Communications in Soil Science and Plant Analysis

ISSN: 0010-3624 (Print) 1532-2416 (Online) Journal homepage: https://www.tandfonline.com/loi/lcss20

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COMMUNICATIONS IN SOIL SCIENCE AND PLANT ANALYSIS
https://doi.org/10.1080/00103624.2019.1689257

Field Evaluation of Ammonium Sulfate versus Two Fertilizer Products Containing Ammonium Sulfate and Elemental Sulfur on Soybeans

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ABSTRACT
Two separate field trials comparing three different commercial sulfur (S) fertilizers were conducted in 2016 and 2017, respectively, to evaluate their initial agronomic effectiveness in increasing soybean grain yield. The S compounds of these products were elemental S (ES) and ammonium sulfate (AS). The fertilizer sources were (1) AS, (2) granular MAP-10 S (5% ES + 5% AS-S) and (3) bulk-blend (bentonite-ES) + (AS) containing 25% ES + 25% AS-S. Rates of total S applied were 0, 5.6, 11.2, 22.4 and 33.6 kg S ha^{-1}. A significant S response in grain yield was observed with all S sources. The grain yield was significantly higher with AS than with the other two S sources at S rates ≤22.4 kg S ha^{-1} of total S applied but equal for all sources above this rate. All data points for the three S sources followed the same S response function based on a quadratic plateau model when the grain yield was plotted versus AS-S rate applied. This suggests that there was no significant ES oxidation from MAP-10S and (ES) + (AS) products to provide soybean crop growth to maturity. The experimentally observed AS-S rate at which the maximum grain yield was attained in the 2 years of fieldwork was 11.2 kg S ha^{-1} while the calculated average AS-S rate based on a quadratic plateau model was 13.4 kg S ha^{-1}.

Abbreviations: AS: ammonium sulfate; ES: elemental S; MAP: monoammonium phosphate; DAP: diammonium phosphate; TSP: triple superphosphate.

ARTICLE HISTORY
Received 30 August 2019
Accepted 1 November 2019

KEYWORDS
Sulfur; fertilizers; soil fertility; plant nutrition

Sulfur (S) is an essential plant nutrient and a S deficiency slows down the formation of amino acids which are required for optimal plant growth and final maximum crop yield. In recent years, soil S deficiency has become a major problem for crop production in many countries due to the extensive and popular use of high-analysis NP fertilizers, e.g., urea, mono-ammonium phosphate (MAP), di-ammonium phosphate (DAP), and triple superphosphate (TSP), which contain little or no S nutrient (Chien et al., 2009). Reduction of SO_2 emissions from industry to the atmosphere triggered by environmental regulations also had a significant effect lowering S deposition from air to soils. Traditionally, the major S fertilizer sources have been gypsum ($CaSO_4$) in single superphosphate, ammonium sulfate (AS), and elemental S (ES). Natural gypsum and phosphogypsum, a by-product of H_3PO_4 production, are used as soil amendments and supply S nutrient as well. Recently, flue gas desulfurized gypsum, a by-product from coal-generated power plants, has also been introduced to farmers.

Because powdered ES particles are dusty, difficult to apply to soils and potentially explosive, recent use of ES as an S source normally is in granular form. For example, a granulated product of powdered ES with 10% bentonite has been introduced to farmers for some time. Recently, several

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fertilizer companies have developed and marketed high-analysis granular NP fertilizers such as TSP, MAP and DAP containing ES particles (Chien et al. 2016). Since ES is almost 100% S, N and P contents are not significantly reduced compared to incorporating AS or gypsum. However, ES is not plant available unless it is oxidized to SO_4-S by soil microbes. It is known that oxidation rate of ES particles increases with decreasing particle size of ES (Boswell and Friesen 1993). Recently, some fertilizers have been developed and marketed granular bentonite-(ES±AS) or NP-(ES±AS) fertilizers containing micronized ES particles (<100 µm). It has been assumed that once the fertilizer granules disintegrate and the ES particles are released back to the original very fine particle size, the rate of ES oxidation in the soils would be rapidly enhanced. In order to make up for a potentially slow ES oxidation from granular ES and NP-ES fertilizers to provide available SO_4-S early in the crop growth, products containing a mixture of (ES + AS) at various S ratios have been introduced to the market. The assumption was that the AS component of the granular (ES+AS) products would supply initial available S while ES oxidation would provide available S for the later stages of crop growth up to maturity. However, these products have not been proven that granular ES products are able to provide available S as effective as SO_4-based sources during the initial or first cropping season following application (Chien et al. 2016).

