

Co-granulated Elemental Sulfur/Sulfate Fertilizers and Their Role in Crop Nutrition

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The effectiveness of S-enhanced ammoniated phosphate fertilizers, with both fast and slow release forms of S, differs based on the growing environment.

The presence of elemental S can be advantageous in environments at risk for leaching of sulfate.

Sulfate-S performs best in environments with less risk of loss, but products co-granulated with a suitable size of elemental S can be equally effective.



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Sulfur-enhanced fertilizers can be an efficient option to deliver sulfur to crops like canola, which can be grown across a variety of climates and soils around the world.

Sulfur (S) is one of the 18 elements essential for plant growth and the fourth after N, P and K in terms of amounts required by crops. It plays a key role in plant nutrition through its activity in photosynthesis and in the synthesis of amino acids and proteins. Sulfur shares a similar behavior to N in soils and plants—it is sensitive to leaching, can be immobilized into organic matter, and is present in different oxidation states. Reduced forms of S include elemental S (ES), iron sulfide minerals present in waterlogged (e.g., paddy rice) soils, and S bound to carbon present in soil organic matter (SOM). Oxidized forms of S include sulfate minerals (e.g., gypsum), sulfate-esters in SOM and sulfate-S present in the soil solution.

Plants take up S from soils predominantly as sulfate via the soil solution. Hence, like N, the availability of S in soils is also affected by mineralization or immobilization reactions with SOM. Another similarity with N is that the oxidized form of S (sulfate) is highly mobile in soils (like nitrate) and can be eas-

ily lost from soils by leaching in higher rainfall environments, hence potentially reducing the efficiency of applied S fertilizer.

Sulfur fertilizers are predominantly either sulfate-based (e.g., ammonium sulfate, gypsum, potassium sulfate) or based on ES [e.g., ES pastilles or ammoniated/calcium-based phosphatic fertilizers containing ES such as S-enhanced triple superphosphate (TSP), monoammonium phosphate (MAP) or diammonium phosphate (DAP)]. Sulfate-based fertilizers provide a source of S (sulfate) that is immediately available for crop uptake but these fertilizers contain relatively low S contents (<25% S) so higher application rates are needed and transport costs are relatively high. Pure ES fertilizers have the advantage that they are the most concentrated form of S (>90% S) and thus application rates and transport costs are lower. However, to become available for plant uptake, ES must first be oxidized in soil to sulfate and hence the supply of S to plants is slower than for sulfate. Fertilizers that combine these two forms of S can provide both a fast and a slow release source of S for crop nutrition. But how quickly is the S released from the ES in these products?

Abbreviations and notes: N = nitrogen, P = phosphorus; K = potassium; S = sulfur; ES = elemental sulfur.

