP was combined with AS or ATS. This is explained by the high sensitivity of pea to the salt effect of seed-placed fertilizer, and also to the fact that peas can effectively access indigenous soil P by acidification of the rhizosphere, and through their strong association with arbuscular mycorrhizal (AM) fungi that extend the root system (Hassan et al., 2012). Also these three soils had relatively good P fertility to begin with as a result of their history of good management with P fertilizer additions made in the past. A noteworthy finding is that there were some significant yield responses of pea to the S fertilization treatments when the S fertilizers were applied alone without MAP such that major salt effects were avoided. For example, at the Brown Chernozem site ATS addition increased pea yield over the control treatment. On the Gray Luvisol, however, there was no significant ($P \leq 0.05$) response to S fertilization in the pea (Fig. 11). The response at the Brown Chernozem site could be related to an indirect soil acidification effect of the ammonium thiosulfate that may have enhanced availability of a micro nutrient like zinc (Anderson, 2015), as this site was relatively calcareous and had the highest pH of the three soils. At the Black Chernozem site, some positive responses of pea yield to S fertilization were observed, such as from AS, ATS and gypsum. This is interesting as canola did not response to S fertilization at this site. This may be explained by the high degree of cleavers weed infestation in the pea plots at this site in 2013. Peas are shallow rooted and the weed competition for nutrients like S close to the soil surface could explain the response of the peas to the S fertilization treatments at the Black Chernozem site.

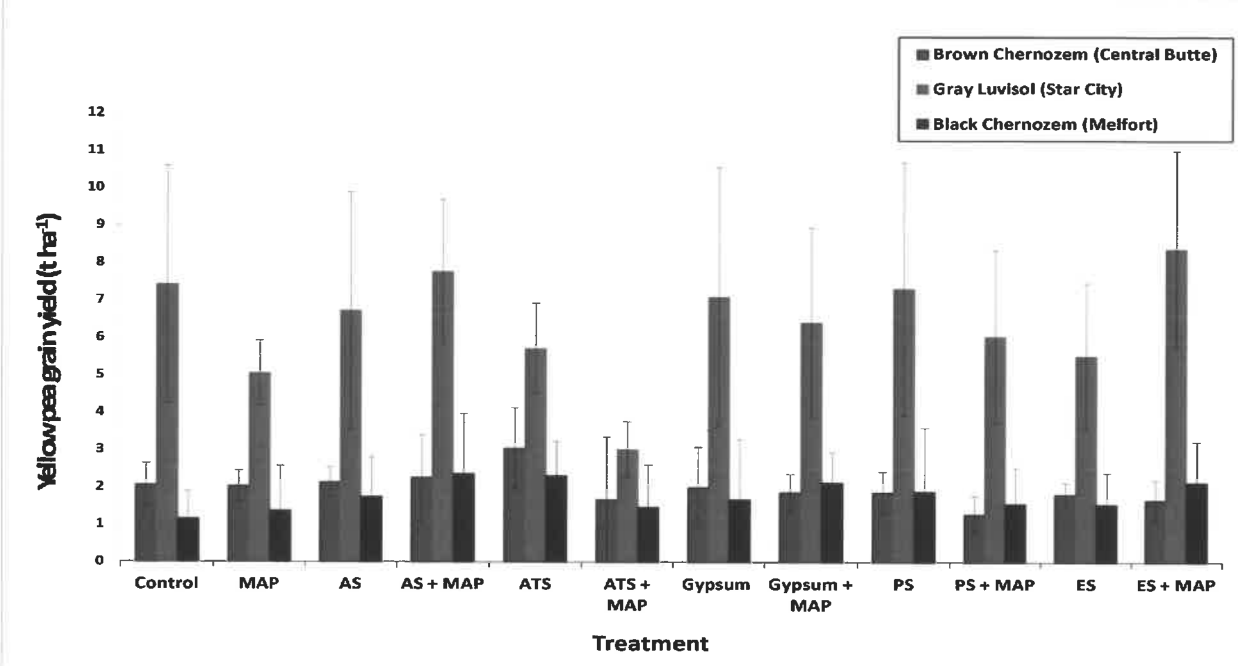


Fig. 11. Yellow pea grain yield (t ha^{-1}) harvested at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) at the field research trials in fall 2013. Error bars denote standard error of the treatment means with N=48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental Sulfur).

In the field in 2013, the fertilizer amendments did not significantly affect P uptake by wheat or canola at the three sites (Table 11). This is in agreement with the lack of fertilizer P effect on yield and can be attributed to the relatively high indigenous P fertility of the soils at the three sites. For peas, the phosphorus uptake at the Gray Luvisol (Star City) site (25-30 kg P ha^{-1}) was significantly higher than the other sites (~ 8 – 10 kg P ha^{-1}), reflecting the high yields achieved at this site compared to Brown Chernozem (Central Butte) which had disease issues and Black Chernozem (Melfort) which had cleavers weed pressure. The only significant ($P \leq 0.05$) effect of fertilization on pea phosphorus uptake was at the Star City site where injury from ammonium thiosulfate reduced yield and therefore P uptake. Injury to peas from seed-placed ATS was also observed in 2014. The Gray Luvisol (Star City) site P uptake (25-30 kg P ha^{-1}) was significantly higher than the other sites (~ 8 – 10 kg P ha^{-1}), reflecting the high yields achieved at this site compared to Brown Chernozem (Central Butte) which had disease issues and Black Chernozem (Melfort) which had cleavers weed pressure. The only significant ($P \leq 0.05$) effect of fertilization on pea phosphorus uptake was at the Star City site where injury from ammonium thiosulfate reduced yield and therefore P uptake.

Table 11. Crop (wheat, canola, pea) uptake of P and S (kg ha^{-1}) at the: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) three field sites in 2013.

Central Butte = CB (Brown Chernozem)
Star City = Herzberg (Gray Luvisol)
Melfort = Armstrong (Gray-Black Chernozem)

WHEAT: P and S Uptake

Treatments	WHEAT											
	Total P Uptake (kg ha)						Total S Uptake					
	Central Butte		Star City		Melfort		Central Butte		Star City		Melfort	
Control	13.7	a	24.30	a	21.23	a	14.5	ab	16.2	bc	22.1	a
Monoammonium Phosphate (MAP)	13.9	a	22.87	a	20.23	a	14.8	ab	15.6	bc	19.1	a
Ammonium Sulfate	12.1	a	21.36	a	23.46	a	17.6	ab	15.3	bc	20.0	a
Ammonium Sulfate + MAP	15.0	a	17.65	a	21.80	a	16.7	ab	14.3	c	21.3	a
Ammonium Thiosulfate	14.9	a	21.61	a	20.79	a	18.4	ab	21.1	ab	23.0	a
Ammonium Thiosulfate + MAP	19.4	a	23.96	a	18.13	a	23.9	a	23.9	a	19.7	a
Gypsum	14.5	a	17.87	a	18.78	a	15.6	ab	17.1	bc	16.7	a
Gypsum + MAP	13.7	a	18.69	a	21.11	a	14.6	ab	16.8	bc	18.9	a
Potassium Sulfate	13.4	a	15.52	a	21.65	a	12.8	b	15.7	bc	21.2	a
Potassium Sulfate + MAP	15.3	a	22.30	a	22.24	a	17.1	ab	20.0	abc	21.2	a
Elemental Sulfur	10.4	a	23.62	a	21.02	a	12.0	b	15.9	bc	16.7	a
Elemental Sulfur + MAP	15.7	a	20.74	a	24.57	a	16.5	ab	15.5	bc	19.5	a
ANOVA												
P Value (0.05)	0.359		0.106		0.925		0.088		<0.0001		0.508	
F Value	1.15		1.75		0.44		2.18		5.33		0.95	
SEM	2.143		2.384		2.697		2.091		1.495		2.003	

Means followed by the same letter are not significantly different at p ≤ 0.05. The multi-treatment comparisons were made using the Tukey's HSD method
* Standard error of mean

CANOLA: P and S Uptake

Treatments	CANOLA											
	Total P Uptake (kg ha)						Total S Uptake					
	Central Butte		Star City		Melfort		Central Butte		Star City		Melfort	
Control	10.9	a	18.1	a	22.4	a	24.0	a	22.0	a	27.3	a
Monoammonium Phosphate (MAP)	12.4	a	23.8	a	22.5	a	28.3	a	21.6	a	29.0	a
Ammonium Sulfate	12.6	a	26.5	a	24.5	a	27.8	a	32.8	a	36.8	a
Ammonium Sulfate + MAP	11.8	a	23.5	a	22.1	a	27.9	a	27.3	a	30.1	a
Ammonium Thiosulfate	10.0	a	23.1	a	18.4	a	26.3	a	41.6	a	32.1	a
Ammonium Thiosulfate + MAP	9.7	a	27.7	a	22.5	a	25.7	a	41.1	a	36.5	a
Gypsum	9.5	a	30.6	a	22.1	a	22.1	a	36.9	a	29.5	a
Gypsum + MAP	12.8	a	23.5	a	24.4	a	27.4	a	28.0	a	30.0	a
Potassium Sulfate	11.9	a	32.3	a	15.4	a	23.0	a	39.4	a	23.4	a
Potassium Sulfate + MAP	14.0	a	27.7	a	19.4	a	29.2	a	37.5	a	27.2	a
Elemental Sulfur	9.9	a	21.3	a	22.8	a	22.7	a	27.3	a	25.1	a
Elemental Sulfur + MAP	13.3	a	21.4	a	18.2	a	29.4	a	19.6	a	23.3	a
ANOVA												
P Value (0.05)	0.778		0.270		0.264		0.953		0.046		0.085	
F Value	0.64		1.30		1.31		0.38		2.13		1.83	
SEM	2.098		3.878		2.536		4.485		5.957		3.254	

[1] Means followed by the same letter are not significantly different at p ≤ 0.05. The multi-treatment comparisons were made using the Tukey's HSD method
* Standard error of mean

PEAS: P and S Uptake

Treatments	PEAS											
	Total P Uptake (kg ha)						Total S Uptake					
	Central Butte		Star City		Melfort		Central Butte		Star City		Melfort	
Control	7.9	a	31.4	a	4.8	a	10.8	a	15.8	a	4.4	b
Monoammonium Phosphate (MAP)	8.3	a	21.3	ab	6.3	a	12.3	a	12.5	a	5.3	ab
Ammonium Sulfate	8.3	a	26.4	ab	7.0	a	10.3	a	18.3	a	8.1	ab
Ammonium Sulfate + MAP	8.8	a	32.5	a	9.1	a	15.1	a	19.7	a	8.3	ab
Ammonium Thiosulfate	10.2	a	21.5	ab	8.6	a	14.3	a	17.3	a	9.7	a
Ammonium Thiosulfate + MAP	5.9	a	13.6	b	5.3	a	11.0	a	9.4	a	5.9	ab
Gypsum	7.7	a	29.7	ab	7.5	a	10.8	a	20.1	a	7.0	ab
Gypsum + MAP	7.3	a	28.6	ab	8.4	a	15.0	a	18.0	a	9.6	ab
Potassium Sulfate	7.2	a	29.6	ab	8.3	a	12.9	a	21.4	a	8.7	ab
Potassium Sulfate + MAP	5.7	a	24.2	ab	6.6	a	12.7	a	16.6	a	7.7	ab
Elemental Sulfur	7.1	a	25.7	ab	6.9	a	8.4	a	15.3	a	6.0	ab
Elemental Sulfur + MAP	7.1	a	32.0	a	8.8	a	9.6	a	15.9	a	7.3	ab
ANOVA												
P Value (0.05)	0.652		0.018		0.174		0.479		0.078		0.020	
F Value	0.79		2.55		1.51		0.99		1.89		2.51	
SEM	1.291		3.726		1.906		2.469		2.964		1.541	

[1] Means followed by the same letter are not significantly different at p ≤ 0.05. The multi-treatment comparisons were made using the Tukey's HSD method
* Standard error of mean

The addition of sulfate and thiosulfate fertilizers increased the uptake of sulfur by the wheat crop (Table 11), particularly at the Brown Chernozem and Gray Luvisol sites. There was no significant ($P \leq 0.05$) effect at the Black Chernozem site. The increased uptake did not translate into any yield increases of the wheat as discussed earlier. The S uptake in the elemental S treatments was similar to the unfertilized control, in agreement with the results of the controlled environment tray study. For canola, the S uptake was significantly increased by fertilization, with SO_4^{2-} and ATS sources having higher S uptake than the elemental S form. Sulfur uptake by peas was generally higher in treatments fertilized with SO_4^{2-} and ATS, especially at the Black Chernozem site where considerable weed (cleavers) competition for nutrient was evident and there was a significant yield response to the added S.

Soil extractable available SO_4 and PO_4 amounts in the seed-row one week (7 days), 4 weeks (28 days) and 8 weeks (56 days) after seeding in the 2013 field season are shown in Figures 12-20. Overall and similar to the findings of the controlled environment study, seven days after seeding, plant available SO_4 content in the seed-row was significantly higher in the SO_4 and ATS fertilizer sources than the unfertilized control and the elemental S fertilizer treatments (Figs. 12-20). Sulfate and ATS sources produced similar high amounts of SO_4 in the seed-row in the week after seeding. Occasionally, gypsum resulted in higher seed-row SO_4 contents than the rest of the treatments, which may be attributed to the slightly soluble nature of gypsum which reduces movement of SO_4 away from where it is placed in the soil (Havlin et al., 2005). Contents of SO_4 in the elemental S fertilizer treatments 7 days after application were not significantly different from control treatments receiving no S fertilizer. This is indicative of lack of oxidation to SO_4 over the seven day period. All SO_4 and ATS fertilizers had large decreases in the content of SO_4 in the seed-row for all crops and all sites from day 7 to day 28, indicating large plant uptake of SO_4 by all crops in the first month after seeding. Although the crops do take up a significant amount of available S in the first month of growth, they can respond to late season applications of sulfate to overcome deficiency of S (Malhi and Gill, 2002). The addition of the MAP fertilizer along with the S did not appear to affect SO_4 contents in the seed-row in the first seven days after seeding.

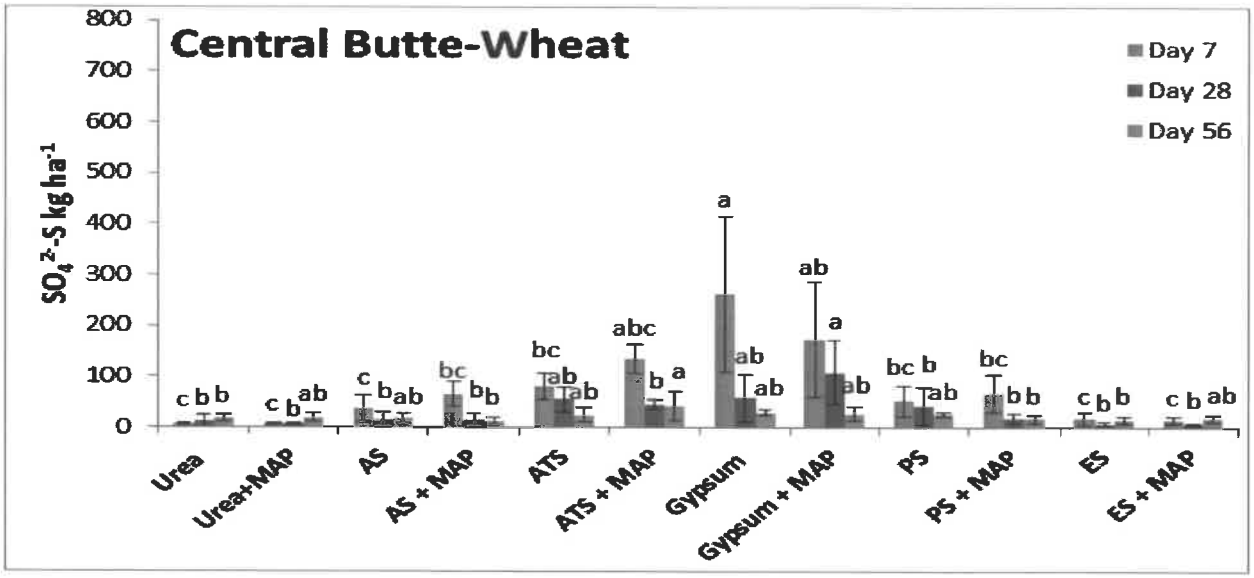


Fig. 12. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in wheat at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

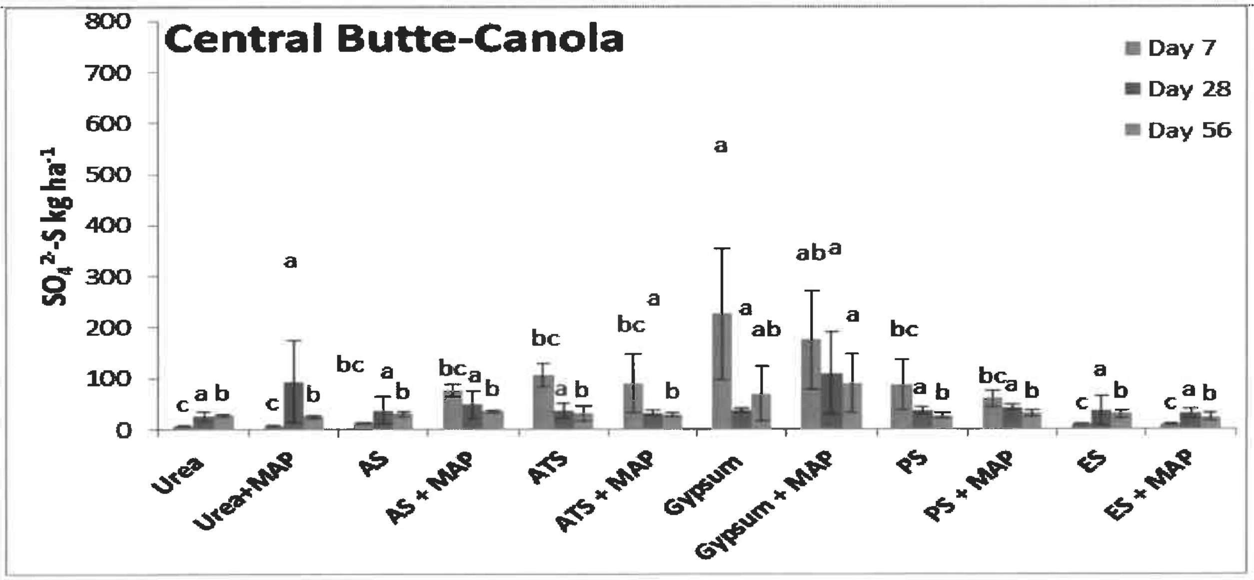


Fig. 13. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in canola at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

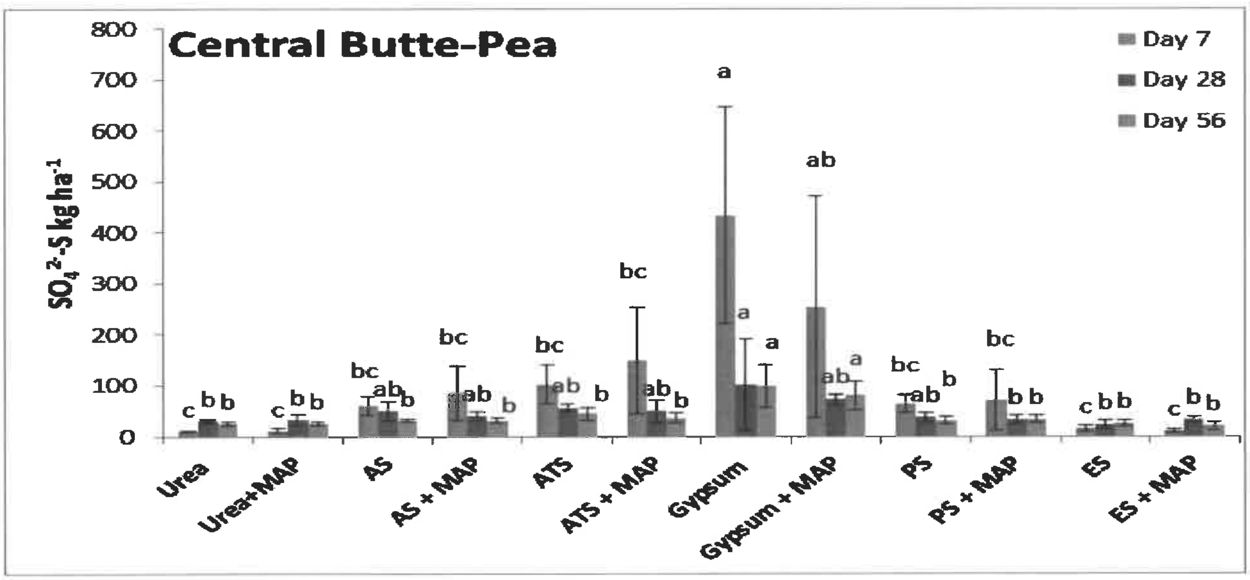


Fig. 14. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in yellow peas at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

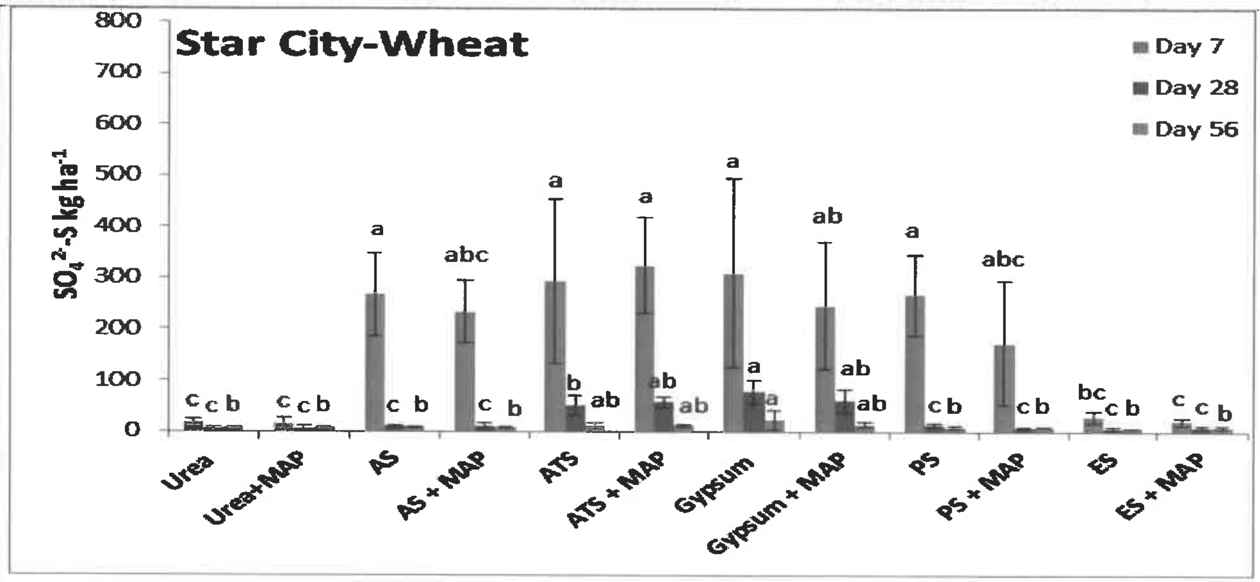


Fig. 15. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in wheat at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \le 0.10$).

