Effect of Cogranulation on Oxidation of Elemental Sulfur: Theoretical Model and Experimental Validation

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Elemental sulfur (ES) is a common S fertilizer source. Elemental S is insoluble in water and hence is not susceptible to leaching and also has the benefit of lower transport/handling costs because it is the most concentrated form of S. However, ES only becomes available to plants when it is oxidized to sulfate (Boswell and Friesen, 1993). Knowledge of the factors that affect ES oxidation is hence required to develop fertilizer recommendations for ES-containing fertilizers.

The oxidation of ES particles is affected by biological, fertilizer, and soil-related factors (Germida and Janzen, 1993). Because ES oxidation is a biologically mediated process, it is strongly influenced by temperature. Janzen and Bettany (1987a) assessed ES oxidation in six soils in Saskatchewan, Canada, at temperatures ranging between 3 and 30°C and found Q10 values (factor increase per 10°C increase) ranging from 3.2 to 4.3. Oxidation of ES is a surficial process, and the rate of oxidation is therefore proportional to the specific surface area of the ES particles. Soil properties also affect the oxidation rate, likely through their effect on the composition and abundance of the microbial community. For instance, Zhao et al. (2015) found that the surface-based oxidation rate of ES in 10 Australian soils ranged between 5 and 52 μg cm⁻² d⁻¹ and was positively correlated with the pH and organic matter content of the soil.
Based on this knowledge, models have been developed that allow estimation of the oxidation of particulate/powdered ES under field conditions to select in favor of fertilizers, depending on environmental conditions and crop type (Chapman, 1996; Watkinson and Lee, 1994). However, commercial ES fertilizers are usually in granular form because of safety and practical considerations (Chien et al., 2011) (e.g., in the form of ES-fortified ammoniated phosphate fertilizers or as pastilles of ES particles bound together by bentonite). Several studies have indicated that oxidation of such granular fertilizers containing ES particles is slower than that of ES particles of the same size mixed through soil (Friesen, 1996; Hu et al., 2002). Friesen (1996) found that the oxidation rate of ES in triple superphosphate (TSP) containing 160 g kg⁻¹ ES decreased with increasing granule size. He hypothesized that the dissolving granule left a cavity in which the ES settles as an aggregate, resulting in less available ES surface with increasing granule size because the total number of granules for a given fertilizer rate is smaller as the granule size is larger. In a recent review paper, Chien et al. (2016) pointed out that cogranulated ES products are usually less effective in the short term than ES particles mixed through soil, which was attributed to a “negative locality effect,” but this effect was not quantified. In a recent study (Degryse et al., 2016), we compared the oxidation of granular ES fertilizers and ES particles in three soils. For all three soils, the oxidation rate was around 0.02 d⁻¹ for ES particles with diameter <100 µm, around 0.005 d⁻¹ for monoammonium phosphate (MAP) fertilizer containing 50 or 75 g ES kg⁻¹, and around 0.0006 d⁻¹ for ES-bentonite pastilles with 900 g ES kg⁻¹.

The aim of the current study was to develop a model that describes the effect of cogranulation of ES with macronutrient fertilizers on its oxidation rate. The model presented predicts the “effective diameter” of cogranulated ES based on the composition of the fertilizer and quantifies the effect of cogranulation on the oxidation rate of ES. This effective diameter corresponds to the diameter of particulate ES that would oxidize at the same rate as the cogranulated ES. To validate the model, a column incubation experiment was performed in which the oxidation rate was determined for ES-fortified MAP fertilizers with varying ES content, granule diameter, and ES particle diameter. Because the aim of this study was to assess the effect of cogranulation, all other factors that may affect ES oxidation (temperature, soil properties, and water content) were kept constant.

**MATERIAL AND METHODS**

**Model Development**

The model presented here was developed from first principles without any fitting to experimental data. Elemental S oxidation is a surficial process, and the rate of oxidation is hence proportional to the surface area. The lower oxidation rate of co-granulated ES can be explained by a reduction in the surface area of ES in contact with the soil. In the analysis below, the surface area of co-granulated ES is represented by the “effective diameter,” which is the hypothetical diameter of ES particles mixed through soil that would oxidize at the same rate as the cogranulated ES.