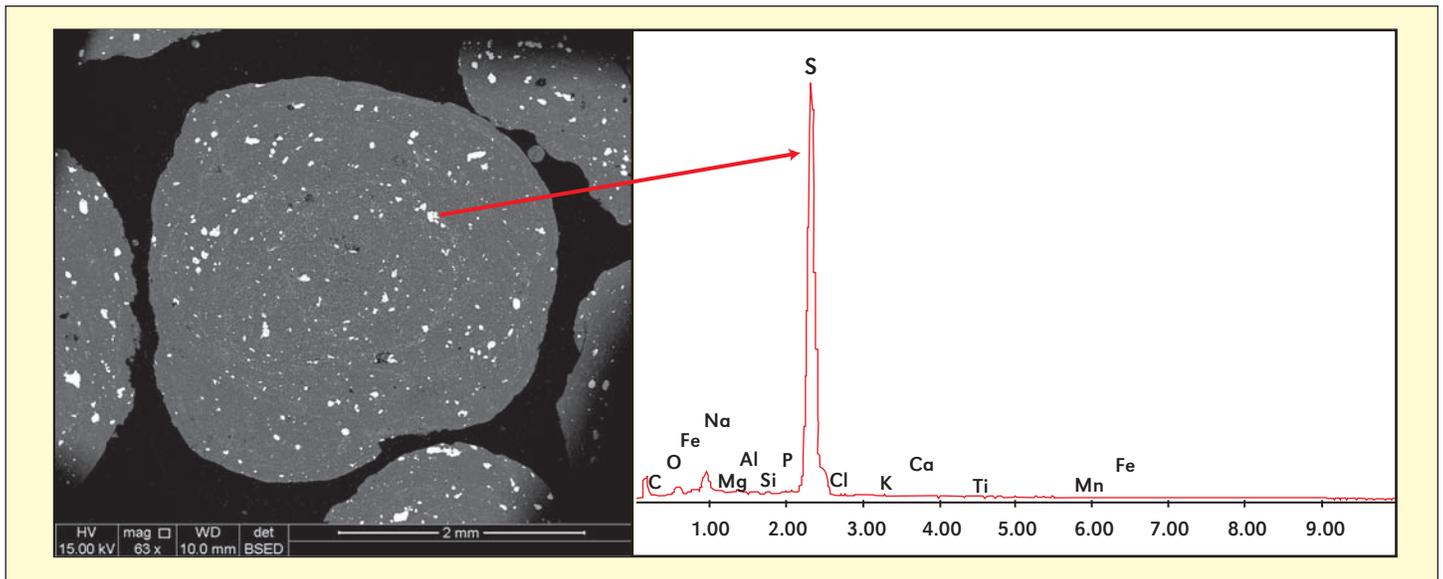


Figure 1. Typical ES/sulfate fertilizer co-granulated with ammonium phosphate and the x-ray analysis of the bright particles in the granule confirming the particles are ES.

Oxidation of ES fertilizers in soil has been studied for decades, and it is well known that the particle size of the ES fertilizer plays a major role in controlling the rate of oxidation and release of sulfate. Research has shown smaller particles oxidize faster because the surface area to volume ratio of a

particle increases as the diameter of the particle decreases. Oxidation of ES is carried out by a wide range of soil microorganisms and therefore is affected by factors that affect microbial abundance and activity in soils. The most important factors are soil temperature and soil pH, but organic C content and to a lesser extent soil water status also play a role. Warm climates with non-acidic soils that are rich in organic matter will oxidize ES the fastest.

Models have been developed to predict oxidation of ES in soil based on the above key factors controlling oxidation assuming the ES is well-mixed throughout the soil.

However, this is rarely the case and ES is usually added to soil in granules or prills/pastilles consisting solely of ES with a binder or dispersant, or coated or co-granulated with other macronutrient fertilizers. Based on greenhouse experiments, it has been observed that ES in these products, despite having small ES particles embedded in the granule (**Figure 1**), oxidizes much slower than ES particles of the same size mixed throughout the soil (Friesen, 1996) with pure ES granules/prills being the slowest.

The oxidation of ES in these co-granulated products was examined in laboratory, greenhouse and field experiments to develop a better understanding of what controls the rate of ES oxidation in these products. Measuring oxidation of ES fertilizer in soils might seem simple at first, as measurement of sulfate produced is a relatively simple chemical procedure. However, sulfate released from ES fertilizers can be leached, taken up by plants, or incorporated into SOM (**Figure 2**), so the increase in sulfate-S may underestimate ES oxidation.