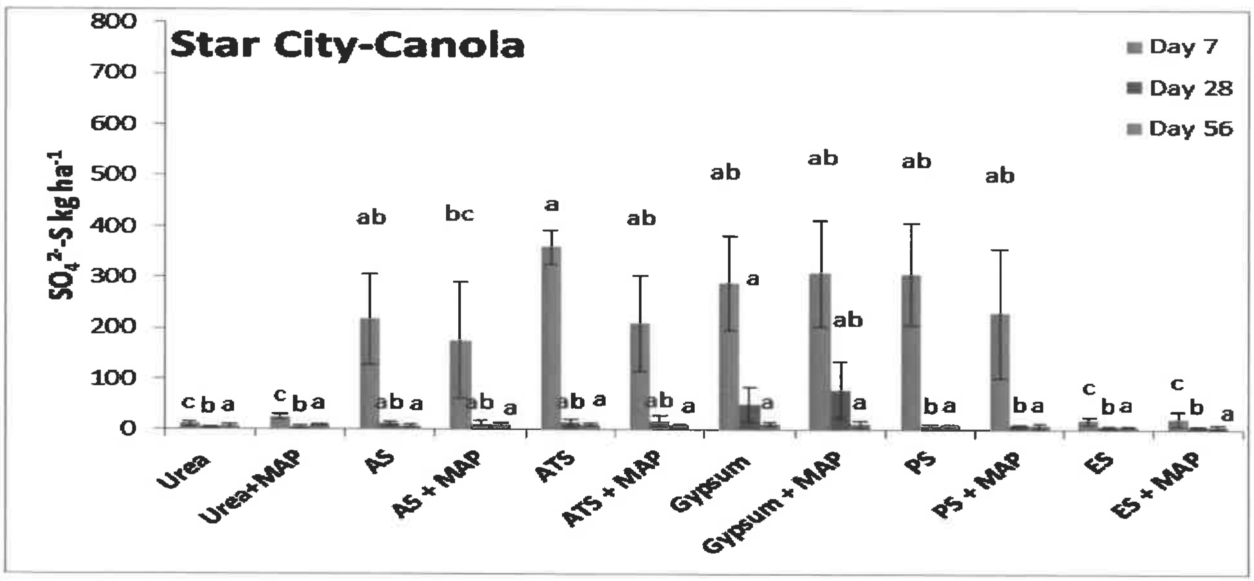


Fig. 16. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in canola at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \le 0.10$).

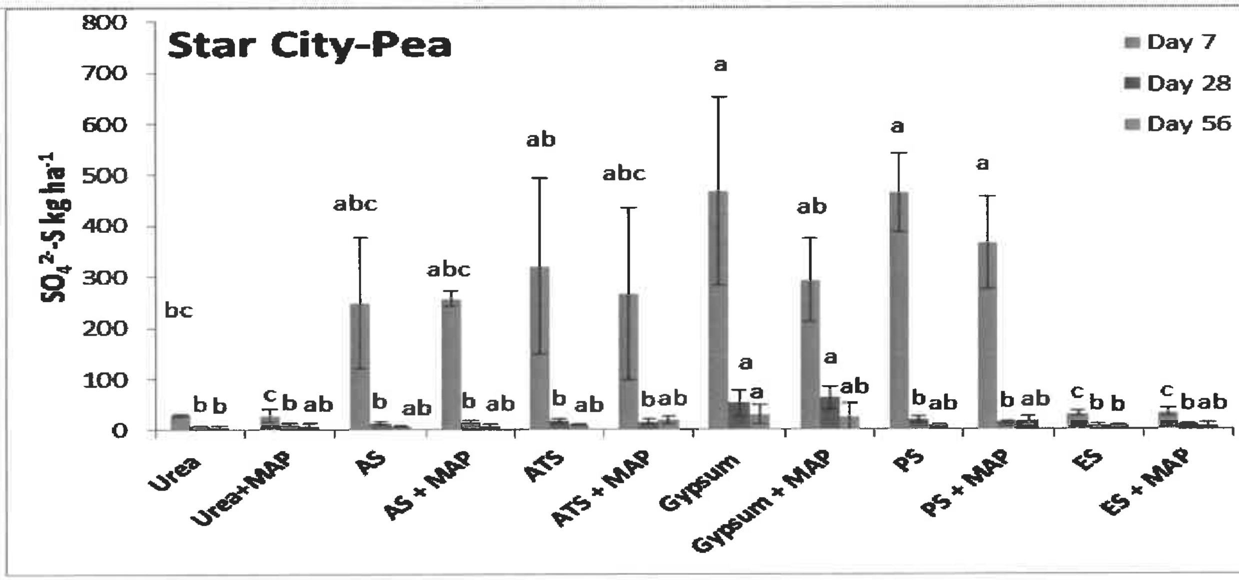


Fig. 17. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in yellow peas at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

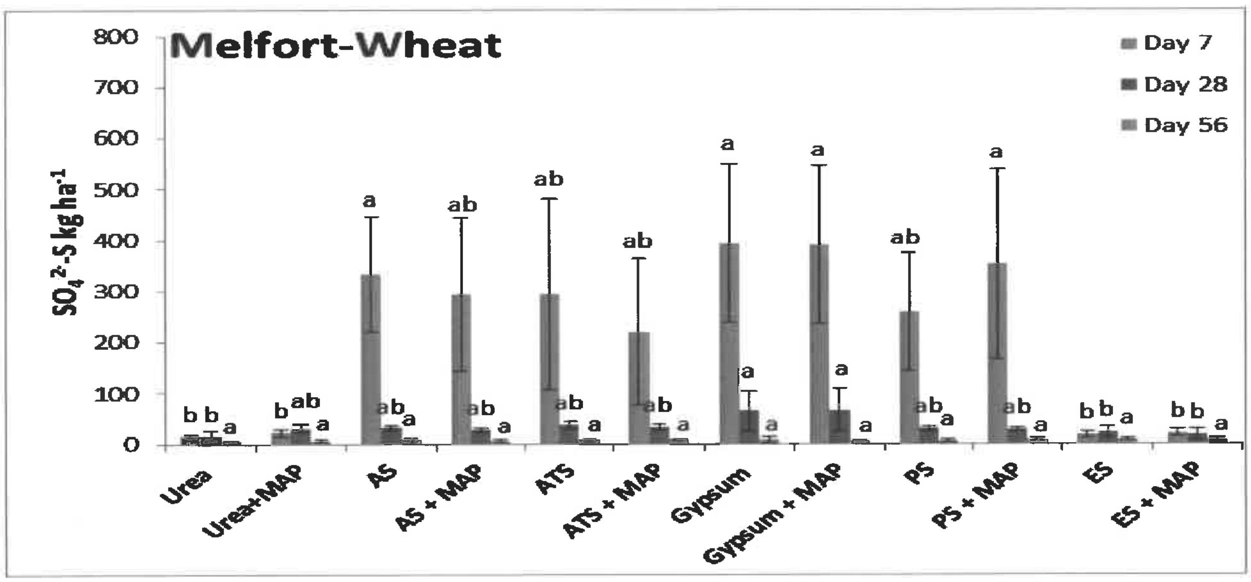


Fig. 18. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in wheat at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

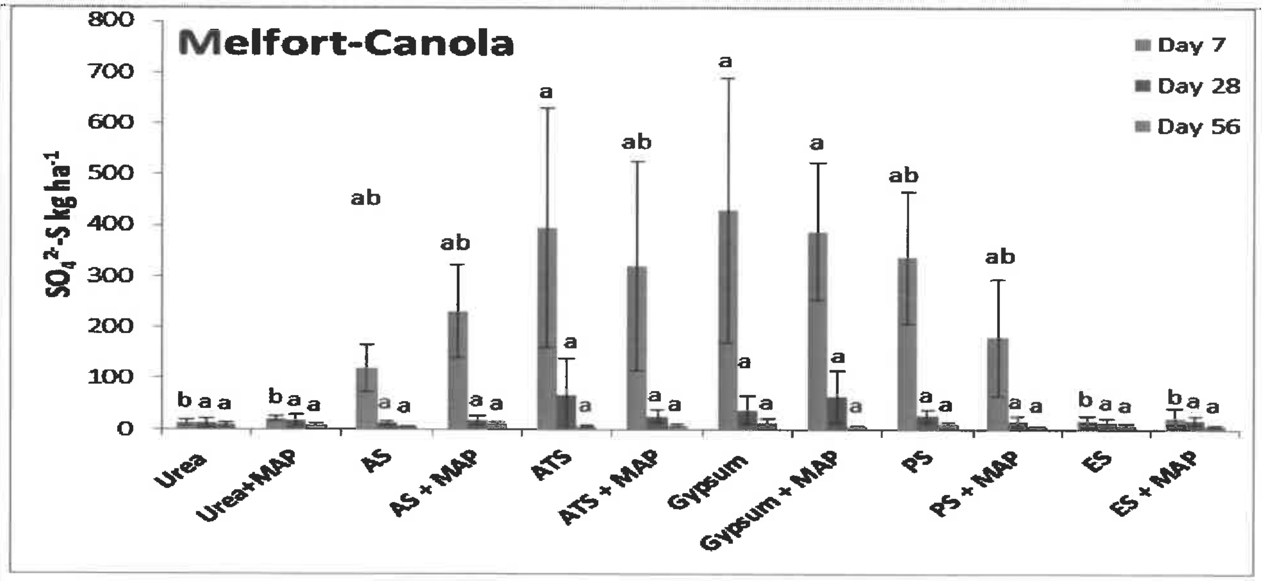


Fig. 19. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in canola at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

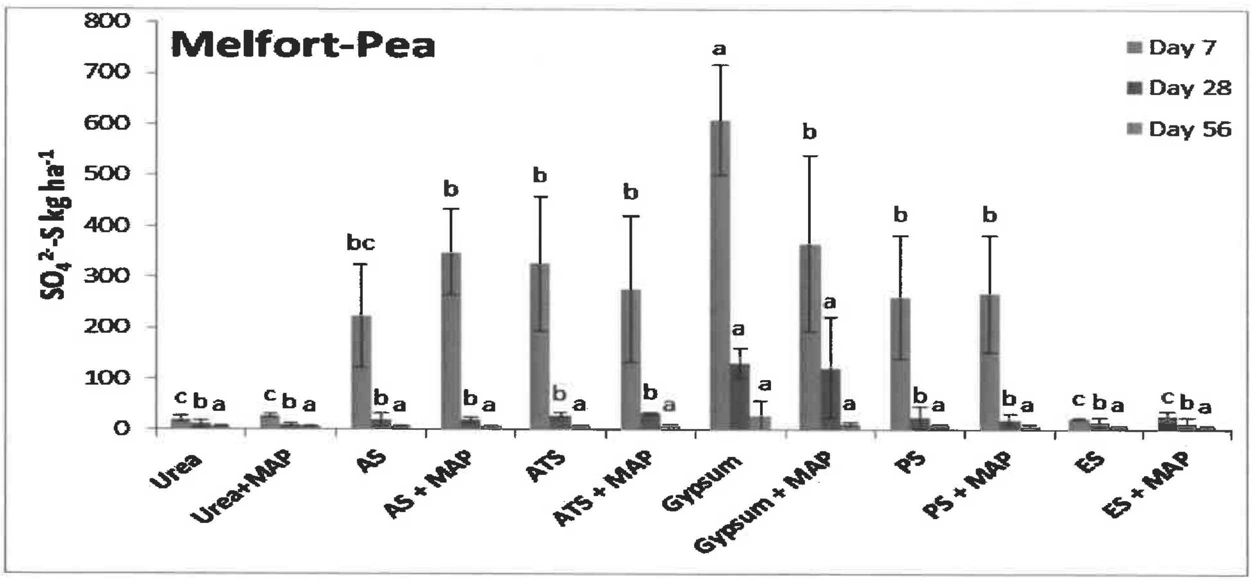


Fig. 20. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in yellow peas at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

The seed-row extractable PO_4-P contents one week (7 days), four weeks (28 days) and eight weeks (56 days) after seeding in 2013 are shown in Figures 21-29. As expected, the addition of MAP significantly increased the content of extractable available PO_4-P in the seed-row seven days after seeding for all crops and sites. Increases in seed-row PO_4 were greatest at the Black Chernozem (Melfort) site (Figs. 27-29) and lowest at the Brown Chernozem (Central Butte) site (Figs. 21-23). This likely reflects greater precipitation of phosphate in less soluble forms at the Brown Chernozem site as a consequence of higher pH and more calcareous nature of the soil (Kar et al., 2011). This is supported by the P XANES data discussed later. The combination of S fertilizer along with the MAP did not appear to significantly affect the extractable PO_4 over MAP alone, except for PS where the addition of MAP along with PS did not have as great an effect on increasing the available PO_4 after 7 days. This was observed generally for all crops and all sites and in 2014 as well. It may be a consequence of the formation of the mineral tarankite, a potassium PO_4 mineral of low solubility. However, no spectroscopic evidence of the tarankite mineral was found. Some evidence of P fixation in this treatment is also found in the 8 week PRS™ anion resin membrane supply rates in the controlled environment tray study. Similar to SO_4, a large depletion in seed row PO_4 content is observed from day 7 to day 28 for all crops, as a consequence of crop uptake of PO_4 from the seed-row early on in its growth cycle (Havlin et al., 2005).

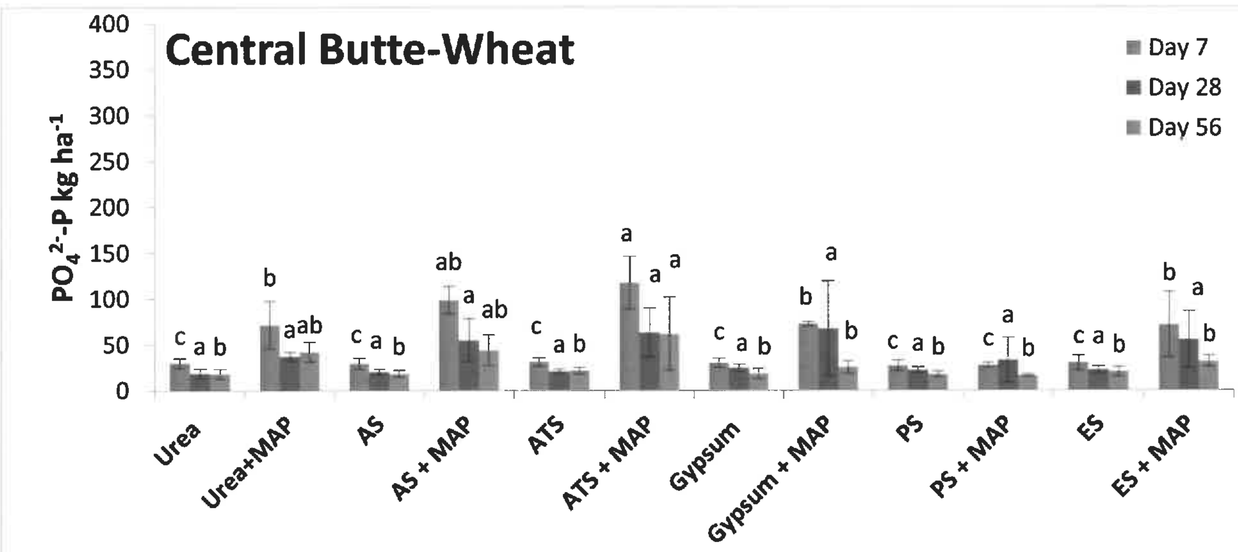


Fig. 21. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in wheat at Brown Chernozem (Central Butte) soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

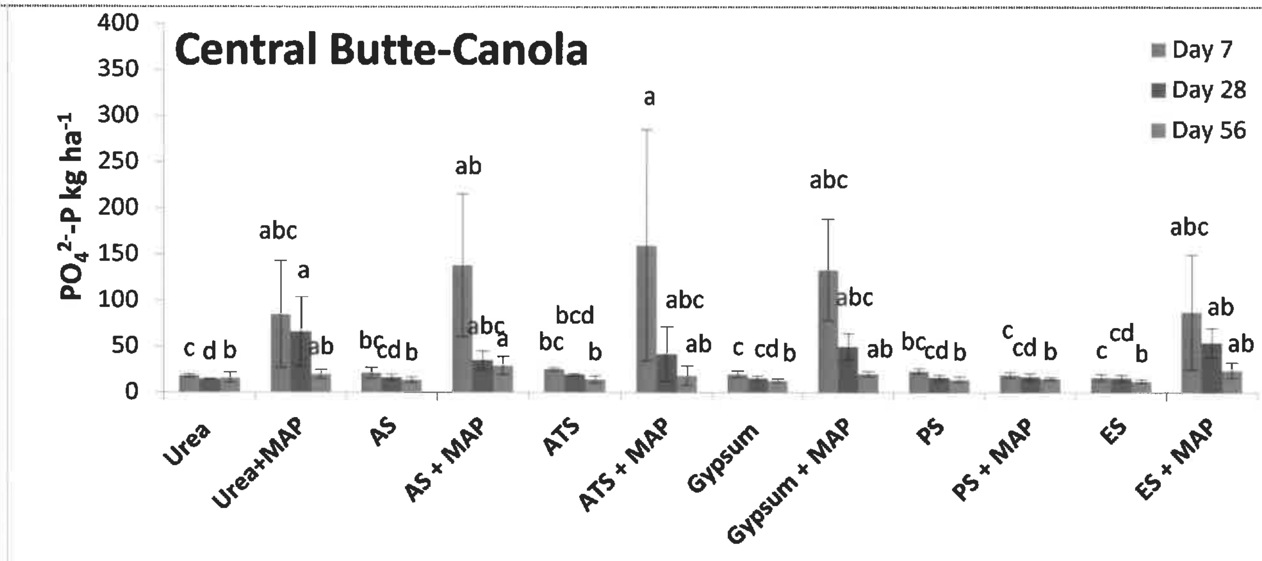


Fig. 22. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in canola at Brown Chernozem (Central Butte) soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