The specific surface area (S, the surface area per unit mass) of a spherical particle is determined as:

\[ S = \frac{A}{\rho V} = \frac{\pi d^2}{\rho \pi d^3/6} = \frac{6}{\rho d} \]  

where \( A, V, \) and \( d \) are the area, volume, and diameter of the spherical particle, respectively, and \( \rho \) is the particle density. Hence, the oxidation rate of ES particles is predicted to be inversely proportional to the particle diameter. The shape of ES particles also influences the specific surface area and hence the oxidation rate (Germida and Janzen, 1993). However, for simplicity and due to the lack of easily gathered shape information, particles are usually considered to be spherical. In most cases, ES particles are close enough to spherical for this assumption to be justified, and using more accurate descriptions (e.g., a spheroidal particle model) has been found to have only a minor effect (around 10%) on predicted oxidation (McCaskill and Blair, 1989).

Given a constant surface-based oxidation rate, the decrease in ES with time for single-size spherical particles follows a cubic equation (Janzen and Bettany, 1987b; Watkinson, 1989):

\[ \frac{m}{m_0} = \left(1 - 10^{-6} \frac{k t S}{3}\right)\left(1 - 0.01 \frac{2k t}{\rho d}\right) \]  

where \( m/m_0 \) is the ES mass relative to the initial mass, \( k \) is the surface-based oxidation rate (μg cm⁻² d⁻¹), \( t \) is time (days), \( S \) is the specific surface area in cm² g⁻¹, \( \rho \) is the density of the ES (2.07 g cm⁻³), and \( d \) is the initial diameter of the ES particles (μm). From Eq. [2] it follows that the time to oxidize 50% of the initial ES corresponds to 21.4 \( d/k \). The dependence of oxidation rate on particle diameter is illustrated in Fig. 1 for values of \( k \) between 5 and 80 μg cm⁻² d⁻¹, which roughly corresponds to the range reported in the literature for a temperature of 25°C (Watkinson, 1989; Zhao et al., 2015).

Although several studies have shown that the oxidation of cogranulated ES is slower than that of ES particles of the same size distributed throughout the soil, to our knowledge no at-
attempt has been made to quantify this effect of granulation. We conceptualized the granule effect as shown in Fig. 2. It is assumed that when the ES particles are held within a macronutrient fertilizer granule (e.g., MAP or other soluble fertilizer), the soluble compounds of the granule will quickly dissolve and diffuse away, even at low water contents (Lawton and Vomocil, 1954). We assume this leaves a (collapsed) granule cavity that contains the fertilizer residue (ES and insoluble fertilizer impurities) with a surface area in contact with the soil corresponding to the surface area of the original granule. Thus, if the area covered by the individual ES particles combined exceeds the surface area of the granule (Case B in Fig. 2), the area of ES exposed to soil corresponds to the surface area of the granule, and hence the effective surface area per mass of ES is:

\[
S_{\text{eff}} = \frac{A_{\text{gran}}}{f_{\text{ ES}} r_{\text{gran}}} = \frac{\pi d_{\text{gran}}^2}{6} f_{\text{ ES}} r_{\text{gran}} \\
\]

where \(A_{\text{gran}}\), \(V_{\text{gran}}\), and \(d_{\text{gran}}\) are the area, volume, and diameter of the fertilizer granule, respectively; \(r_{\text{gran}}\) is the density of the granule (which for fertilizer MAP is 1.86 g cm\(^{-3}\)); and \(f_{\text{ ES}}\) is the mass fraction of ES in the granule. Because the oxidation rate is determined by the specific surface area, we can derive the diameter \(d_{\text{eff}}\) of single-sized ES particles that would oxidize at the same rate as the cogranulated ES by equating Eq. [1] and [3], which gives:

\[
d_{\text{eff}} = d_{\text{ES}} = \frac{f_{\text{ ES}} d_{\text{gran}} r_{\text{gran}}}{\rho_{\text{gran}}} \]

Thus, in this case (Case B in Fig. 2), the effective diameter increases and the oxidation rate decreases proportionally to the ES content and diameter of the granule.