To our knowledge, there is only one published peer-reviewed paper in scientific journal on the granular (ES+AS) products with S ratios of ES:AS at 12:1, 12:3 and 12:4 in a greenhouse study (Matamwa et al. 2018). The results showed that these incorporated granular (ES+AS) products in S availability were less effective than SSP and gypsum in biomass yield of first maize crop (5 weeks). The published information on the field trials for recently marketed NP-(ES+AS) products have been confined mainly to conference proceedings, but not in peer-reviewed scientific journals, as discussed in a review by Chien et al. (2016). Therefore, the objective of this study was to evaluate the initial agronomic effectiveness of AS versus granular NP-(ES±AS) fertilizer products in terms of S availability for soybean growth in two separate years under field conditions. The reported results could be available in the literature for the first time in a peer-reviewed scientific journal.

Materials and methods

The S sources used were commercial-grade granular fertilizer products: (1) AS (21-0-0-24S), (2) MAP-10S (12-40-0-10S) (trade name: MES-10S®) containing MAP-(5% ES + 5% AS-S) and (3) bulk-blend (ES) + (AS) in which granular ES was produced by granulation of ES (90%) with bentonite (10%) (tradename: Tiger 90®). The bulk-blend (ES) + (AS) had a grade of 12-0-0-50S which contained 25% ES and 25% AS-S, the same S ratio of 50:50 between ES and AS-S as that of MAP-10S.

The experiments were conducted at one site in 2016 and at another site in 2017 to evaluate the initial soybean response to S nutrient. The two sites were close to each other located in La Crosses, LaPorte County, Indiana. The soil is a sandy loam classified as Maumee series (sandy, mixed, mesic typic Endoaquolls). Pertinent average soil properties at the two sites that were relevant to S response were pH 6.4, 2.5% organic matter and sandy texture. The low organic matter content in the soil suggested that mineralization of organic S be minimum to provide available S during crop growth.

The two sites were pre-cropped with maize (*Zea mays* L.) treated with all nutrients except S, which depleted soil available S for the following soybean [*Glycine max* (L.) Merr.] in order to enhance S response for soybean. The S sources were broadcast and incorporated in the soil before 2016 soybean planting at Site 1, while the S sources were surface-applied to the soil without incorporation in 2017 at Site 2. The total S rates applied at the two sites were 0, 5.6, 11.2, 22.4 and 33.6 kg S ha^{-1} (0, 5, 10, 20 and 30 lb. S $acre^{-1}$). All other major nutrients except S were applied and balanced to the same adequate levels so that S was the only limiting factor for soybean growth. The plot size was 3 × 12 m with 0.38 m rows. A randomized complete block design (RCBD) was made with four replicates of each treatment. The soybean crop was grown to maturity and harvested. Grain yield was expressed with 13% moisture content.

In this study, soybean grain yield data were presented by regression functions in figures, instead of in tables, to enhance the contrast between the three S sources in grain yield. The significant S response was confirmed by the significance level of the regression functions. The relationship between grain yield and the S rate applied as total S or AS-S from each S source in this study was described by a quadratic plateau model as,

$$Y = Yo + bX + cX^2 \quad (1)$$

where Y is the yield, X is the rate of total S or AS-S applied, Yo is the yield of control, i.e., X = 0, and b and c are coefficients of the response function to be estimated. Because all S sources shared the same control treatment in the RCBD design, Yo is a fixed observed yield value while b and c vary with each S source in Equation (1).

When the S response curve and the linear maximum yield (Ym) plateau intersects at the point of total S or AS-S rate (Xm), the slope (dY/dX) of the S response function should be zero. That is,

$$(dY/dX) = 0 = b + 2cXm \quad (2)$$

$$Xm = -b/2c \quad (3)$$

Substituting (3) into (1),

$$Ym = Yo + b(-b/2c) + c(-b/2c)^2 = Yo - \left(b^2/4c\right) \quad (4)$$

Therefore, the maximum yield (Ym) increase with total S or AS-S over control (Yo) is $\Delta Ym = (Ym - Yo)$ and $\%\Delta Ym = [(\Delta Ym)/(Yo)]x100$ represents relative maximum % grain yield increase with S treatments over the control.