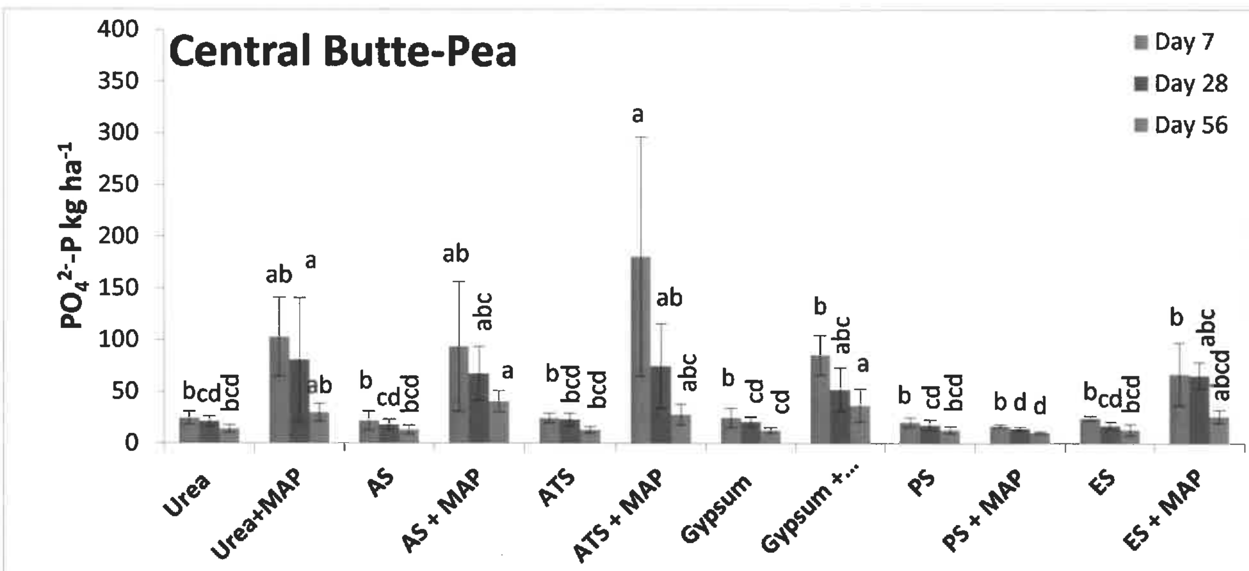


Fig. 23. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in yellow peas at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

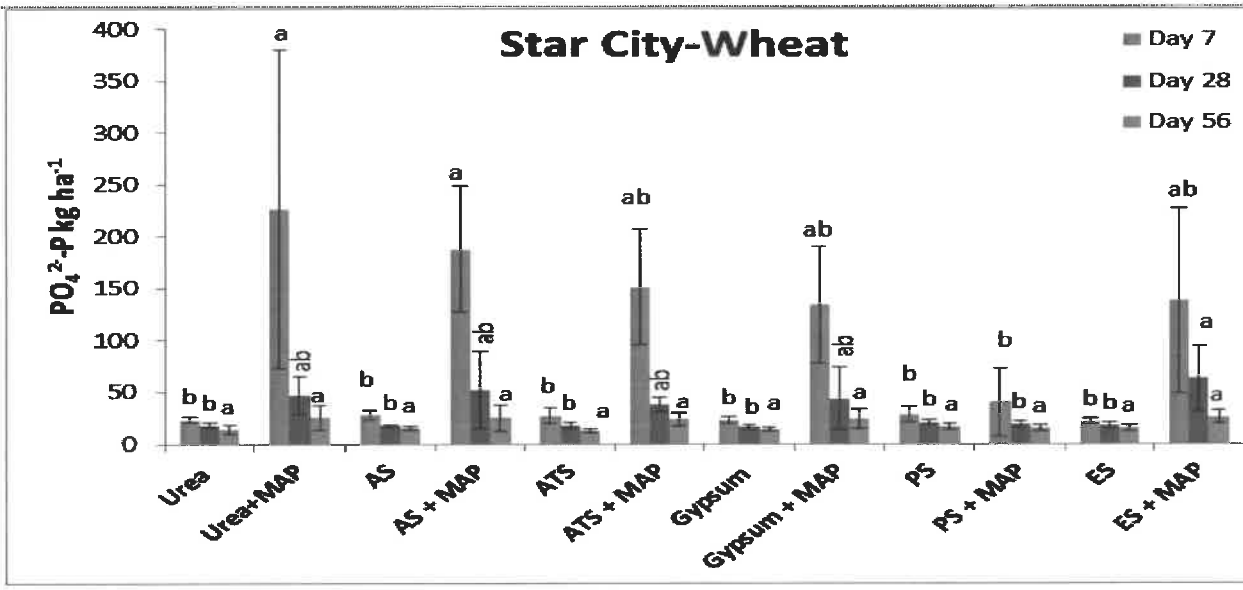


Fig. 24. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in wheat at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

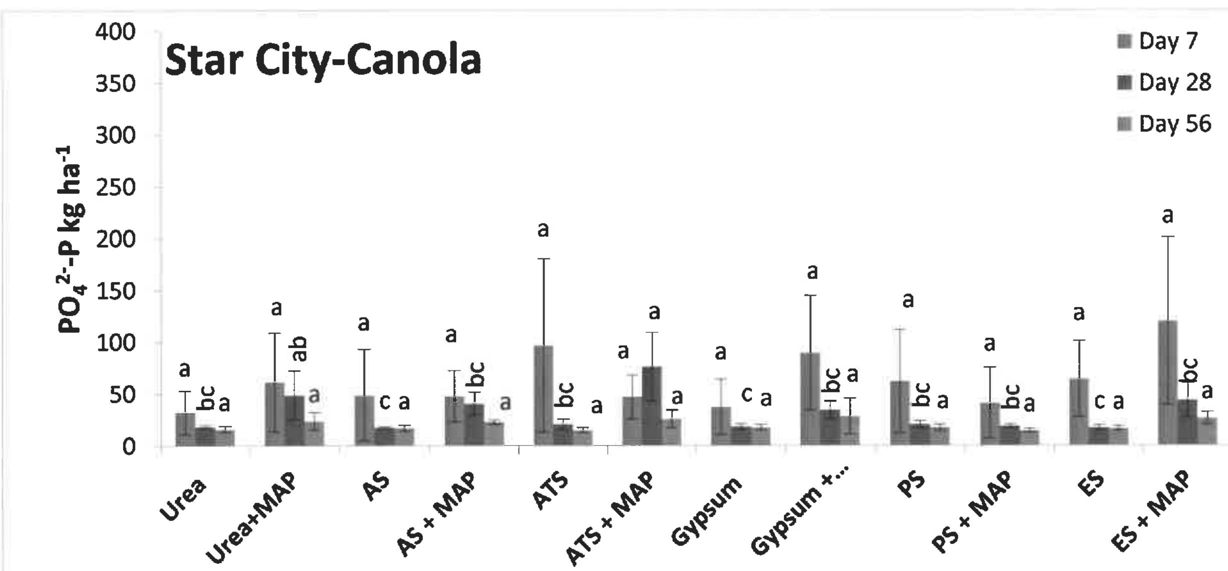


Fig. 25. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in canola at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

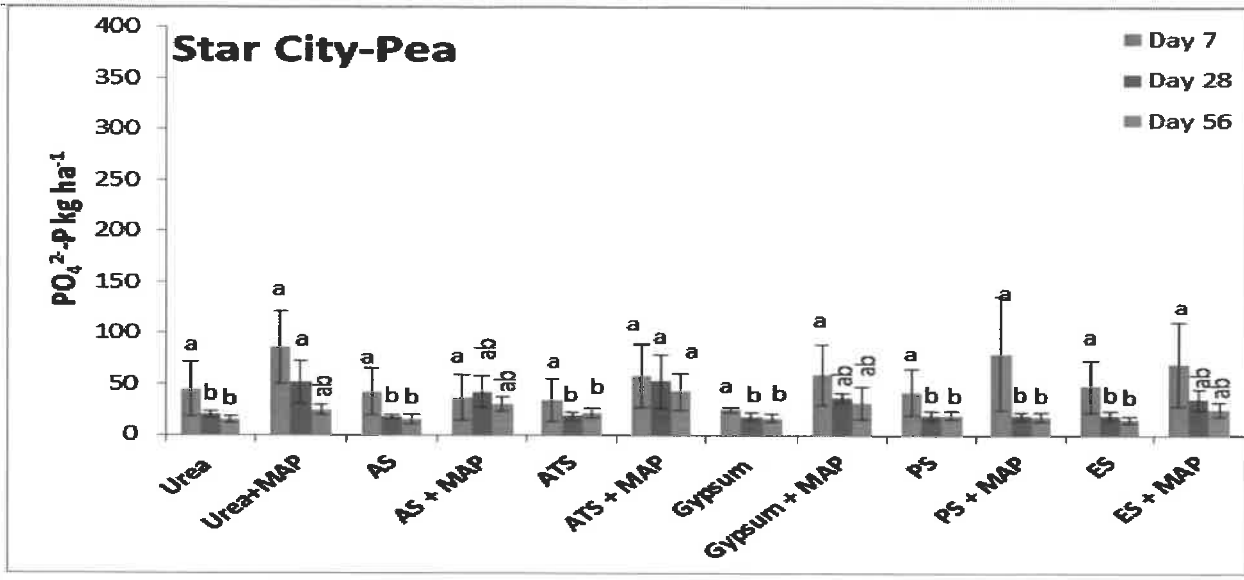


Fig. 26. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in yellow peas at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

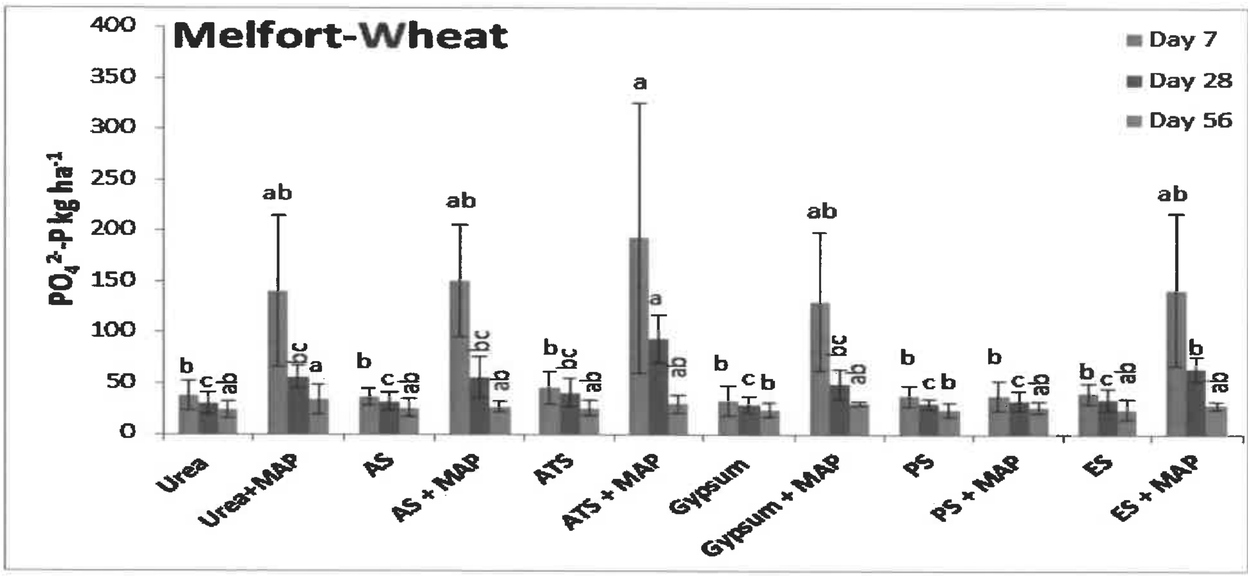


Fig. 27. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in wheat at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

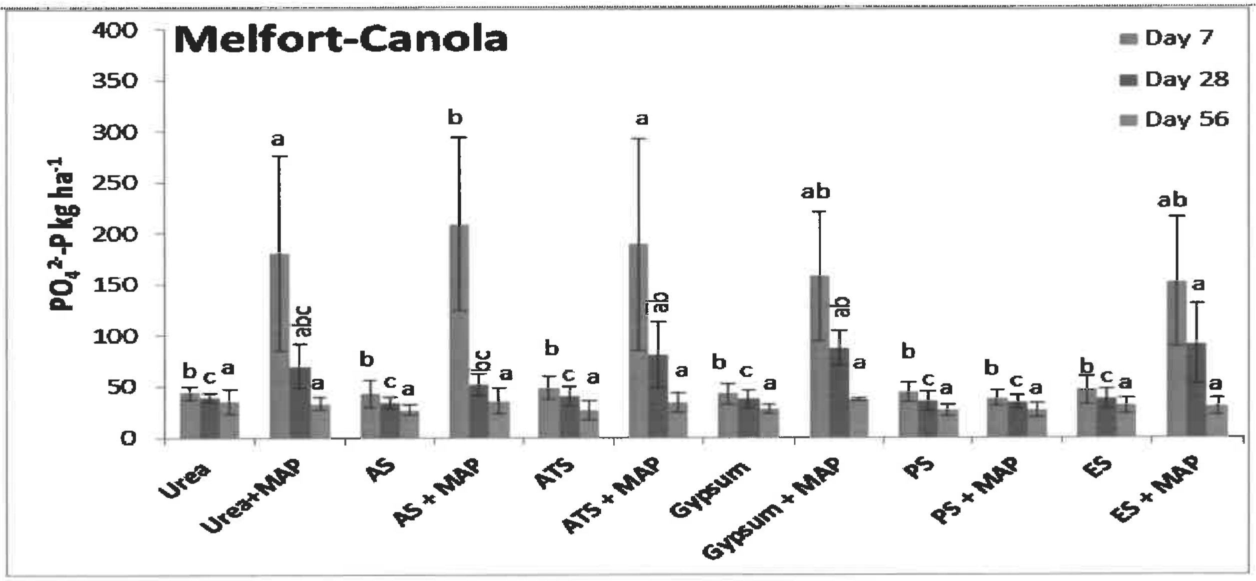


Fig. 28. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in canola at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

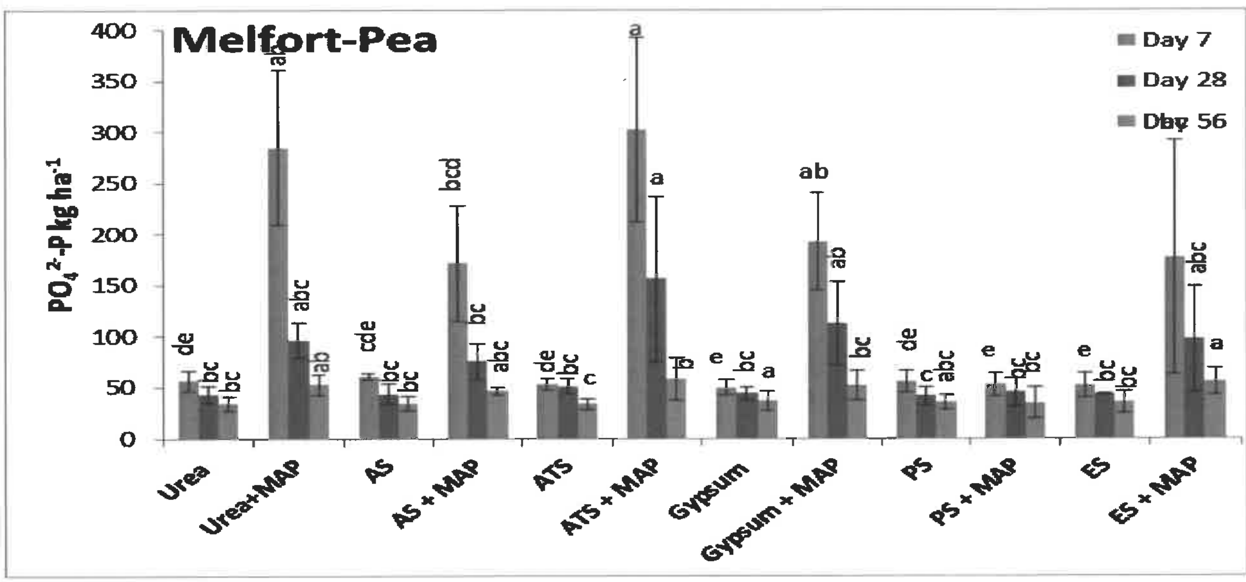


Fig. 29. Mean seed-row extractable phosphate phosphorus content (PO_4-P kg ha^{-1}) in yellow peas at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2013. Error bars are standard deviation of mean with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

2014 Field Study

Generally good growing conditions were experienced at the three Saskatchewan field sites: Brown Chernozem

(Central Butte), Gray Luvisol (Star City), and Black Chernozem (Melfort) regions in 2014 (Fig. 30). At the Central Butte site, May to August growing season precipitation was about 40% greater than normal, while other locations experienced precipitation that was close to normal.

Fig. 30. From top to bottom: yellow peas at Brown Chernozem (Central Butte), wheat at Gray Luvisol (Star City) and canola at Black Chernozem (Melfort) sites in mid-July, 2014.

Of note, the Brown Chernozem site received an abundance of moisture in June and July 2014, measuring 355 mm (14") for the 2014 growing season. For the wheat crop grown at the three field research sites in 2014, there was no significant ($P \leq 0.05$) differences between treatments in grain biomass yields (Fig. 31).

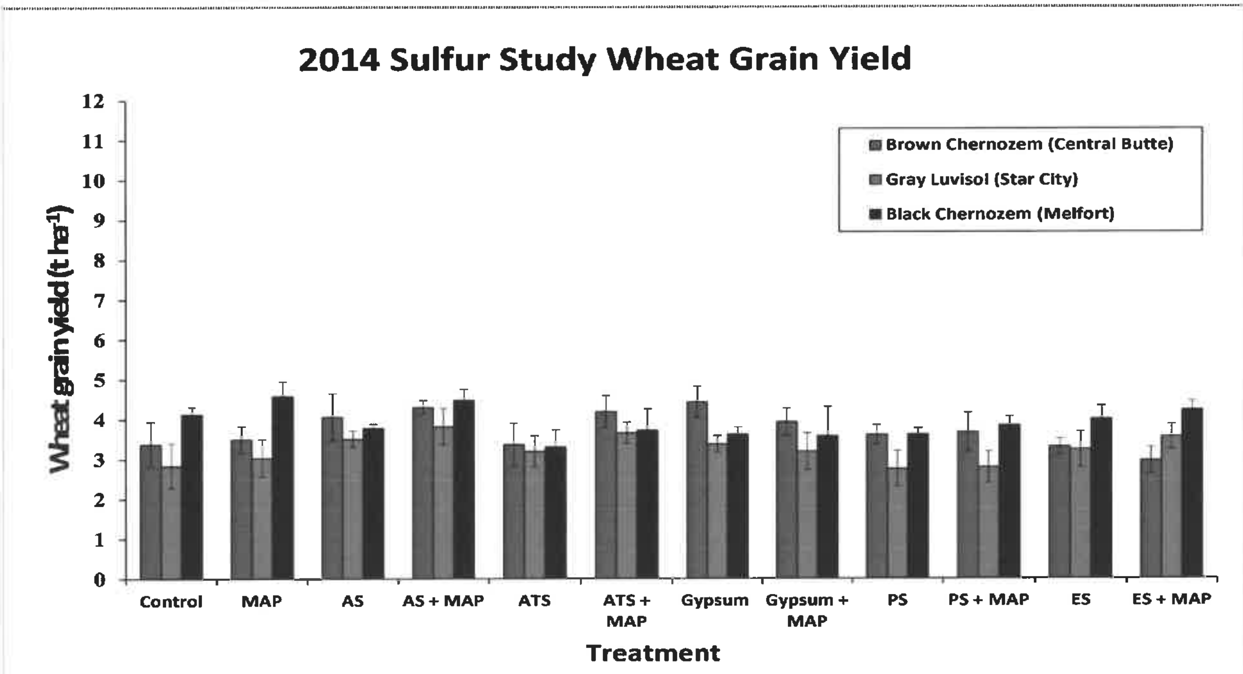


Fig. 31. Wheat grain yield (t ha^{-1}) harvested at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) at the field research trials in fall 2014. Error bars denote standard error of the treatment means with N=48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental Sulfur).