The oxidation of ES in three fertilizers was measured in

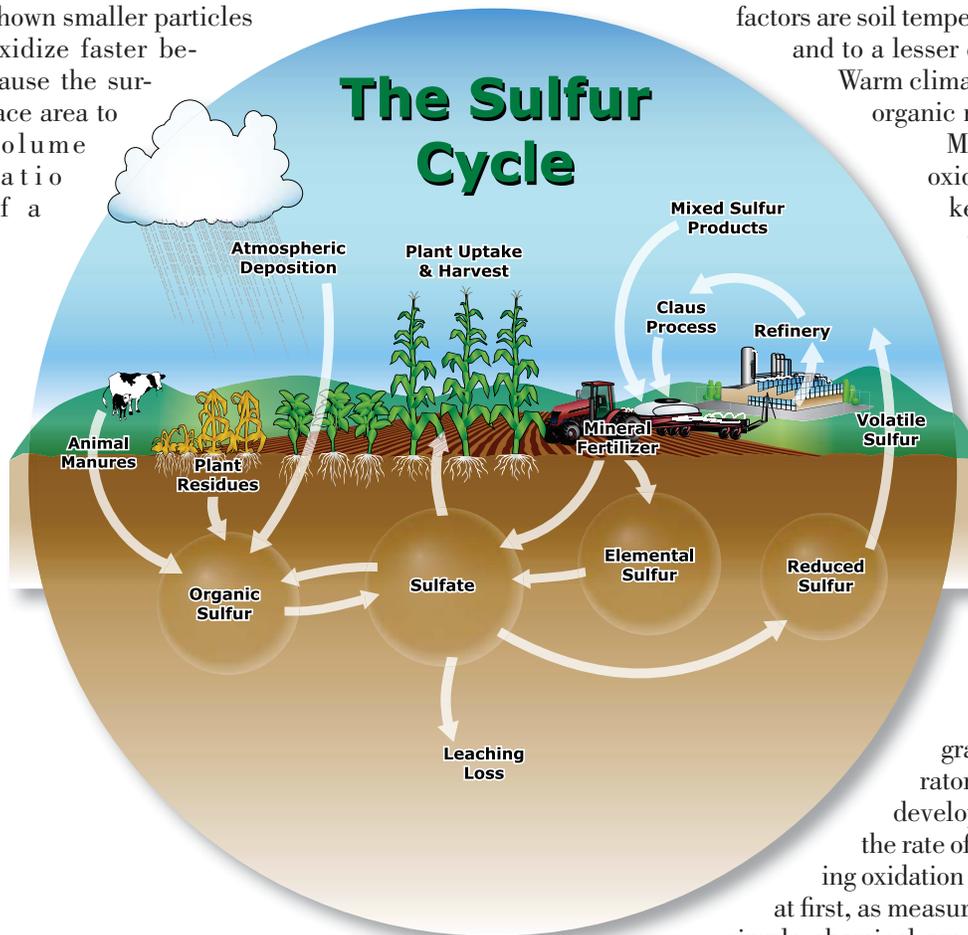


Figure 2. Fate of fertilizer S, added as either elemental S or sulfate in soil. The major pathways of loss for sulfate from soil are removal with harvested crop products, immobilization in soil organic matter (Organic S), and leaching.

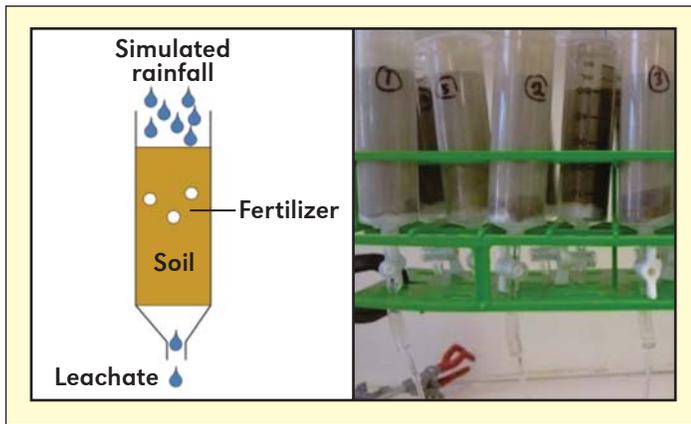


Figure 3. Picture of leaching procedure to measure oxidation of ES in soil (left: schematic diagram; right: columns)

laboratory experiments by regularly leaching sulfate out of the soil to minimize immobilization in SOM (**Figure 3**) and by measuring ES remaining at the end of the experiment (by solvent extraction) to check the mass balance of S.