If the area covered by the individual ES particles is less than the granule surface area (Case A in Fig. 2), the ES particles will act individually, and hence the effective diameter will equal the diameter of the ES particles:

\[
d_{\text{eff}} = d_{\text{ES}} \]

where \(d_{\text{ES}}\) is the ES particle diameter. The transition between these scenarios, when the area covered by the ES particles corresponds to the surface area of the granule, occurs when

\[
f_{\text{ ES}} d_{\text{gran}} = \frac{\rho_{\text{gran}}}{\rho} \]

Once the effective diameter has been determined, calculation of the ES oxidation can be performed in the same way as for homogeneously mixed ES (Eq. [2]) but by using the effective diameter of ES particles instead of the actual particle diameter.

**Experimental Validation with Laboratory-Produced Granules**

To assess if the effect of granule size, ES particle size, and ES content of the fertilizer is well predicted by the model outlined above, a column oxidation experiment was performed using the same methods as described by Degryse et al. (2016). In short, the fertilizer was added to a soil column that was immediately leached to remove all sulfate and then incubated at 25°C and leached at regular time intervals to remove and determine the sulfate that was produced by ES oxidation during the incubation period. The soil used was a calcareous sandy loam soil from South Australia, with a SO\(_4^{2-}\)-S content of 7.1 mg kg\(^{-1}\) and total S content of 279 mg kg\(^{-1}\). The soil is classified as a Calcixerollic Xerofluvent and has a pH (in 0.01 mol L\(^{-1}\) CaCl\(_2\)) of 7.5, organic C content of 17 g kg\(^{-1}\), CaCO\(_3\) content of 110 g kg\(^{-1}\), and cation exchange capacity of 15 cmol c kg\(^{-1}\). The fertilizers used were MAP fertilizers with granule diameters of 1.8 or 3.4 mm; ES contents of 20, 50, 100, or 250 g kg\(^{-1}\); and (equivalent) ES particle diameters of 25 or 60 \(\mu\)m, resulting in 16 granular fertilizer treatments. Furthermore, three treatments were included with ES particles (Sigma Aldrich) that were obtained by sieve fractionation (<20, 20–63, and >63 \(\mu\)m) and mixed through
The distribution of the particles was derived from optical image analysis (Degryse et al., 2016), and, based on this distribution, it was estimated that these particles are oxidized at the same rate as homogeneously sized particles with a diameter of 25, 50, and 100 μm. Also a blank (MAP only) treatment was included. There were three replicate columns for each treatment (60 columns in total).

The fertilizers were made by using the <20- or >60-μm sieved fraction of the reagent-grade powdered ES. The ES was mixed with ground fertilizer-grade MAP in a mortar at the rates specified above. This mixture was wetted, and granules were made by extruding the paste-like mixture through a cylindrical die with a diameter of 1.5 or 3.0 mm and cutting the extrusion into pieces. The “granules” were dried in an oven at 35°C and had an average mass of 6 mg (for the 1.5-mm die) or 40 mg (for the 3-mm die), corresponding to an equivalent spherical diameter of 1.8 or 3.4 mm, respectively. To determine the exact size of the ES particles in the fertilizer, the ES was extracted from the fertilizer (because grinding of the MAP+ES mixture could have affected the ES particle size), and a microscopic image of the ES was taken (Supplemental Fig. S1) and analyzed as described by Degryse et al. (2016). The spherical equivalent diameter of the <20-μm sieved ES particles ranged from approximately 10 to 50 μm. The fact that the upper diameter of the particles was larger than the sieve aperture can be explained by the irregular shape of the particles. Calculation of the oxidation rate by size class (Watkinson, 1989) indicated that these particles would behave similarly as single-sized particles with a diameter of 25 μm (Supplemental Fig. S1). The >60-μm sieved ES particles ranged from approximately 20 to 130 μm and were predicted to behave similarly as single-sized particles with a diameter of 60 μm (Supplemental Fig. S1). The original particles were larger (equivalent diameter of 100 μm), indicating that grinding had indeed affected the ES particle size.