For the wheat crop in 2014, the AS, ATS and gypsum treatments gave the highest mean wheat yields across the sites. Similar to 2013, the ES wheat yields were close to the unfertilized control treatment. Overall, yield increases from S and P fertilizer treatments were not large and often not significant. As was observed in the controlled growth chamber experiments with wheat, canola and yellow peas, there were differences in response of wheat, canola and pea in the field which mainly reflect differences in crop requirements for S, with the high S demand by canola (Malhi et al., 2005a) reflected in greater response compared to wheat (Malhi et al., 2009) and pea. This reflects the relatively low S requirement of wheat. No significant responses of wheat yield to P fertilization were observed, despite two of the three sites testing relatively low according to soil test extractable P. At the Brown Chernozem (Central Butte) site, there was no wheat grain yield response to the application of S at 20 kg S ha^{-1}. Soil available S at this site was lower than was measured in 2013, which could be attributed to the higher than average amount of rainfall received in 2014, that could have moved S lower in the soil profile. Overall, the gypsum treatment had the highest overall grain yield, while ATS plus MAP and AS treatments had higher grain yields (Fig. 31). Upon gypsum application to soil, Ca^{+2} can replace adsorbed Al^{+3} that can increase soil solution Al^{+3} and possibly decrease the soil pH at the microsite such as band-applied gypsum where the localized fertilizer zone pH is depressed (Havlin et al., 2005). This may be of benefit in enhancing nutrient availability, especially in a soil of high pH such as the Central Butte soil. Similar to the Brown Chernozem site, wheat at the Gray Luvisol (Star City) site had a limited response to application of S fertilizers (Fig. 31). Ammonium S plus MAP and ATS plus MAP had the highest grain biomass yields, although not significantly ($P \leq 0.05$) different from the other S fertilizer treatments. At the Black Chernozem (Melfort) site, the MAP and AS plus MAP treatments produced the highest wheat grain yield (Fig. 31). Interestingly the ES and ES plus MAP treatments produced higher, although not significantly ($P \leq 0.05$) different, wheat grain yields compared to the ATS, gypsum and PS S treatments. It is possible that more of the plant available S in the ATS, gypsum and PS S fertilizers were tied up earlier on in the growing season, while ES was converted to plant available S later on in the growing season and was available for plant uptake. In the initial year of application, SO_4-S sources are more effective than ES (Solberg et al., 2007) in increasing yields, however, residual S from ES can become available over time and increase yields in subsequent crops (Janzen and Bettany, 1987; Wen et al., 2003; Solberg et al., 2007). Otherwise, the overall lack of a positive grain yield response by the wheat crop at all three field sites, similar to the 2013 results, reflects the relatively low S requirement by wheat.

The canola at the Brown Chernozem site in 2014 responded to the addition of the MAP fertilizer, with ~1200 kg ha^{-1} yield benefit (Fig. 32). The two other sites had limited response to added P, despite the Star City site testing relatively low in available P. Similar to the wheat at this site, gypsum and soluble SO_4 forms generally produced highest canola yields (Fig. 32). The ATS yielded lowest, suggesting some injury from placement of ATS in the seed-row close to the seed. Under conditions of high soil pH, such as the Brown Chernozem soil, ammonium in these fertilizers will convert to ammonia gas which will accentuate injury potential (Qian et al., 2012). This was also noted at the Gray Luvisol and Black Chernozem sites and was also observed in 2013. The AS may also have been causing some injury when seed placed. As in 2013, seed-placed gypsum and PS produced good canola yield response. More response to S fertilization was observed at the 2014 Brown Chernozem site than the 2013 site. This may reflect a wetter growing season in 2014 that moved the subsoil sulfates deeper in the profile. On the other hand, the 2014 Gray Luvisol site was less responsive than the site at this location in 2013. As the 2014 sites were located in the same general area but on different farm fields, some differences in soil properties may explain the difference in response between the two years.

Response of canola crop grain biomass yield to application of S plus MAP fertilizer tended to be higher in some of the S plus MAP treatments at the Brown Chernozem and Gray-Black Chernozem sites (Fig. 32). Application of S fertilizer has been reported to increase crop yield especially when forms of fertilizer S are added that contain or rapidly produce sulfate, such as AS, ATS, or gypsum (Karamanos and Janzen, 1991; Malhi et al., 2009). At the Brown Chernozem (Central Butte) site, gypsum and PS produced the highest canola grain biomass yields where MAP was added with the S fertilizers, however, these yields were not significantly ($P \leq 0.05$) different from the other S plus MAP treatments, except for the ATS plus MAP, having the lowest canola grain yield (Fig. 32). The gypsum S fertilizer was observed to have the highest overall grain yield and was significantly ($P \leq 0.05$) different from the ATS and ATS plus MAP treatments. As was observed in 2013, The ATS plus MAP treatment had the lowest mean yield and was likely a consequence of some delay in germination and emergence as a result of the liquid ATS fertilizer coming in contact with the seed during seeding and fertilizer application. The seed placed ATS in combination with the MAP fertilizer likely caused a salt effect that hindered emergence and growth of the canola plant. Application of AS and ATS was occasionally less effective in increasing yield and may be explained by some injury created by these fertilizers when placed in close proximity to the seed in the seed-row, especially in the high pH Brown Chernozem soil. Subsoil S was lower at the Brown Chernozem site in 2014 and the canola crop responded to the addition of S fertilizer. In the case of the ES and ES plus MAP treated plots, canola grain yield was observed to be greater, although not significantly ($P \leq 0.05$) greater than the control canola grain yield (Fig. 32). Gypsum is slightly soluble so this could account for the gypsum treatment having the highest overall canola grain yield. Unlike the previous year, canola grain yield at the Gray Luvisol (Star City) site in 2014 was not responsive to the addition of S fertilizer except for the PS and PS plus MAP treatments. The Gray Luvisol site had more subsoil S in 2014, compared to 2013. This could explain why there was a lack of grain yield response at this site. At the Gray Luvisol (Melfort) site, only the PS and PS plus MAP treatments canola grain yields were observed to be greater than the control, although yields were not significantly ($P \leq 0.05$) different (Fig. 32). In 2013, the PS treatment had the lowest canola grain yield, whereas in 2014, the PS treatment had the highest, although not significantly ($P \leq 0.05$) higher grain yield response than the MAP alone and ES plus MAP treatments. The ATS plus MAP treatment was observed to cause delay in germination and emergence in the canola crop, similar to what was observed at the Brown Chernozem site. The effectiveness of ES in supplying S to crops depends largely on time and method of application as this influences the rate of oxidation to plant available sulfate. The oxidization process can occur over a period of months depending upon environmental conditions (Wainwright et al., 1986), thus to assure adequate S availability, ES should be incorporated into the soil as far ahead of seeding as possible to give time for the ES to be oxidized to SO_4-S (Chien et al., 1988, Janzen and Bettany 1987; Wen et al., 2001; Solberg et al., 2003). During the controlled environment tray studies in which wheat, canola and yellow peas were grown over a period of 8 weeks each, there was deemed to be insufficient time to allow for the oxidation of the ES. This was also observed in the field study. During the critical nutrient uptake period in the first few weeks after seeding, there would not have been sufficient time for the oxidation of the ES to a plant available inorganic sulfate form.

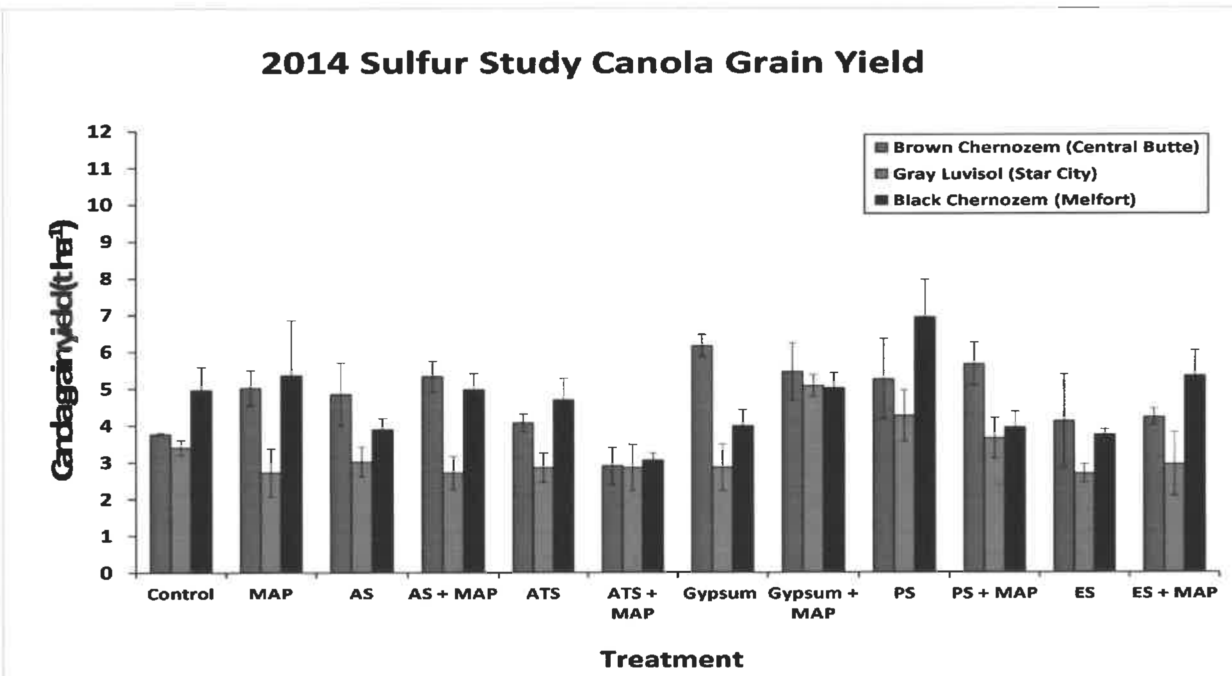


Fig. 32. Canola grain yield (t ha^{-1}) harvested at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) at the field research trials in fall 2014. Error bars denote standard error of the treatment means with N=48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental Sulfur).

Similar to canola, yellow peas also responded positively to fertilization with P at the Brown Chernozem site. Overall, across the sites there was not much response of pea to S fertilization in 2014 (Fig. 33). As for canola, which is sensitive to injury from seed-row placed fertilizer, the ATS treatments appeared to cause some injury. Therefore, especially with crops like pea that are highly sensitive to injury from seed-row placed fertilizer, ATS and AS fertilizers are best placed separate from the seed.

Grain yield response in 2014 of the yellow pea crop grown at the Brown Chernozem site was limited in the S applied treatment plots (Fig. 33). The AS plus MAP treatment was observed to produce the highest grain yield, although this was not significantly ($P \leq 0.05$) different from the other treatments and only slightly higher than the AS alone, MAP and ES treatments (Fig. 33). As with the controlled environment tray study, differences in response of wheat, canola and yellow pea were observed which reflect differences in crop requirements for S, with the higher S demand by canola (Malhi et al., 2005a). The ATS plus MAP treatment was observed to have the lowest grain yields and was attributed to the seed placement of ATS in combination with the MAP fertilizer likely causing a salt effect that hindered emergence and growth of the pea plant, similar to what was observed in this treatment in the canola plots. A lack of response to P fertilization could be due to the high sensitivity of peas to the salt effect of seed-placed fertilizer, and also to the fact that peas can effectively access indigenous soil phosphorus by acidification of the rhizosphere, and through their strong association with arbuscular mycorrhizal (AM) fungi that extend the root system. Soil P was considered to be sufficient at the Brown Chernozem site at the start of the growing season in 2014. In 2013, the addition of MAP to ATS fertilizer in the seed row hindered germination and emergence of peas and this was again observed in 2014, except for the PS plus MAP treatment, which produced a higher grain yield than the PS treatment alone. At the Gray Luvisol site the PS plus MAP produced the highest pea grain yield, although not significantly ($P \leq 0.05$) different from the other S and treatments (Fig. 33). As was observed at the Brown Chernozem site, the ATS plus MAP treatment was observed to have the lowest grain yields and was attributed to the seed placement of ATS in combination with the MAP fertilizer likely causing a salt effect that hindered emergence and growth of the pea plant. At the Black Chernozem (Melfort) site, there was no response of pea grain yield to S fertilization, compared to the control treatment. Again, the ATS plus MAP treatment was observed to have the lowest grain yields.

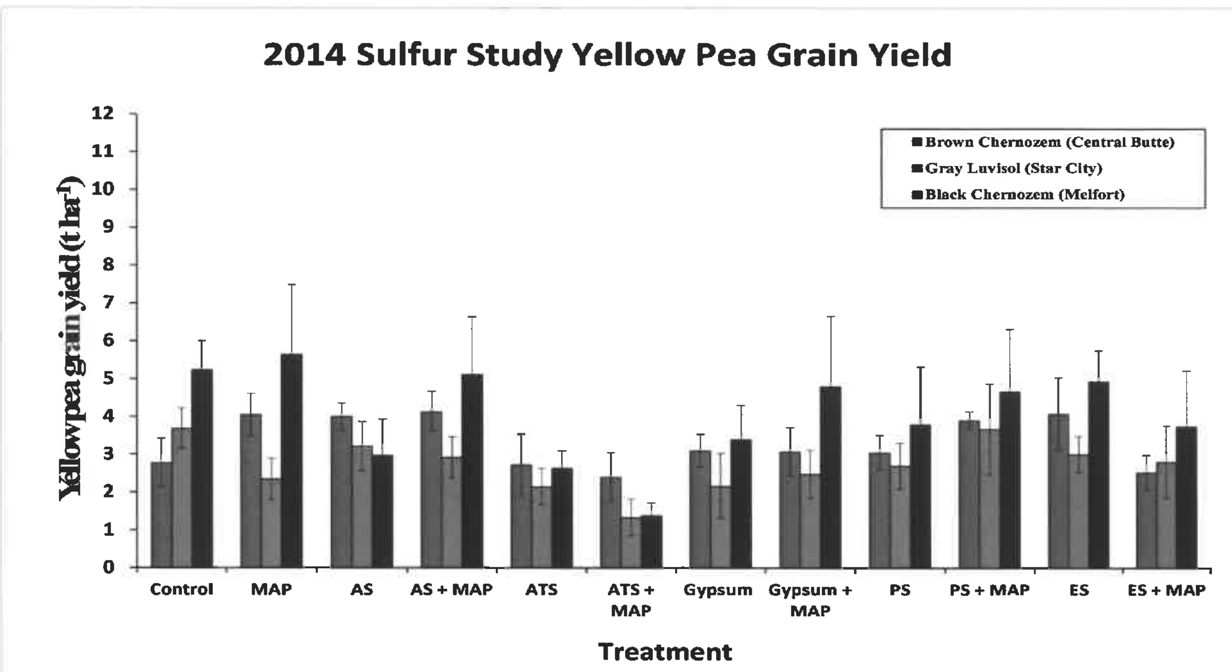


Fig. 33. Yellow pea grain yield (t ha^{-1}) harvested at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) at the field research trials in fall 2014. Error bars denote standard error of the treatment means with N=48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental Sulfur).

The S and P crop uptake data for the 2014 field season is shown in Tables 12, 13 and 14.

At the three field research sites in 2014, the fertilizer amendments did not significantly ($P \leq 0.05$) affect P uptake by wheat (Table 12), canola (Table 13) or yellow pea crops (Table 14) at the three sites. This agrees with the overall lack of crop grain yield response to P fertilization. The ATS plus MAP treatment had lower P wheat and canola uptake at all three sites and lower P uptake in the pea crop at the Gray Luvisol and Black Chernozem sites. With crop yields in the ATS plus MAP treatments being the lowest in the canola and pea crops at all three sites, it is not surprising that the P uptakes were also among the lowest for these two crops.

Table 12. Phosphorus and sulfur uptake (kg ha^{-1}) in wheat grown at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) sites in fall 2014.

Treatments*	WHEAT					
	Total P Uptake (kg ha^{-1})			Total S Uptake (kg ha^{-1})		
	Central Butte	Star City	Melfort	Central Butte	Star City	Melfort
Control	14.0 ab	11.9 a	17.2 ab	15.6 bc	11.7 a	11.8 a
MAP	15.2 ab	11.5 a	20.1 a	15.3 c	10.4 a	14.4 a
AS	17.3 ab	12.8 a	16.7 ab	19.6 abc	14.3 a	12.0 a
AS + MAP	17.3 ab	13.6 a	19.8 a	22.5 a	15.6 a	14.1 a
ATS	14.0 ab	13.0 a	14.9 b	17.7 abc	13.8 a	12.0 a
ATS + MAP	15.8 ab	14.7 a	16.5 ab	19.5 abc	13.8 a	12.3 a
Gypsum	18.4 a	13.4 a	16.4 ab	21.7 ab	13.6 a	12.4 a
Gypsum + MAP	18.4 a	11.0 a	18.1 ab	16.9 abc	12.9 a	13.3 a
PS	15.6 ab	10.4 a	18.0 ab	17.3 abc	11.7 a	12.5 a
PS + MAP	15.8 ab	12.1 a	16.2 ab	17.6 abc	12.5 a	12.4 a
ES	15.2 ab	12.7 a	17.7 ab	16.6 abc	12.8 a	12.1 a
ES + MAP	12.4 b	13.8 a	18.4 ab	14.3 c	13.3 a	12.4 a
P × S Fertlizer effect†						
LSD ($p< 0.05$))	5.40	5.10	4.66	6.38	5.67	3.24
P Value (0.05)	0.855	0.850	0.673	0.581	0.989	0.805
F Value	0.39	0.39	0.64	0.76	0.11	0.46
SEM††	1.86	1.78	1.58	2.19	1.98	1.13

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental sulfur

Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil)

are not significantly different (LSD, p <0.05)
† ANOVA results related to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil
†† Standard error of mean

Table 13. Phosphorus and sulfur uptake (kg ha^{-1}) in canola grown at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) sites in fall 2014.

Treatments*	CANOLA					
	Total P Uptake (kg ha^{-1})			Total S Uptake (kg ha^{-1})		
	Central Butte	Star City	Melfort	Central Butte	Star City	Melfort
Control	16.2 ab	15.9 b	29.4 ab	45.2 bc	15.5 c	27.6 b
MAP	25.1 a	12.7 b	30.9 ab	58.6 abc	12.8 c	27.7 b
AS	22.8 ab	13.5 b	23.4 bc	65.6 ab	20.6 bc	24.3 b
AS + MAP	25.3 a	12.9 b	29.0 ab	58.3 abc	22.9 abc	28.2 b
ATS	17.4 ab	15.0 b	28.3 abc	47.8 bc	23.5 abc	27.1 b
ATS + MAP	14.8 b	14.6 b	19.5 c	38.3 c	18.3 c	19.4 b
Gypsum	25.3 a	12.4 b	22.5 bc	61.1 abc	19.5 c	24.0 b
Gypsum + MAP	25.0 a	24.0 b	29.9 ab	58.8 abc	34.0 a	25.9 b
PS	26.4 a	18.8 ab	37.3 a	58.7 abc	32.6 ab	47.4 a
PS + MAP	27.0 a	14.9 b	23.3 bc	71.4 a	21.9 abc	21.6 b
ES	19.5 ab	11.3 b	23.6 bc	56.9 abc	14.1 c	18.2 b
ES + MAP	19.5 ab	14.9 b	35.3 a	51.6 abc	14.6 c	28.4 b
P × S Fertlizer effect†						
LSD (p< 0.05))	10.51	7.78	9.42	23.82	12.44	11.78
P Value (0.05)	0.719	0.062	0.002	0.570	0.103	0.002
F Value	0.57	2.35	4.59	0.78	2.00	4.71
SEM††	3.51	2.67	3.28	8.07	4.28	4.11

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental sulfur
# Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, p <0.05)
† ANOVA results related to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil

†† Standard error of mean

Table 14. Phosphorus and sulfur uptake (kg ha^{-1}) in yellow peas grown at: Brown Chernozem (Central Butte), Gray Luvisol (Star City) and Black Chernozem (Melfort) sites in fall 2014.