Results and discussion

There was a significant soybean grain yield response to all S fertilizers indicating inadequate soil available S for crop growth in 2016 (Figure 1). The grain yield obtained with AS increased from 3,266 kg ha^{-1} with the control to 3,747 and 3,930 kg ha^{-1} at 5.6 and 11.2 kg S ha^{-1} applied,

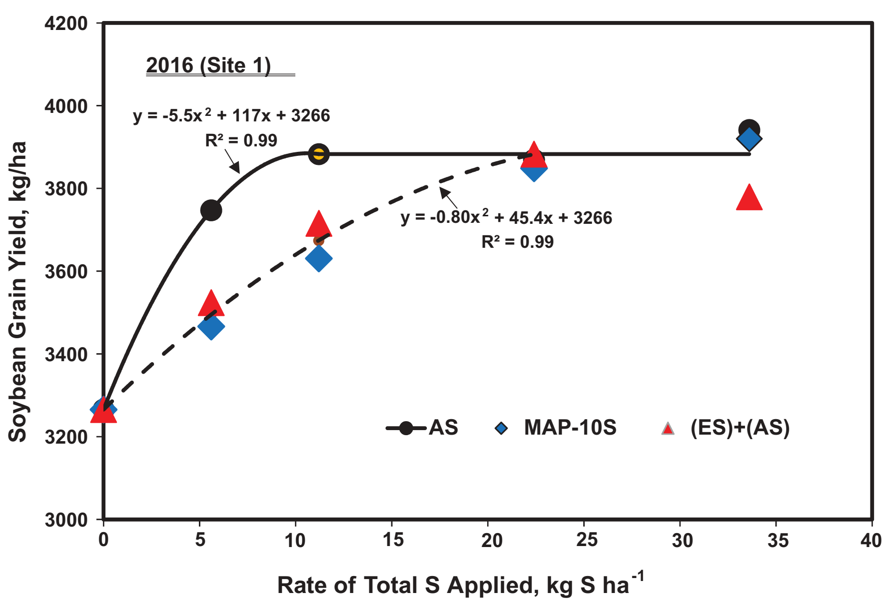

Figure 1. Soybean grain yield obtained with AS, granular MAP-10S, and bulk-blend (ES) + (AS) based on total S rate applied (2016).

respectively. At 11.2 kg ha^{-1} rate, the grain yield appeared to attain the maximum yield plateau through 22.4 to 33.6 kg S ha^{-1} with an average grain yield of 3,900 kg ha^{-1} over the three total S rates applied.

McLaughlin et al. (2015) stated that once NP-(ES±AS) granules have dissolved and soluble NP have diffused from the granule into the soil, a 'collapsed cavity' with ES still remains. A fertilizer product containing a lower ES content would therefore provide more exposure of ES particles' surface area to the soil microbes for ES oxidation as compared to another product containing a higher ES content based on the same total S rate applied.

Based on this concept, ES oxidation of MAP-10S containing 5% ES per granule of MAP-10S would be expected to be higher than (ES) + (AS) containing 90% ES per ES granule for a given total S rate applied in the current study. If so, granular MAP-10S would be expected to provide higher available SO_4-S than (ES) + (AS), which would result in an also higher soybean grain yield response. Furthermore, the number of MAP-10S granules containing ES is 18 times (90/5 = 18) the number of ES granules in (ES) + (AS), which could have further enhanced S uptake by soybean from the oxidized ES because of a closer contact between soybean roots and ES particles in the soil. However, there were no significant differences in grain yield between MAP-10S and (ES) + (AS) across all applied total S rates (Figure 1). This suggests that the available S via ES oxidation, if any, was not significantly influenced by the number of granules containing ES as discussed by McLaughlin et al. (2015).

Alternatively, it suggests that there might not have been a significant oxidation of ES granules to provide available S from MAP-10S and (ES) + (AS) during the seasonal crop growth as discussed by Chien et al. (2016). If so, it may explain why MAP-10S and (ES) + (AS) were equally effective for soybean grain yield across all total S rates applied following the same S response curve (Figure 1) due to the lack of significant ES oxidation and both products having the same amount of AS-S content with ES:AS-S at 50:50 ratio.