Over 12 months, the oxidation of ES prills was slow, oxidation in co-granulated ES/MAP/sulfate fertilizers was faster, and the fastest oxidation was observed when ES was uniformly mixed throughout the soil (**Figure 4**). By contrast, nearly all added S was removed during the first leaching event for the ammonium sulfate treatment (Degryse et al. 2015).

The reason oxidation of ES is slower in co-granulated products (for a given particle size of ES) is that the surface of ES in contact with the soil (and soil organisms) is lower when the ES is co-granulated than when ES particles of the same size are mixed throughout the soil. After the soluble nutrients (N, P) in the granule have dissolved and diffused from the granule, a ‘collapsed cavity’ with ES remains. Further oxidation will depend on the surface of ES in contact with the soil, the granule size, the ES content of the fertilizer, and the diameter of the ES particles (**Figure 5**). Based on these geometrical considerations, we were able to model the reduction in oxidation rate for co-granulated ES fertilizers compared to ES particles mixed throughout soil.

The much slower oxidation for ES pastilles than for S-enhanced MAP fertilizers was confirmed in a pot experiment, in which the S availability to plants was not different from the MAP control. However, the availability of S for the co-granulated fertilizer was higher than for ammonium sulfate in a second crop (**Figure 6**). The low S uptake for the ES pastilles treatment is due to slow oxidation and the relatively low uptake for the AS treatment is due to uptake by the first crop and immobilization in SOM.

Crop recovery of S from the sulfate-S and ES in co-granulated products containing both forms of S was measured by labeling with an enriched stable isotope— ^{34}S . Labeled ^{34}S products were manufactured where either the ES or the sulfate-S was labeled and used in field trials at various locations in North and South America.

As expected, where sulfate leaching is a potential risk after fertilization (e.g., fall applications in North America) the ES in the fertilizer was a more effective source than the sulfate-S (**Figure 7**). On the other hand, where sulfate leaching was not significant, the sulfate-S source had the highest initial avail-