Treatments*	PEAS					
	Total P Uptake (kg ha^{-1})			Total S Uptake (kg ha^{-1})		
	Central Butte	Star City	Melfort	Central Butte	Star City	Melfort
Control	12.6 a	16.9 ab	18.8 a	9.8 ab	9.7 ab	8.7 a
MAP	16.9 a	12.0 ab	15.9 a	13.9 ab	7.1 b	10.1 a
AS	11.5 a	19.2 ab	10.5 a	13.0 ab	13.9 a	5.7 a
AS + MAP	12.7 a	15.4 ab	18.3 a	14.5 a	10.2 ab	10.4 a
ATS	11.5 a	12.3 ab	11.0 a	9.0 b	8.2 ab	6.2 a
ATS + MAP	16.0 a	9.5 ab	6.6 a	9.8 ab	6.2 b	4.6 a
Gypsum	17.6 a	11.7 ab	14.2 a	11.6 ab	9.4 ab	7.4 a
Gypsum + MAP	17.9 a	12.8 ab	18.4 a	14.2 a	8.3 ab	10.2 a
PS	11.9 a	14.7 ab	15.0 a	10.9 ab	10.3 ab	7.8 a
PS + MAP	14.1 a	17.4 ab	15.9 a	12.7 ab	11.1 ab	9.7 a
ES	14.5 a	14.1 ab	14.9 a	12.4 ab	9.1 ab	7.8 a
ES + MAP	12. 0	17.9 ab	13.7 a	11.4 ab	11.3 ab	6.8 a
P × S Fertlizer effect†						
LSD (p< *0.05)*)	6.45	9.06	12.80	5.15	6.44	6.29
P Value (0.05)	0.481	0.655	0.739	0.808	0.775	0.713
F Value	0.92	0.66	0.55	0.45	0.50	0.58
SEM††	2.25	3.11	4.34	1.80	2.25	2.10

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental sulfur

Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, p <0.05)

† ANOVA results related to the phosphorus (P) x sulfur (S) fertilizer interaction effect independently for each soil

†† Standard error of mean

Total S uptake for the wheat crop were affected by fertilization at the Central Butte (Brown Chernozem) site (Table 5). The wheat crop was observed to have significantly ($P \leq 0.05$) greater S uptake in the AS plus MAP treatment, compared to the control, MAP and ES plus MAP treatments, however, the S uptake was not significantly ($P \leq 0.05$) greater than the other S treatments (Table 12). There was no significant ($P \leq 0.05$) effect on wheat S uptake at either the Star City (Gray Luvisol) or Melfort (Black Chernozem) sites, which is in agreement with a lack of wheat crop response to S at those two sites (Table 12). At the Brown Chernozem site, canola S uptake was highest reflecting high yield and crop S demand, and significantly ($P \leq 0.05$) greater in the PS plus MAP treatment, compared to the control, ATS and ATS plus MAP treatments (Table 6). Canola S uptake was lowest in the ATS plus MAP treatment, consistent with this treatment having the lowest canola grain yield response at this site, compared to the other S fertilizer treatments (Table 6). At the Star City site, the gypsum plus MAP had the highest overall canola S uptake, however, this was not significantly ($P \leq 0.05$) greater than the AS and PS treatments combined with MAP. The ES and ES plus MAP treatments had the lowest overall S uptake, consistent with lower canola grain yields at this site. At the Melfort site, the PS treatment had significantly ($P \leq 0.05$) higher S uptake in the canola crop compared to all other treatments (Table 13). Again, the ATS plus MAP treatment had the lowest overall mean S uptake compared to all other treatments. The lower canola grain yield in the ATS plus MAP treatment affected S uptake. Sulfur uptake by the pea crop at all three sites was lowest in the ATS plus MAP treatment, reflecting the negative salt effect that the ATS fertilizer had on sensitive pea seeds affecting emergence, germination and subsequently, grain yield and S uptake (Table 14). In plots amended with AS and MAP, S uptakes in the peas was generally, although not significantly ($P \leq 0.05$) greater at the Brown Chernozem and Black Chernozem sites (Table 14).

Soil extractable available sulfate and phosphate amounts in the seed-row one week (7 days), 4 weeks (28 days) and 8 weeks (56 days) after seeding in the 2013 field season are shown in Figs. 34 through 42.

Overall, seven days after seeding, plant available SO_4-S content in the seed-row was significantly ($P \leq 0.05$) higher in the AS, ATS, gypsum and PS with MAP additions, compared to the control, MAP alone and ES with and without MAP at the Brown Chernozem site (Fig. 34, 37 and 40). By 28 and 56 days after seeding, soil available S in all the S treatments had decreased to levels under 10 mg SO_4-S kg^{-1} with the exception of the gypsum plus MAP treatment. These findings for 2014 season are similar to those for 2013. The slightly soluble properties of gypsum reduce movement of SO_4-S away from where it is placed in the soil, thus slightly more SO_4-S was made available over time. This trend was observed at both the Gray Luvisol (Fig. 35) and Black Chernozem (Fig. 36) sites in the wheat crop seed row soil samples. Soil SO_4-S was observed to be the highest in the gypsum and gypsum plus MAP treatments at the Gray Luvisol and Black Chernozem sites in the wheat crop seed-row soil samples (Figs. 37 and 40). At all three sites (Figs. 35, 38 and 41), the gypsum and gypsum plus MAP treatments in the canola crop were observed to be significantly greater than all other S treatments at 28 days after seeding which is due to its slightly soluble nature, maintaining sulfate concentrations in the vicinity where the S fertilizer was placed. However, this did not affect plant S uptake in the canola crop at all three sites. In 2014, as in 2013, at all three sites for the wheat (Figs. 34, 35 and 36), canola (Figs. 37, 38 and 39) and yellow pea (Figs. 40, 41 and 42) crops, contents of SO_4-S in the ES fertilizer treatments seven days after application were not significantly ($P \leq 0.10$) different from control treatments receiving no S fertilizer. A lack of oxidation to SO_4-S over the seven day period would account for lower seed row available S. All SO_4 and ATS fertilizers had large decreases in the content of SO_4-S in the seed-row for all crops and all sites from day 7 to day 28, indicating large plant uptake of SO_4-S by all crops in the first month after seeding (Figs. 16 through 24), again consistent with the 2013 results. Overall, the large drop in soil extractable SO_4-S, 28 days after seeding, indicated that the majority of plant S uptake occurred within the first several weeks and indicates a benefit of seed placing S for encouraging plant S uptake early in the growth cycle.

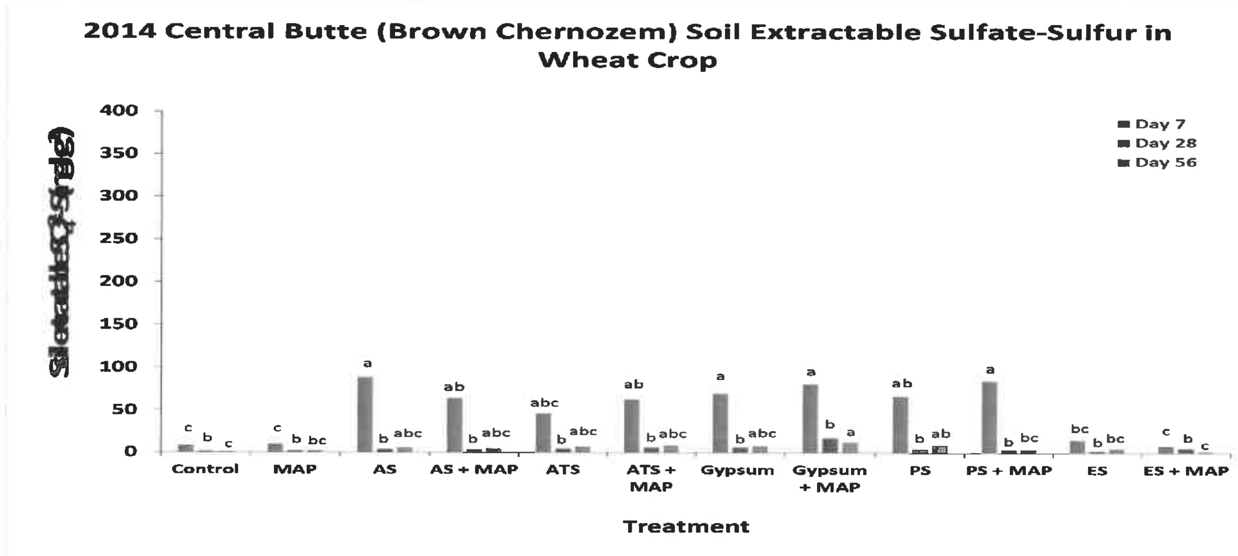


Fig. 34. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in wheat at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

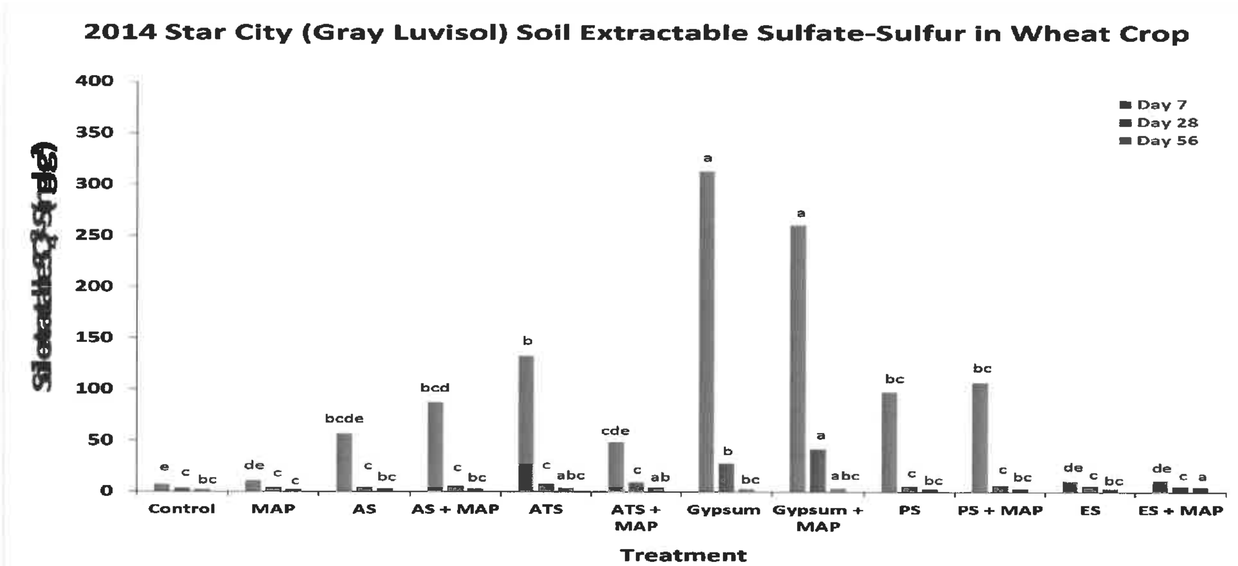


Fig. 35. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in wheat at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

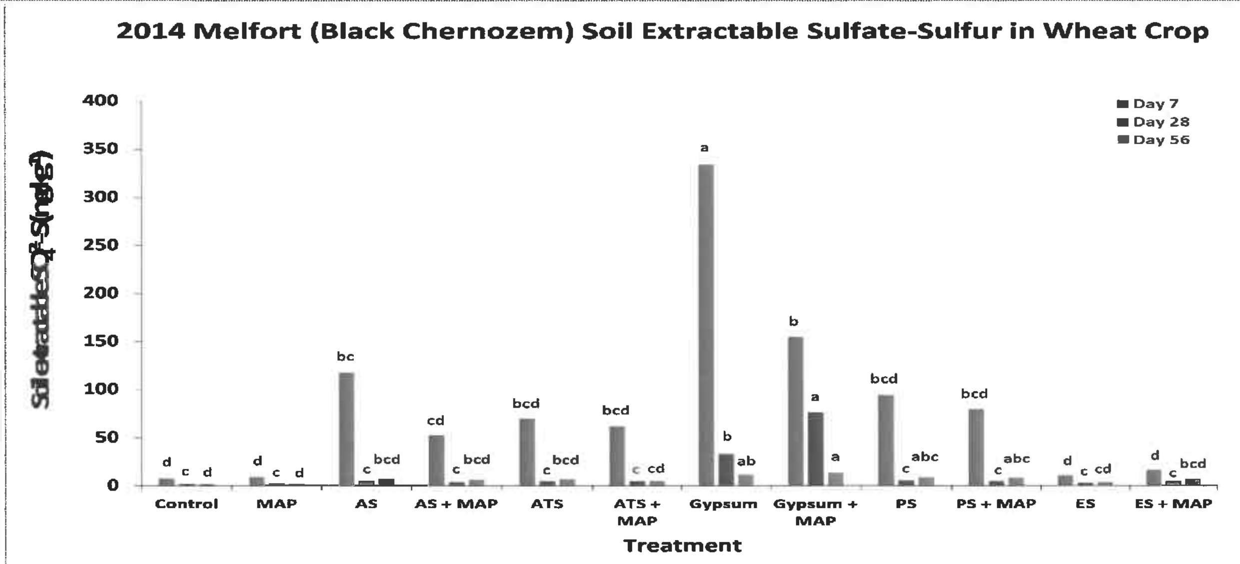


Fig. 36. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in wheat at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

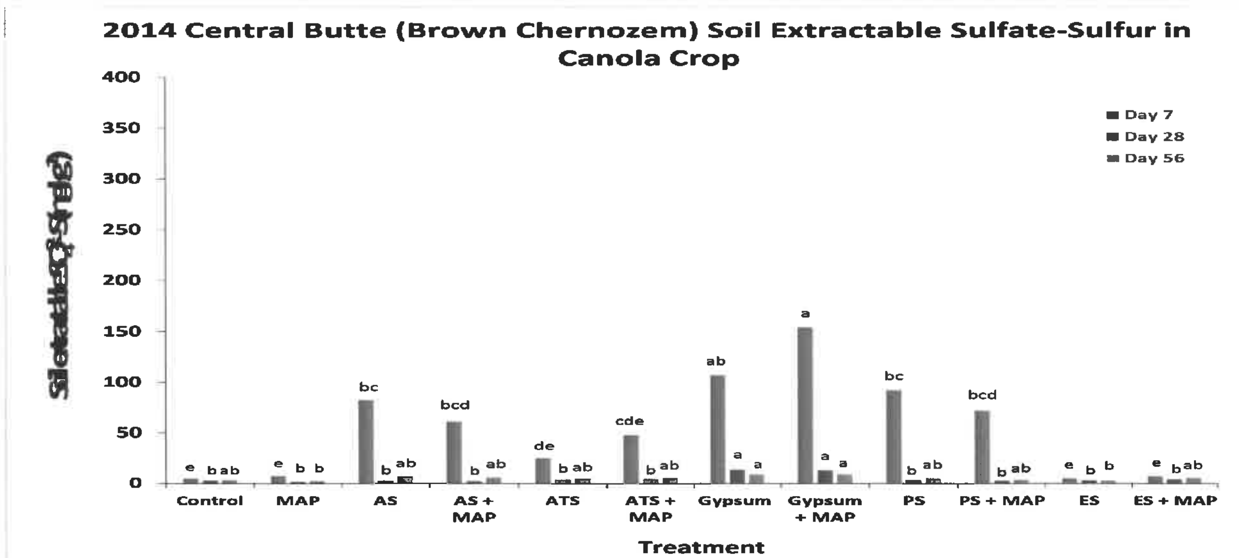


Fig. 37. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in canola at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

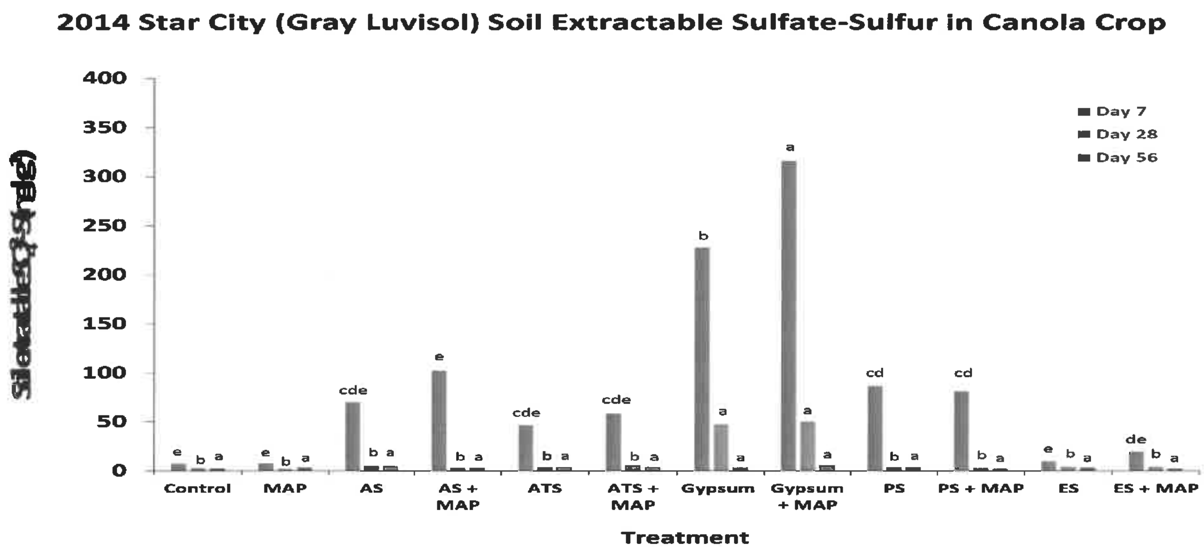


Fig. 38. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in canola at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

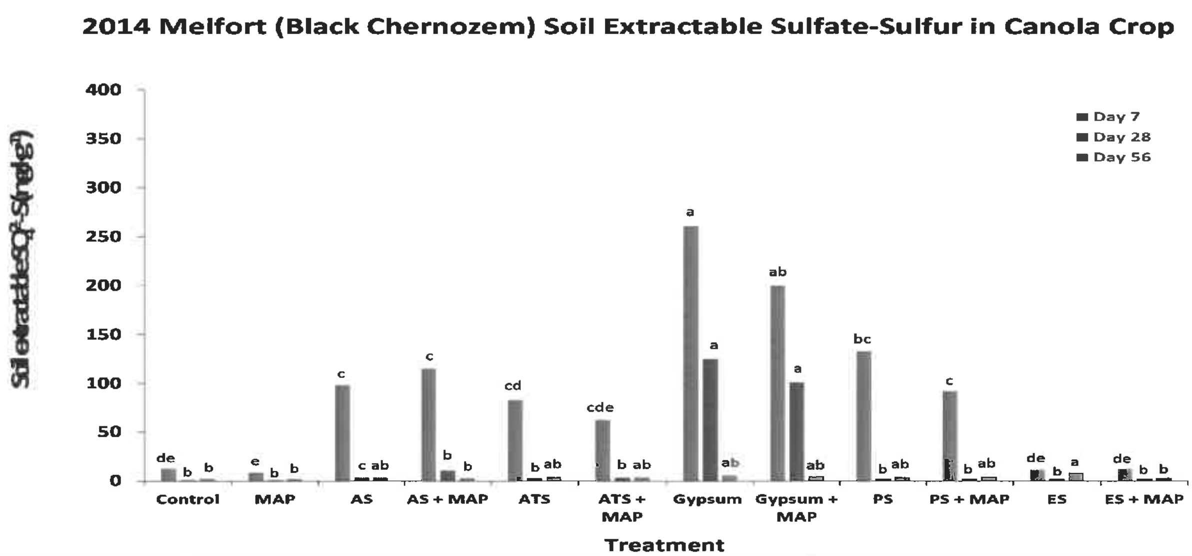


Fig. 39. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in canola at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

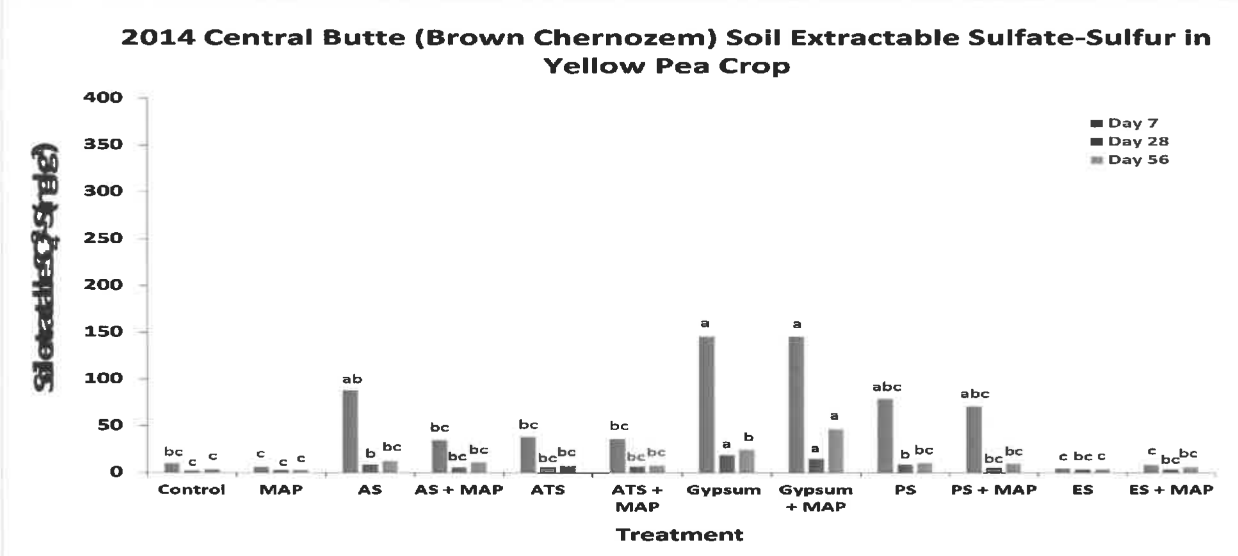


Fig. 40. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in yellow peas at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