In Figure 1, soybean grain yields of both MAP-10S and (ES) + (AS) were significantly lower than that of AS at 5.6 and 11.2 kg S ha^{-1} applied. It shows that ES oxidation of these two fertilizer products containing ES, if any, was inadequate to provide available SO_4-S during the initial soybean growing season. There were no significant differences in grain yield among the three S sources at 22.4 and 33.6 kg S ha^{-1}. At 22.4 kg S ha^{-1} applied, both MAP-10S and (ES) + (AS) provided 11.2 kg AS-S ha^{-1}, which appeared to attain the maximum grain yield with AS applied alone. The fact that MAP-10S and (ES) + (AS) applied at 22.4 and 33.6 kg S ha^{-1} attained the same maximum yield obtained with AS alone suggests the absence of significant ES oxidation from these two fertilizer products during soybean growth to maturity.

It should be noted that comparing agronomic effectiveness of various S sources should be based on multiple S rates, rather than just at a single rate (Chien et al. 2016). For example, had the current study compared the three S sources at a single rate of 22.4 or 33.6 kg S ha^{-1}, the conclusion could have been that all three were equally effective S sources given similar soybean grain yields reached at such S rates. This would have been a misleading conclusion as often reported in the literature (Chien et al. 2016) since AS was actually more effective in boosting soybean grain yields than MAP-10S and (ES) + (AS) at lower S rates as shown in Figure 1.

To determine the contribution of available SO_4-S to crop growth from possible ES oxidation of the NP-(AS±ES) fertilizer products, Chien et al. (2016) developed a simple method in lieu of the expensive labeled S isotopic technique. It plots crop yield or S uptake versus AS-S rate, instead of total S rate, applied from each S source. The difference in crop yield between the response functions of (ES +AS) and AS alone represents the yield increase attributed to the contribution of ES oxidation to provide available S to crop growth. In case that the two S response functions are overlapped by the same a single S response function, it suggests that there is no significant ES oxidation from (ES+AS) to contribute available S for crop yield and the AS component alone is responsible for any crop yield increase.

A plot of soybean grain yield versus AS-S rate applied from the three S sources in 2016 is shown in Figure 2. The data points of all the S sources followed the same quadratic plateau function. This

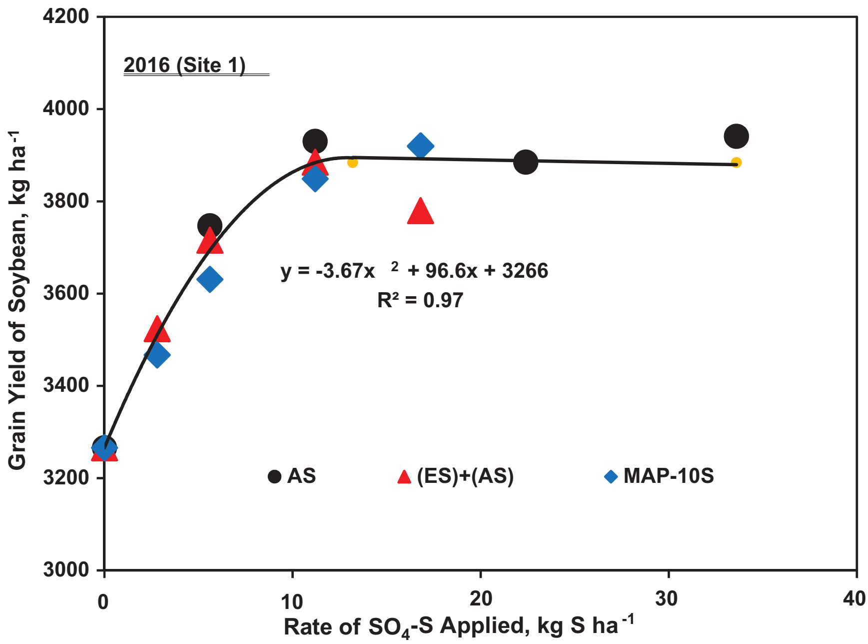

Figure 2. Soybean grain yield obtained with AS, granular MAP-10S, and bulk-blend (ES) + (AS) based on AS-S rate applied (2016).

suggests that there was no significant ES oxidation from MAP-10S and (ES) + (AS) to increase grain yield. Otherwise, the S response curve of MAP-10S and (ES) + (AS) should be above that of AS alone. The AS-S rate (Xm) and the maximum grain yield (Ym) were estimated from the response function as 13.2 kg S ha^{-1} and 3,905 kg ha^{-1}, respectively (Figure 2). The estimated % ΔYm increase in soybean grain yield over control was $\Delta Ym = [(3905 - 3266)/(3266)]x100 = 20\%$. Experimentally, the S rate of AS alone at which the maximum grain yield appeared to be attained was 11.2 kg S ha^{-1} (Figure 1) close to the calculated value of 13.2 kg S ha^{-1} based on the quadratic plateau model (Figure 2).