The dry soil (50 g per column) was mixed with granular MAP+ES fertilizer equivalent to 10 mg ES or with 10 mg ES particles and with MAP granules as required to balance the MAP rate (490 mg MAP per column). The soil was packed into the column (60-mL removable Luer Lock syringe; outer diameter, 3 cm) to an approximate bulk density of 1.4 g mL−1, corresponding to a height of approximately 5 cm. The base of the column was covered with a layer of glass wool and acid-washed sand prior to packing. The columns were wetted by slowly pumping distilled deionized water from the bottom of the column using a peristaltic pump (at a flow rate of 10 mL h−1) until 1 cm of water appeared above the column. The columns were immediately leached with 35 mL of water and then brought to field capacity by applying a suction equivalent to 100 cm of water. Preliminary testing had shown that 35 mL was sufficient to remove nearly all sulfate from the soil column (Degryse et al., 2016). The columns were weighed and transferred to an incubator regulated to 25°C. The columns were leached with 35 mL of water at 1-wk intervals for the first 4 wk, 2-wk intervals for the next 4 wk, and 4-wk intervals thereafter (total experimental duration of 20 wk). The collected leachates were filtered through a 0.45-μm membrane filter and analyzed for S by inductively coupled plasma optical emission spectroscopy.

Elemental S analysis was performed at the end of the experiment. The soil was taken from the columns after the last leaching event, dried at 60°C, and homogenized thoroughly with a grinder. Approximately 2 g of soil was weighed into a vial, and 10 mL of chloroform was added. The suspensions were shaken end-over-end for 2 h and centrifuged at 4600 g for 20 min. An aliquot of the supernatant was pipetted and diluted 10-fold with methanol. The ES concentration was determined by high-performance liquid chromatography (Agilent).

**Data and Statistical Analysis**

To evaluate the recovery of ES-derived S in the leachates, correction was made for S derived from the soil as follows:

\[
ES \text{ recovery (\%) } = \frac{S_{\text{treat}} - S_{\text{ctr}}}{ES_{\text{applied}}} \times 100
\]

where \( S_{\text{treat}} \) and \( S_{\text{ctr}} \) are the cumulative amounts of S leached in the ES fertilizer treatment and control (MAP only) treatment, respectively, and \( ES_{\text{applied}} \) is the amount of ES applied (mg S per column).

Three-way ANOVA was used to assess the effects of ES content in the fertilizer, granule size, and ES particle size on recovery of ES in the leachates and in the soil using SPSS software Version 22 (SPSS Inc.).

Although there was no fitting involved in the derivation of the model, curve fitting was performed to quantify the observed oxidation rates for the experimental treatments. The leaching curves (ES recovery in the leachates as a function of time) were described using the cubic model but with inclusion of a lag-time, which was apparent for most treatments:

\[
m = \frac{m_0}{1 - 0.0097k \frac{t - t_{lag}}{d_{eff}}}
\]

for \( t \geq t_{lag} \) \hspace{1cm} [7a]

\[
m = \frac{m_0}{1}
\]

for \( t < t_{lag} \) \hspace{1cm} [7b]

Technically the oxidation rate is not zero during the lag phase, but it is much lower than the steady-state rate after the lag period, likely because of the exponential growth of S-oxidizing organisms. Therefore, the lag period, when present, is usually distinctive as a period with almost no oxidation (Watkinson and Blair, 1993), justifying this mathematical description. Given the incomplete recoveries pointing to immobilization of sulfate, immobilization was also taken into account using a Michaelis–Menten type equation (Degryse et al., 2016):

\[
I = \frac{I_{max} [SO_4^- - S]}{K_m + [SO_4^- - S]} \hspace{1cm} [8]
\]

where \( I \) and \( I_{max} \) are the actual and maximal immobilization rates (mg S kg⁻¹ d⁻¹), \([SO_4^- - S]\) is the SO₄⁻S concentration, and
in the soil. About 6 mg of S leached in this first leaching event (Supplemental Fig. S2), mainly originating from the MAP fertilizer, which contains about 1.2% sulfate-S. After the first leaching event, the control (MAP only) treatment showed a slow but steady release of S, pointing to mineralization of soil organic S, at a rate of 8.6 µg S d⁻¹ (corresponding to 172 µg S kg⁻¹ d⁻¹).