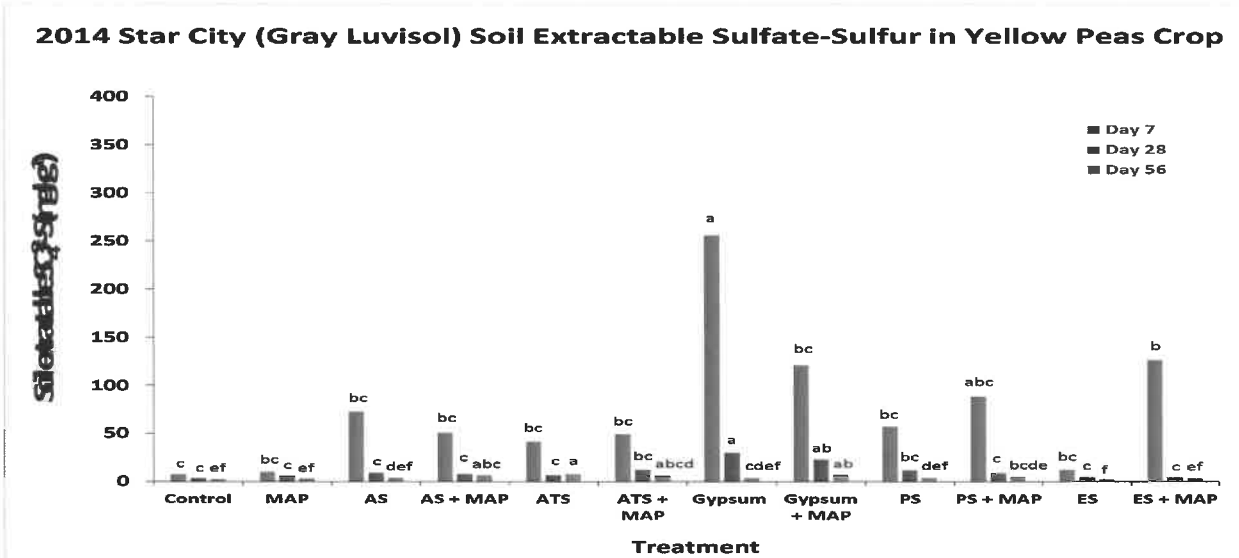


Fig. 41. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in yellow peas at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

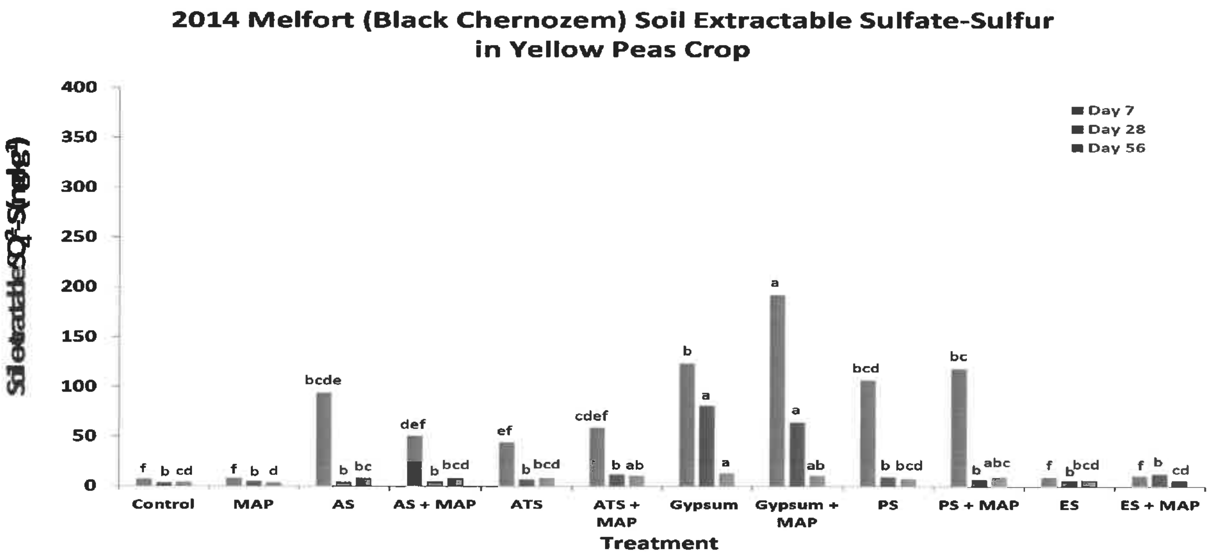


Fig. 42. Mean seed-row extractable sulphate-sulfur content (SO_4-S kg ha^{-1}) in yellow peas at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

The seed-row extractable PO_4-P contents one week (7 days), four weeks (28 days) and eight weeks (56 days) after seeding in 2014 are shown in Figs. 43 through 51. As was observed in the 2013 field season, in 2014 the addition of MAP significantly increased the content of extractable available PO_4-P in the seed-row one week (7 days) after seeding for all crops at all three field research sites (Figs. 43 through 51). Increases in seed-row PO_4--P at one week after seeding were greatest at the Black Chernozem site (Figs. 45, 48 and 51). This likely reflects greater precipitation of fertilizer PO_4-P in less soluble calcium phosphate reaction products at the Brown Chernozem (Figs. 43, 46 and 49) and Gray Luvisol (Figs. 44, 47 and 50) sites as a consequence of higher soil pH and the more calcareous nature of the soil. The combination of S fertilizer plus MAP did not appear to significantly affect the extractable PO_4-P in the S plus MAP treatments compared to the MAP alone treatment, although the mean extractable phosphates after seven days were frequently higher when S was combined with MAP compared to MAP alone. Similar to SO_4-S, a large depletion in seed row PO_4-P content is observed from week one (day 7) to week four (day 28) for all crops at all three sites, as a consequence of crop uptake of PO_4-P from the seed-row in the first several weeks of the wheat, canola and yellow pea crops growth cycle.

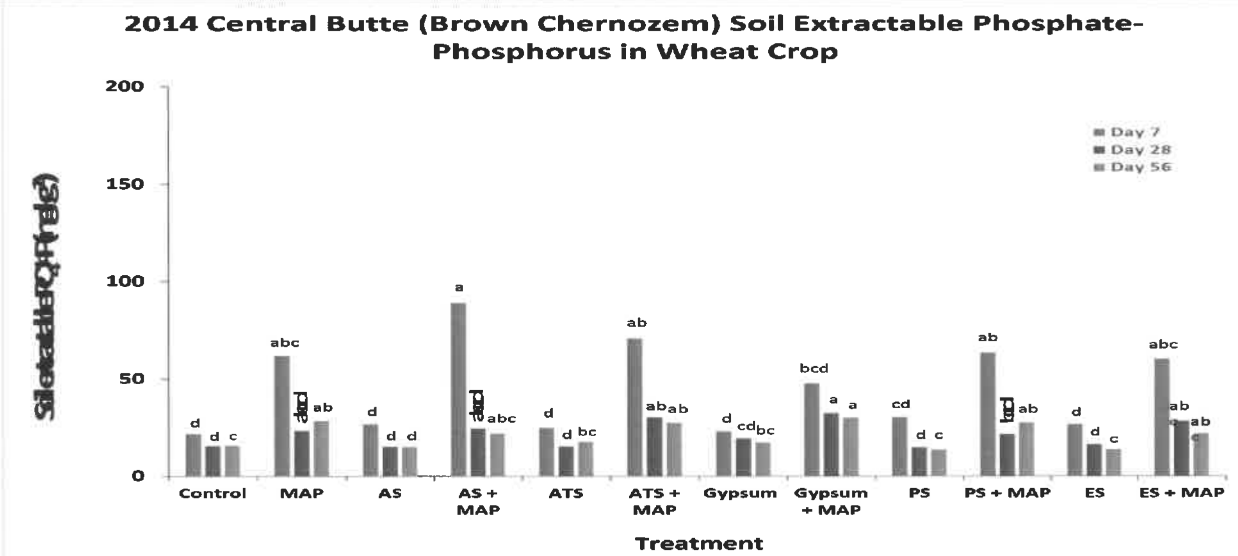


Fig. 43. Mean available seed-row extractable phosphate-phosphorus content (PO_4-P kg ha^{-1}) in wheat at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

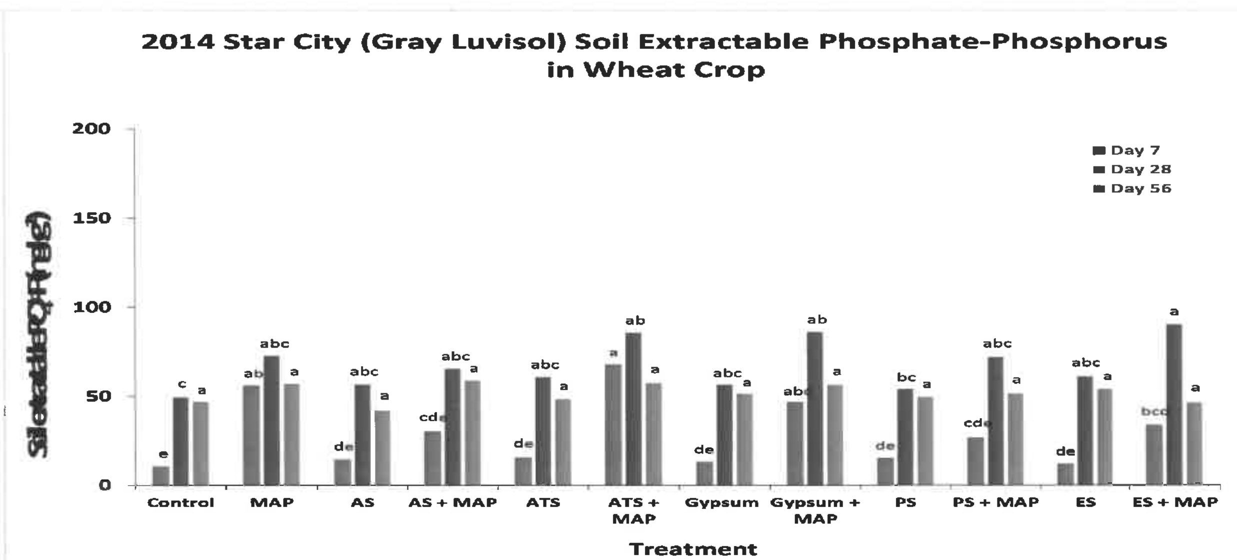


Fig. 44. Mean available seed-row extractable phosphate-phosphorus content (PO_4-P kg ha^{-1}) in wheat at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

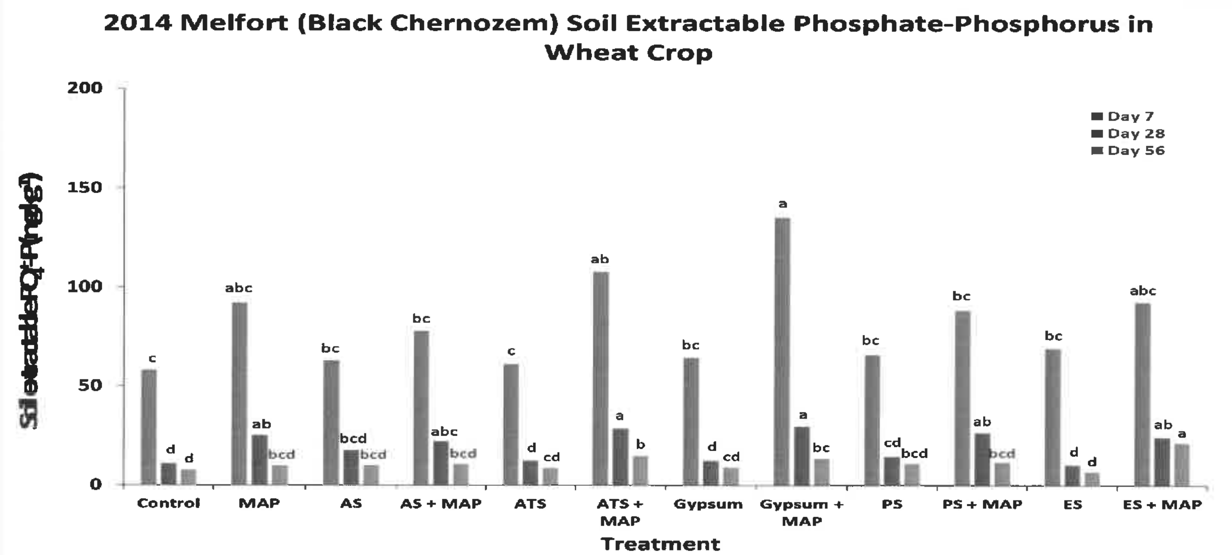


Fig. 45. Mean available seed-row extractable phosphate-phosphorus content (PO_4-P kg ha^{-1}) in wheat at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

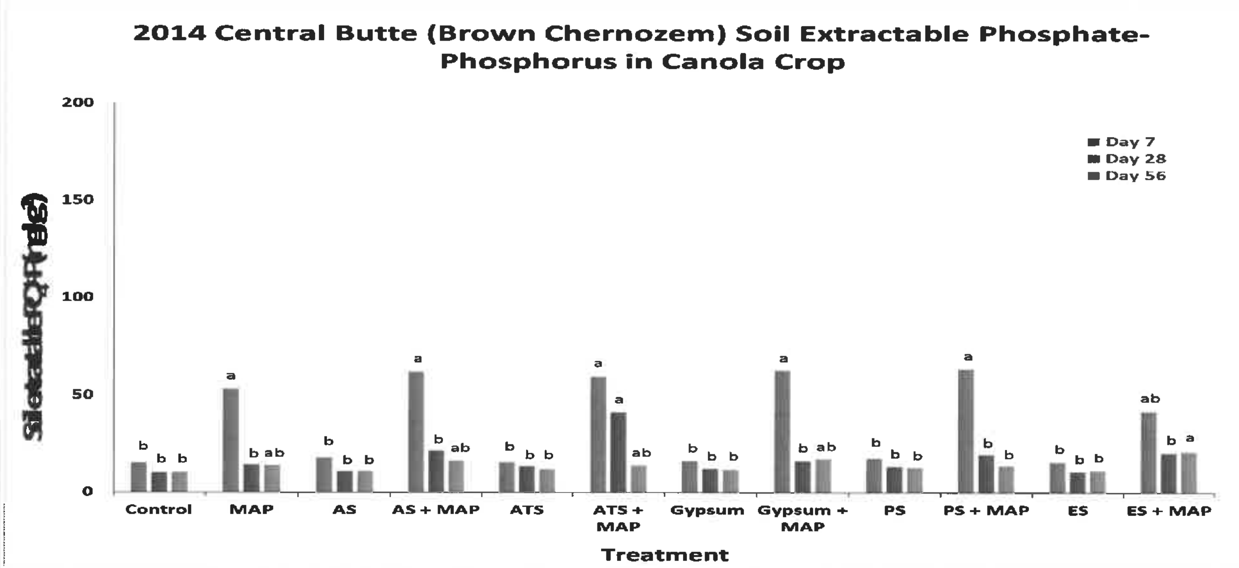


Fig. 46. Mean available seed-row extractable phosphate-phosphorus content (PO_4-P kg ha^{-1}) in canola at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

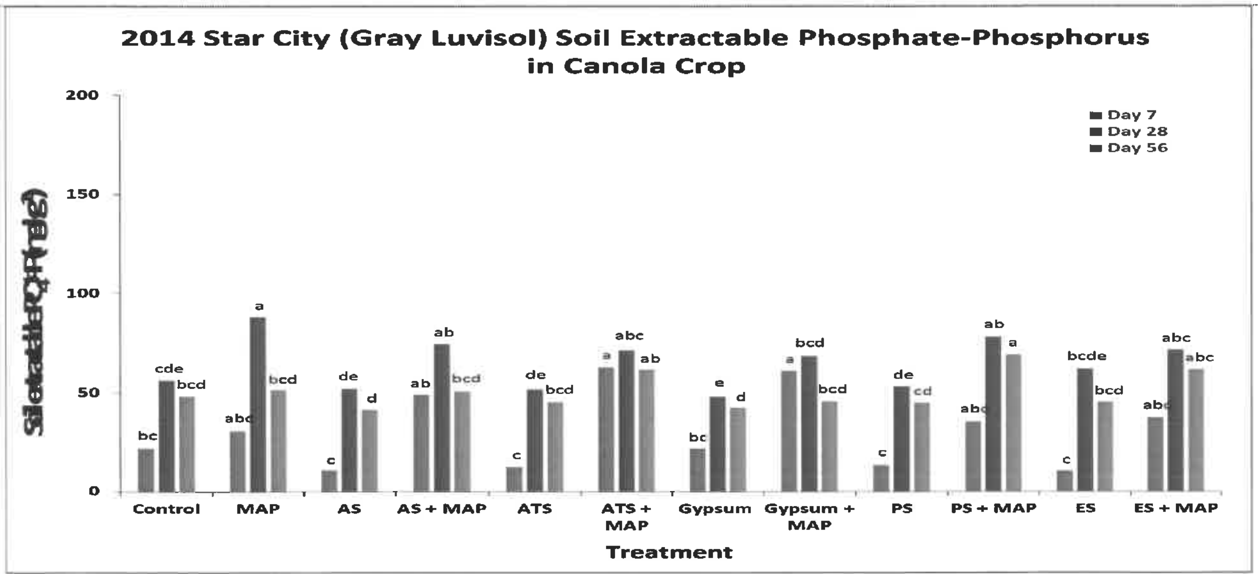


Fig. 47. Mean available seed-row extractable phosphate-phosphorus content (PO_4^--P kg ha^{-1}) in canola at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

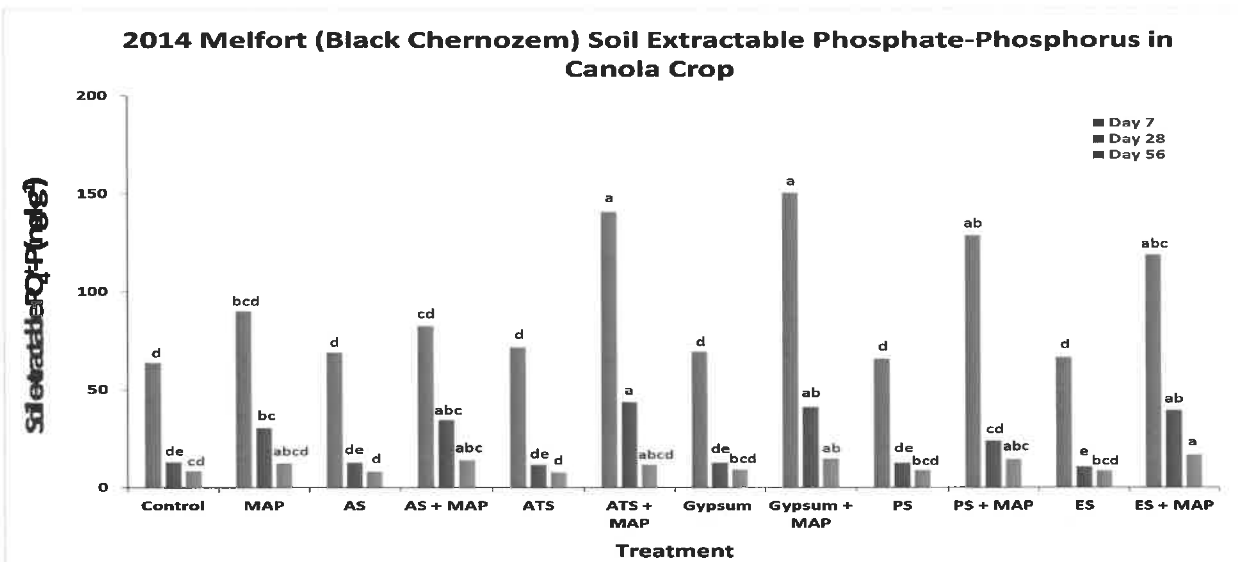


Fig. 48. Mean available seed-row extractable phosphate-phosphorus content (PO_4-P kg ha^{-1}) in canola at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

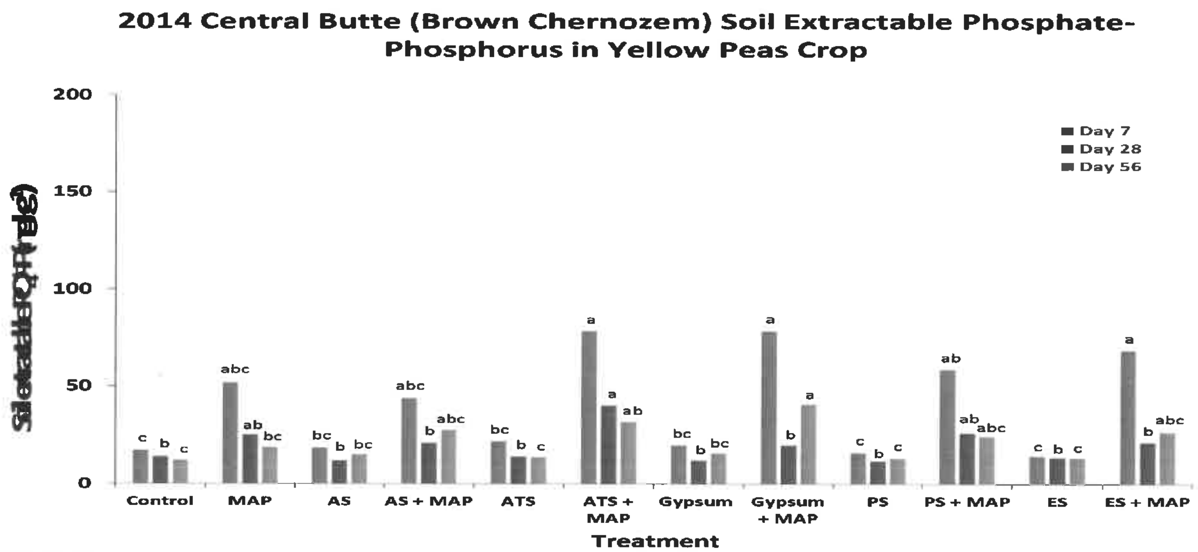


Fig. 49. Mean available seed-row extractable phosphate-phosphorus content (PO_4-P kg ha^{-1}) in yellow peas at Brown Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq$ 0.10).