The lack of significant ES oxidation to provide available SO_4-S to soybean grain yield (Figure 2) is most likely due to the "locality effect" on ES oxidation as discussed by Chien, Mercedes, and Villagarcia (2011), Chien et al. (2016, 2017). In general, rapid effective ES oxidation would be expected if the very fine micronized ES particles (<100 μm) that were used in MAP-10S and (ES) + (AS) fertilizer products had been thoroughly mixed with the soil. The concept of locality effect implies that when the ES granules disintegrate or dissolve and release micronized ES particles in the soil, the ES particles are still localized in cluster form with limited dispersion around the applied granule site due to the fact that ES is water-insoluble. Furthermore, ES is hydrophobic and the released ES particles tend to form larger aggregates that further decrease ES oxidation (Friesen 1996). Consequently, little granular ES oxidation of MAP-10S and (ES) + (AS) fertilizer products occurred during the soybean growth cycle as observed in the current study.

Soybean grain yield results for the three S fertilizer sources in 2017 are shown in Figure 3. Both MAP-10S and (ES+AS) were less effective than AS but the two products were about the same in grain yields at lower total S rates (<22.4 kg S ha^{-1}) applied. It is interesting to note that the grain yield with (ES) + (AS) appeared to be lower than that with MAP-10S at 33.6 kg S ha^{-1} in 2016 when fertilizer S was incorporated with tillage (Figure 1) whereas the reverse was observed at 22.4 and 33.6 kg S ha^{-1} in 2017 when fertilizer S was surface applied with no-till (Figure 3), although the differences were statistically non-significant. We do not have possible explanation for the observation and future trials may provide more information to account for this observation.

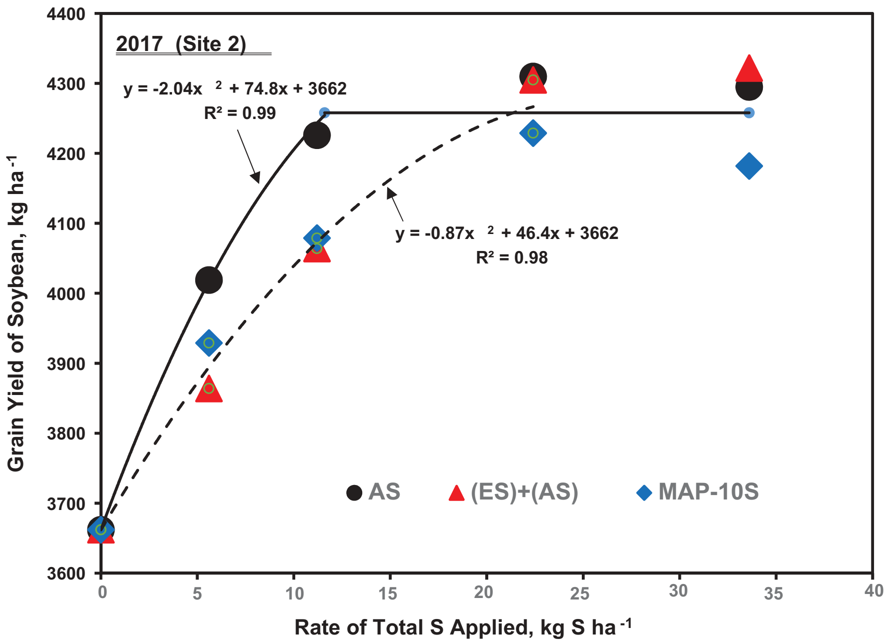

Figure 3. Soybean grain yield obtained with AS, granular MAP-10S, and bulk-blend (ES) + (AS) based on total S rate applied (2017).