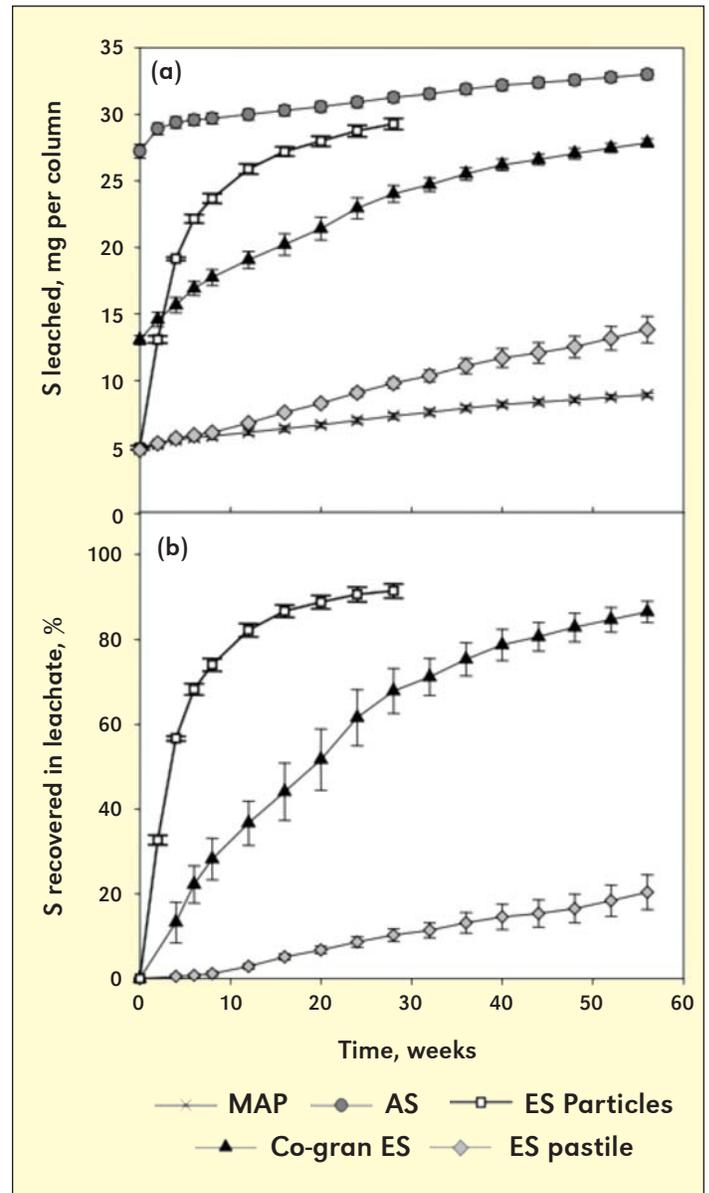


Figure 4. (a) Release of sulfate-S in the leachates and (b) recovery of sulfate-S derived from the oxidation of ES. The soil (pH 6.3, 73% sand, 2.8% organic carbon) was incubated with MAP or various S-containing fertilizers (24 mg S added) at 25°C over 12 months and leached at regular intervals (Degryse et al., 2015). MAP = monoammonium phosphate; AS = ammonium sulfate; ES = elemental S particles (diameter of 65 μm) mixed through soil; Co-gran = elemental S/sulfate in MAP; ES pastille = elemental S pastille with 90% ES and 10% bentonite. Error bars equal standard errors of four replicates.

ability to the crop and ES was a slower release source later in the season and in subsequent seasons. As stated previously, speed of oxidation was primarily controlled by temperature and soil pH.

Summary

A model is now being developed to predict the oxidation of ES in co-granulated products based on particle size of the ES, granule diameter, ES content of the fertilizer, and the environmental variables that control oxidation rate (principally

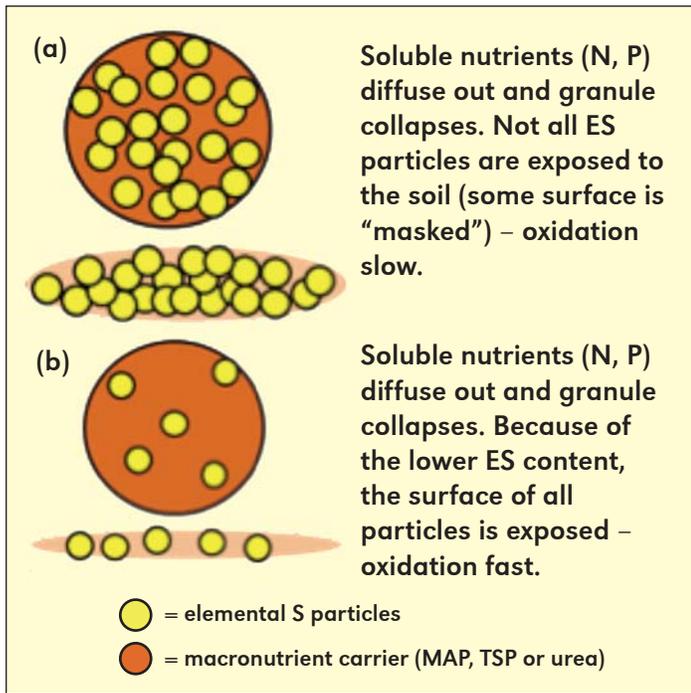


Figure 5. Schematic of dissolution of granulated fertilizers containing ES for a granule with (a) high or (b) low ES content.

soil temperature and soil pH). After validation, this model should allow the tailoring of fertilizer S formulation to meet crop demand in various environments and growing conditions.