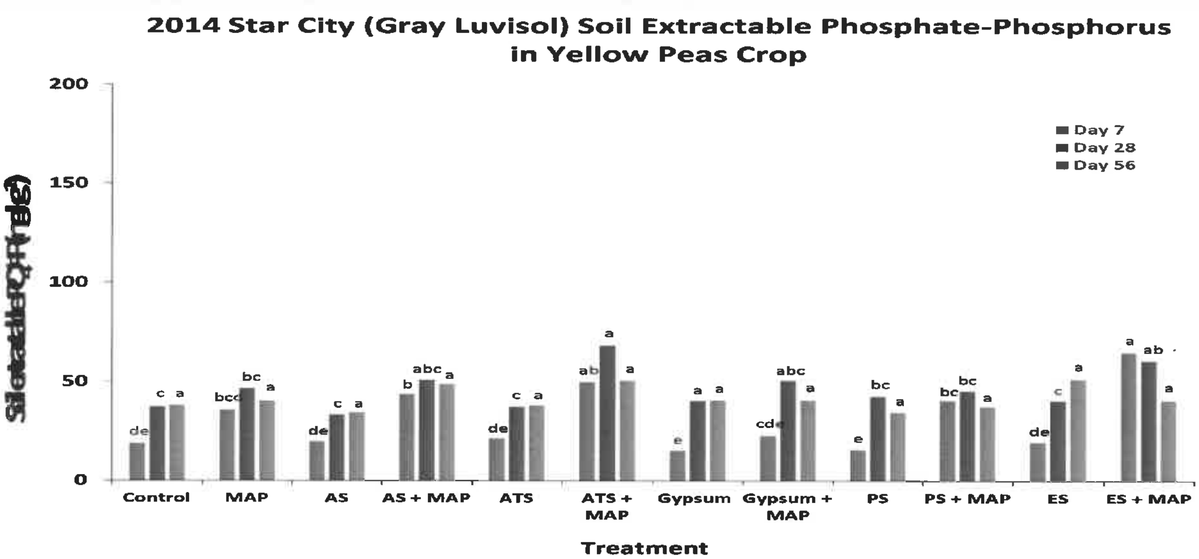


Fig. 50. Mean available seed-row extractable phosphate-phosphorus content (PO_4-P kg ha^{-1}) in yellow peas at Gray Luvisol soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

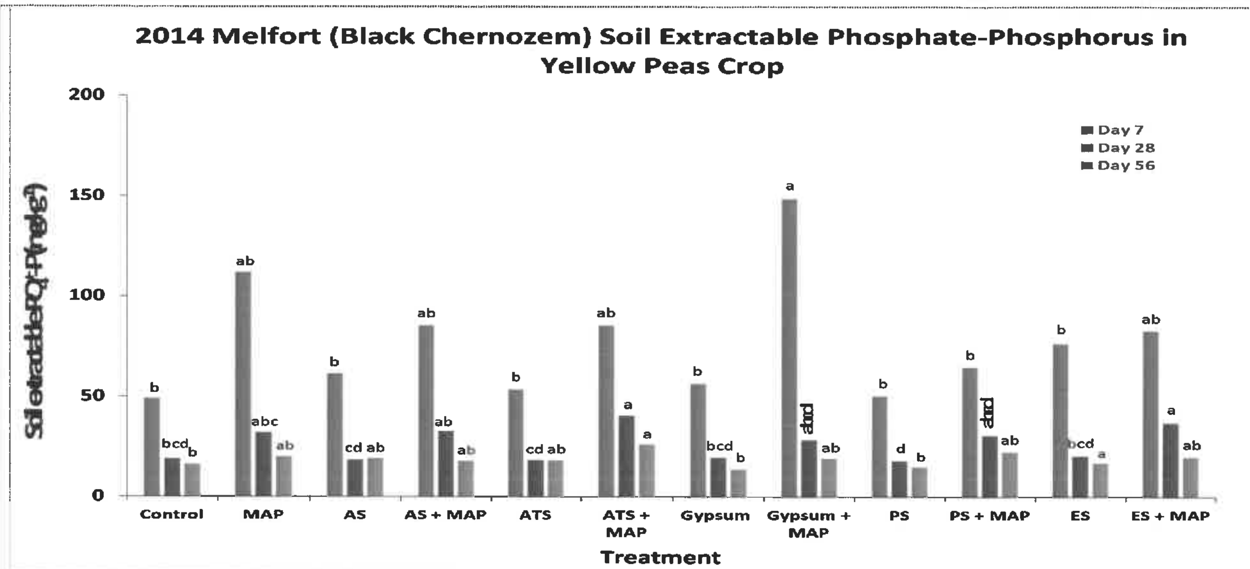


Fig. 51. Mean available seed-row extractable phosphate-phosphorus content (PO_4-P kg ha^{-1})in yellow peas at Black Chernozem soil after: one week (7 days), four weeks (28 days) and 8 weeks (56 days) in fertilizer amended soil in 2014. Treatment means followed by the same letter are not significantly different with N = 48 and n = 4. (MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate. For a treatment, means with different letters are significantly different (Tukey's HSD, $P \leq 0.10$).

2015 Field Study

One field site, the 2014 Central Butte site, was maintained beyond the original planned one year period in order to assess longer term effects of the S fertilization. In 2015, wheat was grown on the 2014 canola plots at the Brown Chernozem site. No N, S and/or MAP fertilizer was applied in 2015. Wheat yields were not significantly different amongst the treatments (Fig. 52). Overall, yields were approximately half of the yields observed in 2014. This is a consequence of the depletion of nutrients by the 2014 canola crop. By 56 days after seeding in 2014, the canola plots had less than 10 mg soil extractable SO_4-S kg^{-1} and less than 21 mg soil extractable PO_4-P kg^{-1} across all treatments.

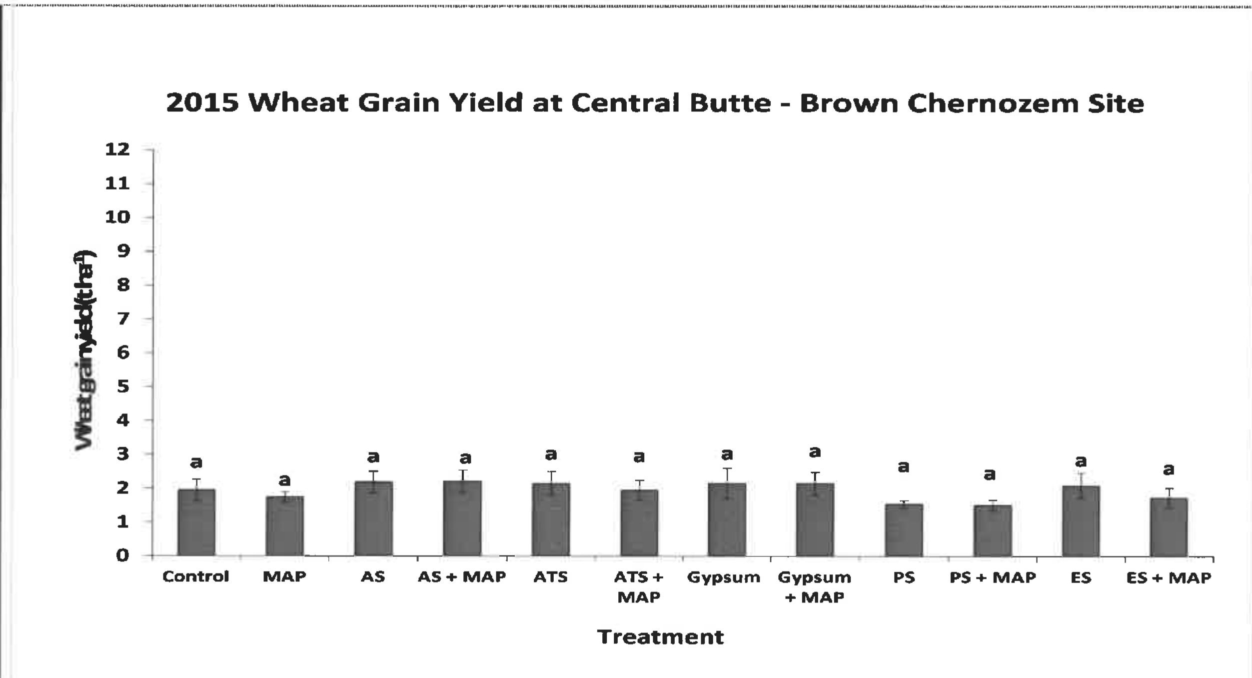


Fig. 52. Wheat grain yield (t ha^{-1}) in fall 2015 at Brown Chernozem (Central Butte) field research trial that received S and P fertilizer treatments in spring of 2014. Error bars denote standard error of the treatment means with N=48 and n = 4. (MAP=Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental Sulfur).

Wheat grain plant S uptake at the Brown Chernozem site in 2015 was highest in the AS and AS plus MAP and significantly ($P \leq 0.10$) greater than the PS and PS plus MAP treatments (Table 15). All other S treatments and the control treatment had similar S uptakes in the plant grain component. Straw plant S uptake was highest in the AS, AS plus MAP, ATS and Gypsum plus MAP treatments (Table 15). The straw contained slightly more S compared to the grain for each treatment. The similarity in S uptake by the wheat in 2015 among S treatments is in agreement with similar low levels of residual sulfate in the seed-row among treatments 56 days after seeding of the canola in 2014. Lower S uptake by wheat in the PS treatments in 2015 may be explained by this treatment having the highest uptake of S by canola in 2014, thereby depleting the sulfate to a greater extent. Higher S uptake by the 2015 wheat crop in the AS treatments may reflect mineralization of some of the fertilizer S applied in 2014 that was immobilized in soil organic matter. No evidence of continued oxidation of the elemental S was found in the form of grain and S straw uptakes in the ES treatments in the 2015 wheat crop that were significantly higher than the unfertilized control.

Table 15. Sulfur uptake (kg ha^{-1}) in 2015 wheat grain and straw grown on canola stubble at Brown Chernozem (Central Butte), site.

Treatments*	WHEAT Total S Uptake (kg ha^{-1}) Grain		Straw	
Control	3.3	ab	5.4	a
MAP	3.0	ab	4.0	ab
AS	4.1	a	5.7	a
AS + MAP	4.0	a	5.3	a
ATS	3.4	ab	5.5	a
ATS + MAP	3.3	ab	5.2	ab
Gypsum	3.3	ab	4.0	ab
Gypsum + MAP	3.3	ab	5.7	a
PS	2.6	b	2.8	b
PS + MAP	2.9	b	3.6	ab
ES	3.2	ab	4.5	ab
ES + MAP	3.1	ab	4.8	ab
LSD ($p < 0.10$)	1.16		2.36	
P Value (0.10)	0.62		0.55	
F Value	0.82		0.89	

* MAP = Monoammonium Phosphate; AS = Ammonium Sulfate; ATS = Ammonium Thiosulfate; PS = Potassium Sulfate and ES = Elemental sulfur

Means (P ×S sources; N = 48 and n = 4) with the same letter in the same column (for a soil) are not significantly different (LSD, p <0.10)

Detection of Sulfur Fertilizer Reaction Products Using XANES Spectroscopy

Sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy was used to identify sulfur species in soils from the three sites receiving S fertilizers. The Sulfur K-edge XANES spectra of S reference compounds exhibited the main white line peaks at different energy levels, showing how the oxidation state affects the energy level (Fig. 53A), allowing identification of S compounds based on peak shift. The XANES results showed that the different applied S fertilizers behaved differently, with different S species formed in the seed-row of canola in the different soils (Brown, Black, and Gray) (Fig. 53B to 53F) over time.

The XANES spectroscopy revealed that the sulfate from sulfate fertilizer sources tended to remain in the seed-row over the eight weeks to a greater extent in the Brown and Black Chernozem soils compared to the Gray soil. This is explained by the Gray site having the highest canola plant S uptake and is consistent with a greater observed reduction in SO_4-$^{2-}$ concentration observed in the seed-rows at the Gray site from week 1 to week 8.

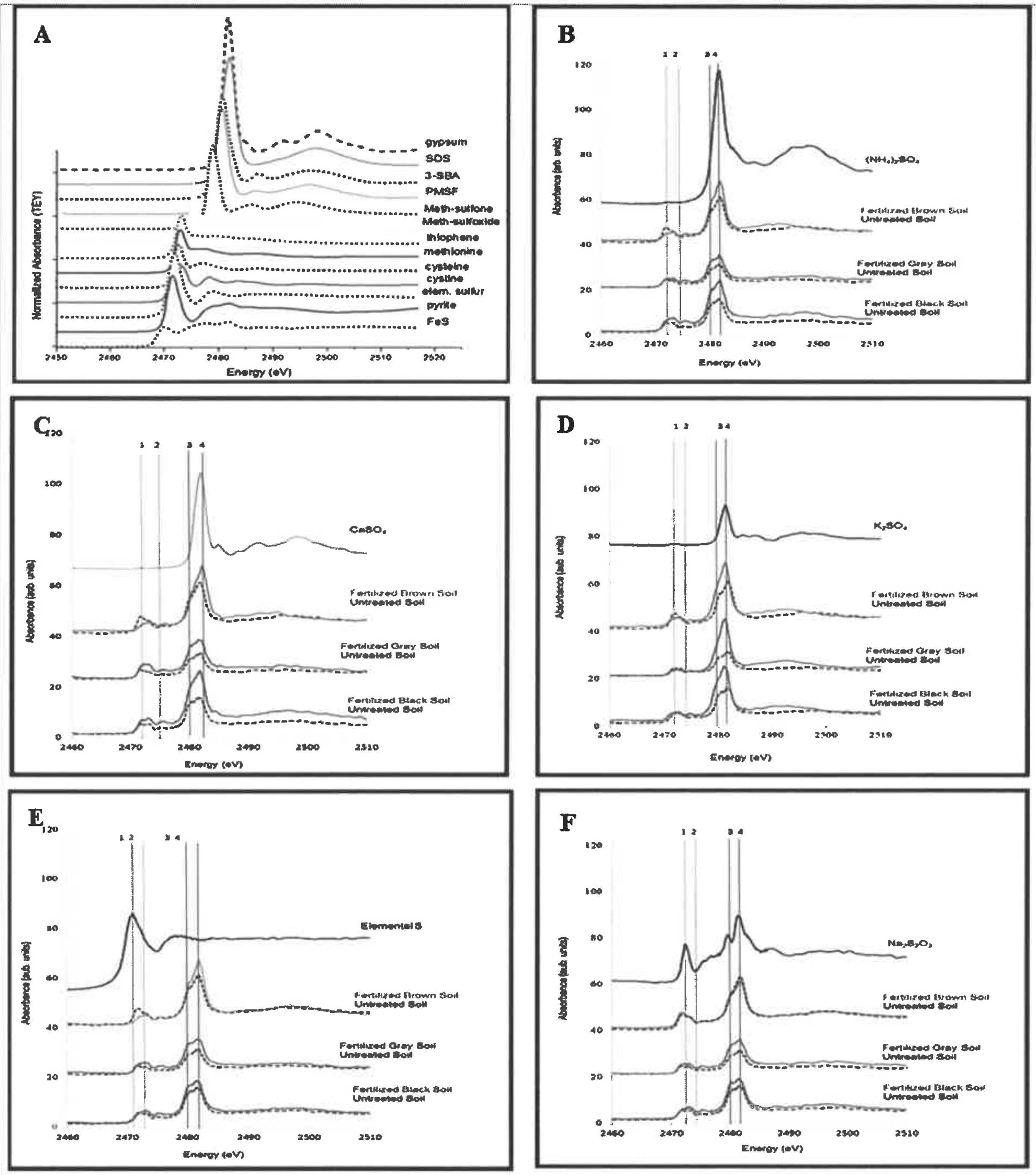


Fig. 53. S K-edge XANES of S reference compounds (A) and three different soils receiving ammonium sulfate (B), gypsum (C), potassium sulfate (D), elemental S (E), and ammonium thiosulfate (F) fertilizers in spring of 2013. Green, orange and purple colored lines represent the fertilized Brown, Black and Gray soils respectively, and black dashed line represents the comparative untreated soil. Dashed lines denote different S species as follows: (1) elemental S (2) thiols (3) ester sulfates (4) inorganic sulfate.

It is evident that there is some transformation of the SO_4- to thiols, ester sulfates, and also residual inorganic sulfate forms of S identified in the soils (Fig. 53B) after 8 weeks of plant growth. The formation of thiols, and particularly ester SO_4^{-2-} is interesting, as ester SO_4^{-2-} are believed to be largely microbial in origin and considered to be a labile, easily mineralized form of organic S in soils (Schoenau and Malhi, 2009). Some of these compounds may be re-mineralized to sulfate the following season as noted in the 2015 field data. These findings provide evidence for microbial immobilization of fertilizer S into organic forms.

Application of calcium sulfate fertilizer (Figure 53C) showed the same trend as AS but thiols were only identified in the Gray Luvisol and Black Chernozem soils. A greater degree of thiol and ester SO_4-$^{2-}$ formation in the Black and Gray soils may reflect a greater intensity of microbial activity in these soils due to higher organic matter content. A similar transformation pattern was observed after application of PS fertilizers (Figure 53D). At the end of 8 weeks, sulfur remaining from the potassium sulfate application could be identified as mainly being inorganic sulfate and ester sulfate.

Elemental S is insoluble in soil and unavailable for plant or microbial use until it is oxidized to SO_4-$^{2-}$ by S oxidizing microbes in the soil (Malhi et al., 2005). The ES fertilizer in the three soils soil appeared to undergo some oxidation in the eight weeks after application (Fig. 54).

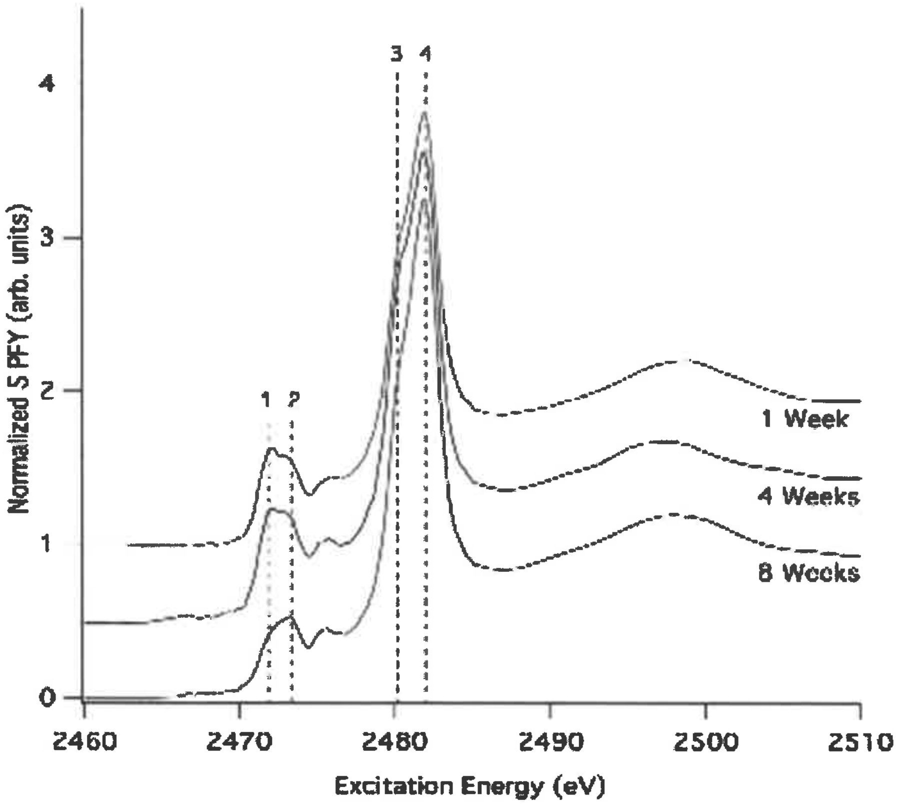


Fig. 54. Reduction in elemental sulfur peak (line 1) as a result of oxidation in soil.