The same quadratic plateau function was used to fit the 2017 data with a plot of grain yield versus the rate of AS-S applied from the three S sources (Figure 4). The estimated AS-S rate (Xm = 13.7 kg S ha^{-1}) at which the maximum grain yield (Ym = 4,273 kg ha^{-1}) was thus attained. The estimated % ΔYm increase in soybean grain yield over the control was [(4,273–3,622)/(3,622)] x 100 = 18%. The grain yields obtained in 2016 and 2017 were different due to seasonal changes and fertilizer S application methods. It was no-till in 2016 while in 2017 was tilled that may result in different observed parameters such as Yo = 3,266 kg ha^{-1}, Ym = 3,905 kg ha^{-1} in 2016 and Yo = 3,622 kg ha^{-1}, Ym = 4,273 kg ha^{-1}, in 2017. However, the estimated parameters for both years based on the quadratic plateau model were relatively the same such as Xm = 13.2 kg AS-S ha^{-1}, ΔYm = 639 kg ha^{-1}, % (ΔYm/Yo) = 20% in 2016 and Xm = 13.7 kg AS-S ha^{-1}, ΔYm = 650 kg ha^{-1}, % (ΔYm/Yo) = 18% in 2017. The experimentally observed AS-S rate at which the maximum grain yield was attained in 2 years was 11.2 kg S ha^{-1} while the calculated average AS-S rate based on the quadratic plateau model was 13.4 kg S ha^{-1}. All these results suggest that the conclusions as drawn from the field evaluations of the initial agronomic effectiveness in S availability from AS compared with MAP-10S and (ES) + (AS) for soybean grown to maturity in the state of Indiana in 2016 and 2017 may be considered to be relatively the same as reported in this study.

Conclusion

Field trials in two different years clearly show that ES oxidation of granular MAP-10S and bulk-blend (ES) + (AS) was not significant to provide available SO_4-S during the first seasonal soybean growth to maturity. Thus, the results did not support manufacturers' claims that their fertilizer products can provide available S as effectively as or more effectively than SO_4-based sources during the first season of application. Comparisons of granular ES or (ES+AS) products with SO_4-S fertilizers should be based on multiple S rates (low to high), rather than just at a single high rate which can result in misleading conclusions. Granular ES, NP-(ES±AS) and bulk-blend (ES) + (AS) products may have agronomic residual or long-term S effect as influenced under the conditions of

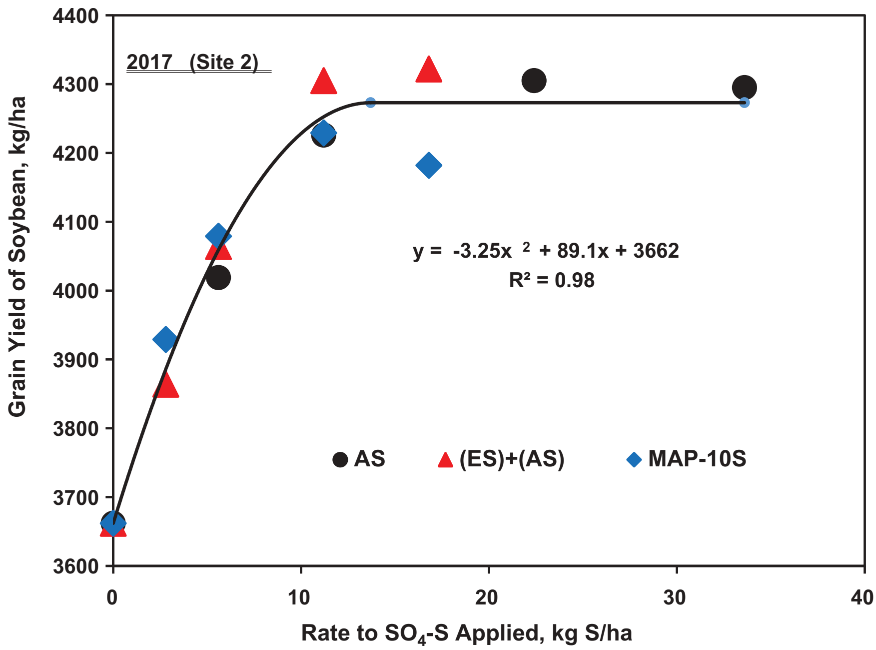

Figure 4. Soybean grain yield obtained with AS, granular MAP-10S, and bulk-blend (ES) + (AS) based on AS-S rate applied (2017).

different agro-climate, soil types, crop species, and cropping system. However, this has not been reported well in scientific literature and future field trials are highly recommended to address this issue.

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