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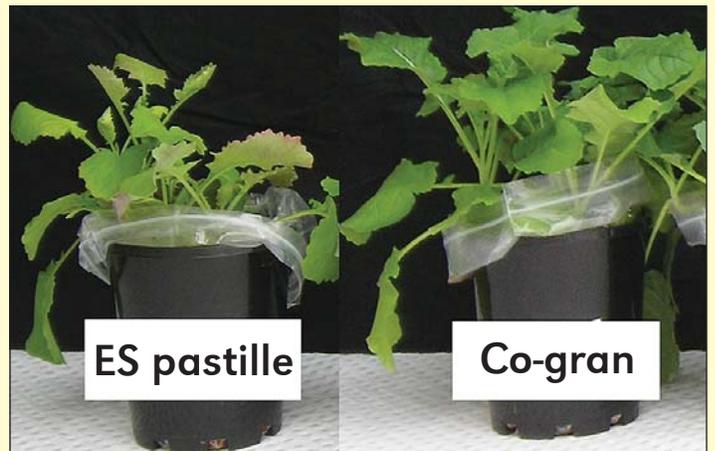
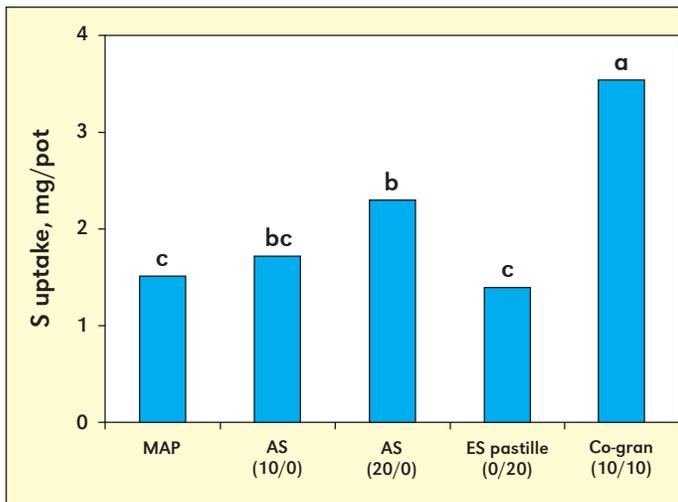


Figure 6. Left - Sulfur uptake by a second canola crop grown in pots. Fertilizer treatments were monoammonium phosphate (MAP) only (control), ammonium sulfate (AS), ES pastilles or S-enhanced MAP fertilizer (numbers in brackets are amount of sulfate-S/ES added with the fertilizer in mg per kg soil). Different letters above the bars indicate significant ($p < 0.05$) differences between treatments. **Right** - Canola grown with S-enhanced MAP fertilizer (ES pastilles on left side; Co-gran on right).

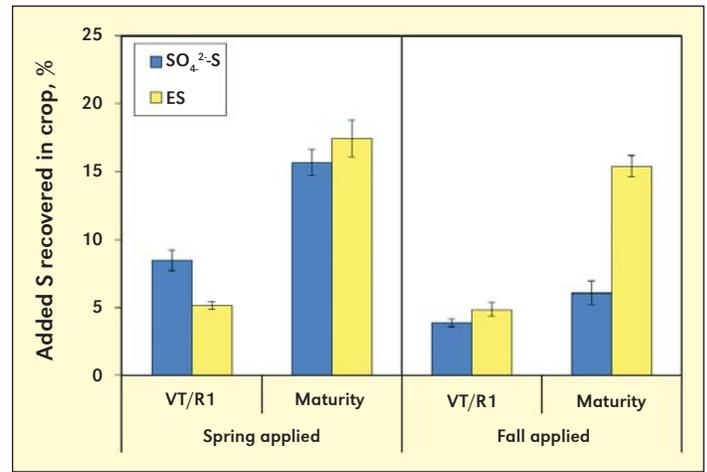


Figure 7. The percentage of added S recovered in corn (above-ground biomass) at tasseling and maturity for the sulfate-S (SO₄²⁻-S) or elemental S (ES) in S-enhanced MAP fertilizer as measured through stable isotope ³⁴S labeling for spring- and fall-applied fertilizers (Trial in Illinois, 2013-2014). Error bars represent standard errors of four replicates.

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