This is also evident by an elemental S peak in the fertilized soil that was not different from the unfertilized soil at the end of the eight weeks. In the Brown soil, there was concomitant formation of thiols and inorganic SO_4-$^{2-}$ forms (Figure 53E), with these forms along with ester SO_4-$^{2-}$ identifiable in the Black and Gray soils. Sulfate concentrations in the seed-row were very low in the elemental S treatments at all three sampling times, indicating that SO_4-$^{2-}$ formed from oxidation must have been rapidly assimilated by canola roots. The ATS (Figure 53F) spectra results showed that this fertilizer transformed into elemental S and inorganic SO_4-$^{2-}$ forms. This is expected as it is known that thiosulfates, when added to soil, forms colloidal elemental S and AS (Havlin et al., 2014). Formation of ester SO_4^{-2-} form was also observed in the Black Chernozem soil after 8 weeks of plant growth (Figure 53F). The reduced peak height difference between fertilized and untreated soils in ES and ATS applied soil compared to those receiving SO_4^{-2-} is likely a consequence of slow release of $SO_4^{-2-}$by oxidation such that SO_4^{-2-} produced was readily assimilated by plant roots as it was produced. It was also observed that more S remained in the Black Chernozem soil compared to the Brown Chernozem and Gray Luvisol soils in the AS, gypsum and PS fertilizers amendments. This could reflect microbial immobilization of the applied SO_4^{-2-} followed by mineralization later in the season.

Detection of Phosphorus Fertilizer Reaction Products With and Without Sulfate Fertilizer Using XANES Spectroscopy

Phosphorus K-edge X-ray absorption near edge structure (XANES) spectroscopy was used to identify P species in soils from the two sites receiving P fertilizer addition with or without different S fertilizers. The P K-edge XANES spectra of P reference compounds exhibited the main white line peaks at different energy levels, showing how the oxidation state affects the energy level (Fig. 55), allowing identification of P compounds based on peak shift. The XANES results showed that the applied P fertilizer behaved differently with soil type and when incorporated with S fertilizer which formed different P species in the seed-row of canola in the different soils (Brown and Black,) (Table 16) over time.

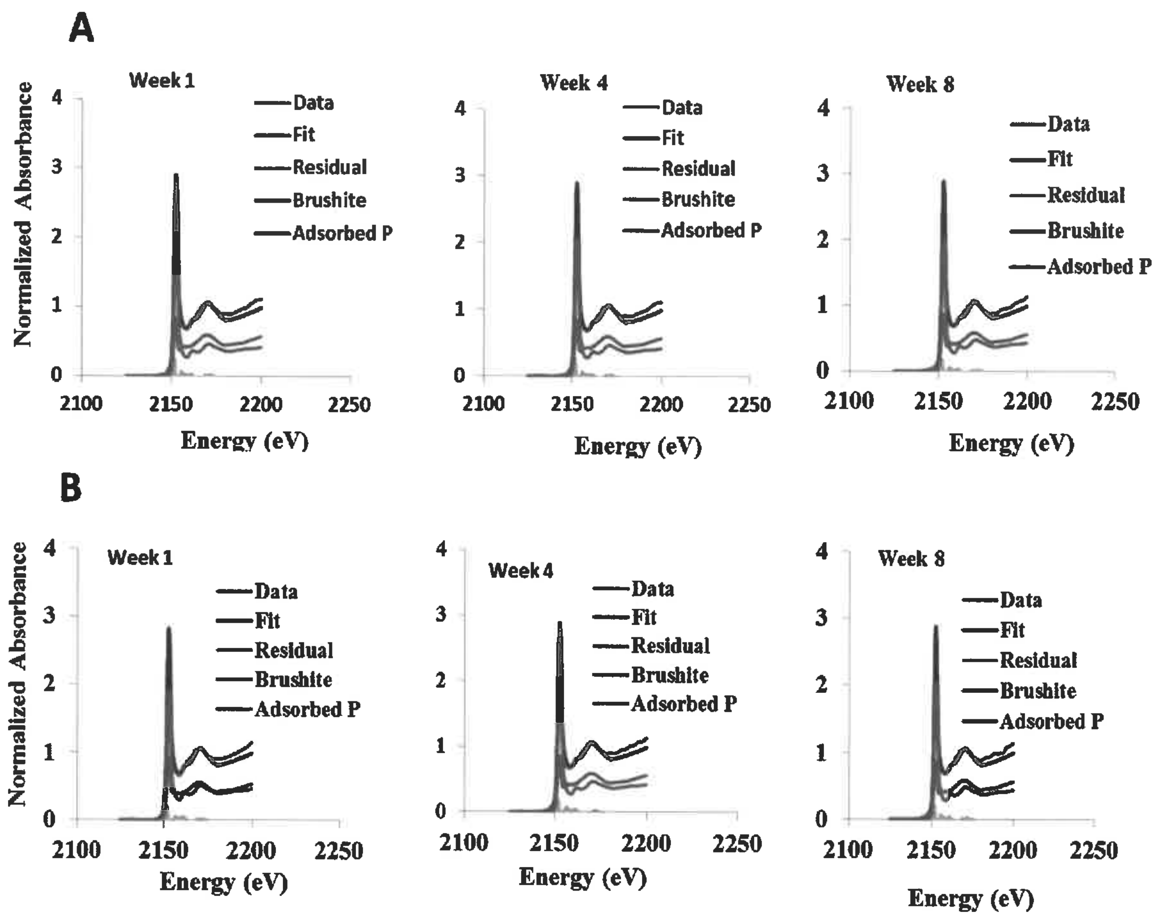


Fig. 55. Linear Combination XANES fit of differential XANES spectra of mono-ammonium phosphate fertilizer applied (A) Brown Chernozem and (B) Black Chernozem soil over time.

The fitting results for MAP fertilizer treated soil added with or without S fertilizer showed that P was mainly present as adsorbed P and as brushite (dicalcium phosphate) in both the Brown and Black Chernozem soils. The XANES spectroscopy results showed (Fig. 55 and Table 16) that in the Brown Chernozem soil, the adsorbed P form was lower initially but it increased over time. In the Brown Chernozem soil, by week 8 a significant portion of the Ca-P appears to have been transformed into adsorbed P in the presence of sulfate. This likely reflects the effect of the sulfate reacting with Ca in this highly calcareous soil resulting in increased dissolution of the Ca-P (brushite) (Kumaragamage, et al., 2004), with the phosphate liberated subsequently reacting with sorbing surfaces in the soil. In the Black Chernozem soil, the addition of sulfate had little effect on the distribution of P between Ca-P and adsorbed form.

Table 16. Linear combination phosphorus X-ray absorption near edge structure (P XANES) fitting results showing

proportions of phosphorus compounds in the phosphorus fertilized soils.

Soil sample	Time	Brushite	Adsorbed P	Apatite
		%		
Brown Chernozem Soil				
P with no S fertilizer	Week 1	52	47	-
	Week 4	41	57	-
	Week 8	43	56	-
P with K_2SO_4 fertilizer	Week 1	56	42	-
	Week 4	57	42	-
	Week 8	28	69	-
Black Chernozem Soil				
P with no S fertilizer	Week 1	45	52	-
	Week 4	42	56	-
	Week 8	43	55	-
P with K_2SO_4 fertilizer	Week 1	45	54	-
	Week 4	42	57	-
	Week 8	49	50	-

Phosphorus K-edge X-ray absorption near edge structure (XANES) spectroscopy was successfully used to identify P species formed from P fertilizer in the soil in the presence and absence of K_2SO_4 fertilizer. Overall, the XANES spectroscopy showed that one week after fertilizer application, P species present in the seed-row included similar proportions of adsorbed and poorly crystalline phosphate forms in both Saskatchewan soils. However, for the Brown Chernozem, the P formed initially as brushite appeared to convert to the adsorbed form in the presence of the potassium sulfate in the last 4 weeks. This could reflect reaction of the sulfate with calcium in the soil to form gypsum which induces the dissolution of the brushite and entry of P into adsorbed forms. However, the XANES did not indicate why available P measured in the seed-row tended to be lower for the potassium sulfate + MAP treatments compared to MAP alone in the first week following application as noted in the seed-row extractable sulfate measurements. The findings from the XANES analyses that labile P forms, including slightly soluble brushite (dicalcium phosphate) and adsorbed P were produced in the seed-row with and without sulfate is in agreement with the observations in the field that application of S fertilizer along with MAP did not greatly affect extractable, available phosphate in the seed-row.

9. Conclusions and Recommendations: *Highlight significant conclusions based on the previous sections, with emphasis on the project objectives specified above. Provide recommendations for the application and adoption of the project.*

1) Soluble sulfates (ammonium sulfate, potassium sulfate), thiosulfate and gypsum ($CaSO_4$) are effective in providing early supplies of plant available sulfate in the seed-row for use by crops. Early supply of sulfate appears to be important for plant S uptake and yield. For sensitive crops like canola and yellow pea, ammonium thiosulfate and ammonium sulfate can cause injury when placed in close proximity to seed and are best placed separate from the seed.
2) Gypsum is an effective source of plant available S, producing good crop response and effectively maintaining supply of plant available sulfate in the seed-row. Elemental sulfur is least effective in

increasing seed-row sulfate supply and providing plant available sulfur to plants over short-term (first weeks after application).

3) Canola responds most consistently and to the greatest extent to application of sulfur fertilizer. Wheat and pea are generally less responsive, reflecting lower sulfur requirements and greater ability of rooting system to remove S from the soil.
4) Wheat, canola and especially peas are not highly responsive to phosphorus fertilizer addition on soils with a history of phosphorus fertilization. This suggests that residual P from previous years fertilization is effective as a supply of available phosphorus.
5) Wheat, canola and pea take up the majority of fertilizer sulfur and phosphorus applied in the seed-row in the first weeks after seeding and application of sulfur and phosphorus fertilizer.
6) Fertilizer sulfur products that supply sulfate and/or acidify the soil may slightly enhance the supply of plant available phosphorus from fertilizer phosphorus placed in the seed-row with the sulfur fertilizer.
7) Limited yield response to addition of S fertilizers may be anticipated in soils in the Brown soil zone when there are adequate supplies of sulfate sulfur in the sub-soil. However, under conditions of unusually high moisture, responses to S fertilization may be observed even in soils with subsoil sulfates. Soils of high organic matter and with good mineralization capacity for S such as Black Chernozems also show reduced response. Under conditions of intense weed competition, peas may respond favourable to S fertilization as a result of their shallow rooted nature.
8) The SXRMB beamline at the Canadian Light Source synchrotron was used successfully to identify different sulfur species formed in the soil from addition of sulfur fertilizers, and to follow their transformations in the soil in the growing season following application. Using the CLS, thiols and ester sulfates were identified as short-term products formed from seed-row placed sulfur fertilizers in our prairie soils that likely originate from microbial immobilization of fertilizer sulfur. The oxidative release of plant available sulfate from reduced forms like elemental sulfur was also shown to occur in the prairie soils using the XANES beamline, pointing to the utility of the synchrotron in tracking the fate of S in prairie soils. The ability to track the oxidation of reduced sulfur fertilizers like elemental S into more oxidized forms and eventually into plant available sulfate over time is of particular interest, as new fertilizer products become available to growers in Western Canada.
9) Phosphorus K-edge X-ray absorption near edge structure (XANES) spectroscopy was successfully used to identify P species formed from P fertilizer in the soil in the presence and absence of sulfate fertilizer. XANES spectroscopy showed that one week after fertilizer application, P species present in the seed-row included similar proportions of adsorbed and poorly crystalline phosphate forms in both Brown and Black Chernozem Saskatchewan soils. The phosphorus formed initially as brushite in the Brown Chernozem soil appeared to convert to the adsorbed form in the presence of the potassium sulfate in the last 4 weeks. This could reflect reaction of the sulfate with calcium in the soil to form gypsum which induces the dissolution of the brushite and entry of P into adsorbed forms.

10. Success stories/ practical implications for producers or industry: *Identify new innovations and /or technologies developed through this project; and elaborate on how they might impact the producers /industry.*

The Canadian Light Source synchrotron was used for the first time to track the fate of fertilizer S and P together in soils and shed light on the kinds of fertilizer reaction products formed and their availability to plants. This breaks ground for further studies using the synchrotron in soil-plant nutrient studies.

11. Patents/ IP generated/ commercialized products: *List any products developed from this research.*

None

12. List technology transfer activities: *Include presentations to conferences, producer groups or articles published in science journals or other magazines.*

T. King, J.J. Schoenau, H. Ahmed, R. Hangs, S.S. Malhi and R. Urton. 2016. Response to Seed-Row Placed S Fertilization. 2016 Soils and Crops Workshop, March 15, Prairieland Park, Saskatoon, SK.

G. Kar, J.J. Schoenau and D. Peak, 2016. P and S Fertilizer Reaction Products in Seed-Row as Revealed by XANES Spectroscopy. 2016 Soils and Crops Workshop, March 15, Prairieland Park, Saskatoon, SK.

J.J. Schoenau, T. King, G. Kar, H. Ahmed, R. Hangs and D. Peak. 2016. Following The Fate of Different Sulfur Fertilizers in Prairie Soils. CropSphere Conference. January 11, TCU Place, Saskatoon, SK.

H. Ahmed, J.J. Schoenau, T. King and G. Kar, 2016. Effects of Seed-Placed Sulfur Fertilizers on Canola, Wheat and Pea Yield, Sulfur Uptake and Soil Sulfate Concentrations Over Time in Three Prairie Soils. Submitted to J. Plant Nutr. In Review.

G. Kar, J.J. Schoenau and D. Peak, 2016. Transformation and Fate of Seed-Row Placed Sulfur Fertilizers in Prairie soils. Manuscript In preparation for Soc. Soil Sci. Am. J. for Review.

G. Kar, J.J. Schoenau and D. Peak, 2015. Sulfur Species Formed in The Seed-Row of Sulfur Fertilized Soils As Revealed By K-Edge XANES Spectroscopy. Canadian Society of Soil Science Annual Meeting. July 5-10, Montreal, QC.

J.J. Schoenau, T. King, G. Kar, H. Ahmed, R. Hangs and D. Peak. 2015. Following the Fate of Different Sulfur Fertilizers in Prairie Soils. Canadian Society of Soil Science Annual Meeting. July 5-10, Montreal, QC.

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H. Ahmed, J.J. Schoenau, T. King and G. Kar, 2015. Effects of Seed-Placed Sulfur Fertilizer Forms on Wheat, Canola and Pea Yields Under Controlled Growth Conditions in Three Saskatchewan Soils. 2015 Soils and

Crops Workshop Proceedings, March 16, Prairieland Park, Saskatoon, SK.

C. Fatteicher, T. King, J.J. Schoenau, G. Kar and R. Urton, 2015. Effects of Starter Sulfur and Phosphorus Fertilizers on Sulfate Content in the Seed-Row of Saskatchewan Soils Seeded to Canola and Peas. 2015 Soils and Crops Workshop Proceedings, March 16, Prairieland Park, Saskatoon, SK.

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J.J. Schoenau, 2014. Fate of Seed-Row Placed Sulfur Fertilizers. Saskatchewan Ministry of Agriculture Agronomy Research Update Conference. December 9, Saskatoon, SK.

G. Kar, J.J. Schoenau and D. Peak, 2014. Transformations and Fate of Seed Placed Sulfur Fertilizers in Presence of Plants in Two Different Soil Zones of Saskatchewan. Abstracts of the 2014 ASA-CSSA-SSSA Annual Meetings, Nov 2-5, Long Beach, CA.

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J.J. Schoenau, 2014. Soil Nutrition and Management for Canola. Canola Discovery Forum, Oct. 22-23, Saskatoon, SK.

T. King, J. Schoenau, G. Kar, R. Urton, R. Hangs and S.S. Malhi. 2014. Effects of Seed-Placed Sulfur and Phosphorus Fertilizers on Wheat, Canola and Pea Yields. 2014 Soils and Crops Workshop, March 11, Prairieland Park, Saskatoon, SK.

G. Kar, J. Schoenau and D. Peak. 2014. Fate of Seed-Placed Sulfur Fertilizers in Brown Saskatchewan Soils as Assessed by X-Ray Absorption Near Edge Spectroscopy. 2014 Soils and Crops Workshop, March 11, Prairieland Park, Saskatoon, SK.

J.J. Schoenau, 2014. Crop Tolerance to Seed-Row Placed Fertilizers. Manitoba Ag Days, January 23, Brandon, MB.

J.J. Schoenau. 2013. Response of Crops to Seed-Placed Sulfur and Phosphorus Fertilizers. 2013 Saskatchewan Ministry of Agriculture Agronomy Research Update Laboratory Tour, December 11, University of Saskatchewan, Saskatoon, SK.

13. List any industry contributions or support received.

Project jointly funded by Agriculture Development Fund, Saskatchewan Canola Development Commission, Saskatchewan Pulse Growers, and Western Grains Research Foundation.

14. Is there a need to conduct follow up research? *Detail any further research, development and/or communication needs arising from this project.*

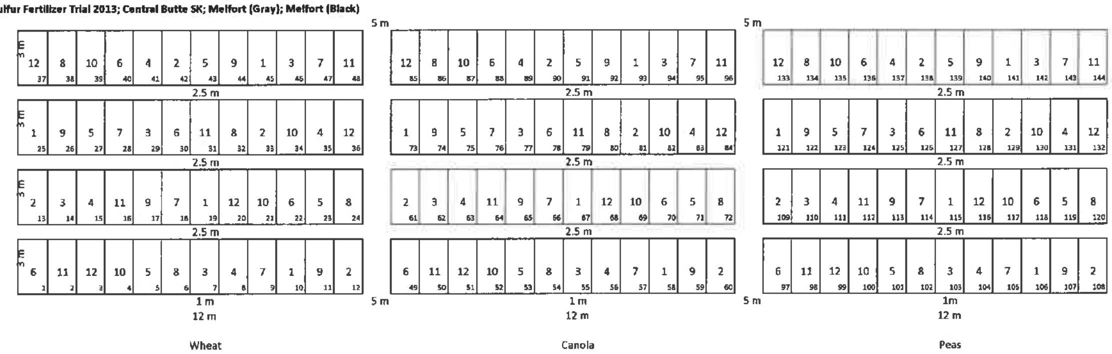
Evaluations of release of S from mineralization of soil organic matter as affected by management would be useful to document the impact of modern management practices: no-till, high S fertilization, increased legume and canola in rotation, higher yields on soil available S supplying power.

15. Acknowledgements. *Include actions taken to acknowledge support by the Ministry of Agriculture and the Canada-Saskatchewan Growing Forward 2 bilateral agreement.*

Acknowledgements at the end of papers and presentations that acknowledge the funding agencies. Signage in field trials.

16. Appendices: *Include any additional materials supporting the previous sections, e.g. detailed data tables, maps, graphs, specifications, literature cited*

Sulfur Fertilizer Trial 2013; Central Butte SK; Melfort (Gray); Melfort (Black)



Treatments		
1	Control (N only)	100 kg N ha-1
2	Control (N + P only)	100kg N ha-1; 20 kg P2O5 ha-1
3	AS	100kg N ha-1; 20 kg S ha-1
4	ATS	100 kg N ha-1; 20 kg S ha-1
5	Gypsum	100 kg N ha-1; 20 kg S ha-1
6	Potassium sulfate	100 kg N ha-1; 20 kg S ha-1
7	Elemental S	100 kg N ha-1; 20 kg S ha-1
8	AS + P	100 kg N ha-1; 20 kg P2O5 ha-1; 20 kg S ha-1
9	ATS + P	100 kg N ha-1; 20 kg P2O5 ha-1; 20 kg S ha-1
10	Gypsum + P	100 kg N ha-1; 20 kg P2O5 ha-1; 20 kg S ha-1
11	Potassium sulfate + P	100 kg N ha-1; 20 kg P2O5 ha-1; 20 kg S ha-1
12	Elemental S + P	100 kg N ha-1; 20 kg P2O5 ha-1; 20 kg S ha-1

Plot Dimensions: 1 m wide x 3 m length

Total Plot Area: 19.5 m x 46 m
2.5 m pathways between blocks
5 m pathway between crops

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