For the ES particles, about 50% of added ES was recovered in the leachates after 7, 20, and 80 d for the ES particles with an equivalent diameter of 25, 50, and 100 µm, respectively (Supplemental Fig. S2), indicating faster oxidation with decreasing particle diameter. For the granular ES fertilizers, there was a very clear effect of ES content of the fertilizers, with slower oxidation as the ES content of the fertilizer increased (Fig. 3), as also evident from the significant effect of ES content on the total recovery of added ES in the leachate (P < 0.001, ANOVA) (Fig. 4A). At the end of the experiment, 77 to 92% of added ES was recovered in the leachate for the fertilizers with 20 g ES kg⁻¹ (kES = 0.02), but only 11 to 29% was recovered for the fertilizers with 250 g ES kg⁻¹ (kES = 0.25). Smaller granule size generally resulted in faster oxidation (P < 0.001, ANOVA) (Fig. 4A). For the granules with 50 to 250 g ES kg⁻¹, about twice as much of the added ES was recovered in the leachates for the small granules than for the large granules (Fig. 4). The ES particle size had no significant effect on the amount of S leached by the end of the experiment (Fig. 4A), but closer inspection of the leaching curves indicated that there was an effect for the small granules (dgrain 1.8 mm) with low ES content (20 or 50 g ES kg⁻¹), for which it took about twice as long to reach 50% recovery with the small (dgrain 25 µm) (Fig. 3A) than with the large ES particle size (dgrain 60 µm) (Fig. 3B). At higher ES content or with the large granules, there was no obvious effect of ES particle size on oxidation rate.

Analysis of ES remaining in the columns at the end of the experiment confirmed these trends. More ES was left in the soil with increasing fertilizer ES content and for the larger granule size (Fig. 4B). Also the effect of ES particle size was significant (P = 0.0011) but not very large. In the treatments with the fastest oxidation, most of the ES applied was recovered in the leachates by the end of the experiment, resulting in near full recovery. However, in treatments with slower oxidation (<50% of applied ES recovered in leachates), the sum of ES recovered in the leachates and ES remaining in the soil was only around 70%, likely because of immobilization of ES-derived sulfate into the soil organic matter pool.

### Experimentally Derived Effective Diameters

Fitting the cubic model to the treatments with the ES particles with an equivalent diameter of 25, 50, and 100 µm (Supplemental Fig. S2) indicated a surface-based oxidation rate of approximately 61 µg cm⁻² d⁻¹, which agrees reasonably well with the value of 52 µg cm⁻² d⁻¹ that was derived by Zhao et al. (2015) for the same soil at the same temperature (25°C) but using a different method (closed incubation and 1000 mg ES kg⁻¹).

Using this estimate for the surface-based oxidation rate (k), d_eff and tlag (Eq. [7]) were derived for the cogranulated

**RESULTS AND DISCUSSION**

**Sulfur Leaching and Elemental Sulfur Analysis**

The columns were leached immediately after fertilizer application to remove the sulfate present in the MAP fertilizer and

<table>
<thead>
<tr>
<th>Fertilizer composition and predicted effective diameter</th>
<th>Fitted (observed) oxidation parameters</th>
<th>Lag time</th>
<th>d_eff</th>
</tr>
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<tbody>
<tr>
<td>d(grain)</td>
<td>d_ES</td>
<td>f_ES</td>
<td>d_eff</td>
</tr>
<tr>
<td>-----------</td>
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<tr>
<td>1.8</td>
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<td>32</td>
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<td>0.05</td>
<td>81</td>
<td>3 (1)</td>
<td>70</td>
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<tr>
<td>0.10</td>
<td>162</td>
<td>7 (2)</td>
<td>154</td>
</tr>
<tr>
<td>0.25</td>
<td>404</td>
<td>7 (3)</td>
<td>332</td>
</tr>
<tr>
<td>60</td>
<td>0.02</td>
<td>60</td>
<td>4 (1)</td>
</tr>
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<td>0.05</td>
<td>81</td>
<td>8 (2)</td>
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<tr>
<td>0.10</td>
<td>162</td>
<td>11 (2)</td>
<td>135</td>
</tr>
<tr>
<td>0.25</td>
<td>404</td>
<td>7 (4)</td>
<td>347</td>
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<tr>
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<td>0.02</td>
<td>61</td>
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<td>11 (2)</td>
<td>195</td>
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<td>7 (3)</td>
<td>270</td>
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<td>556</td>
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<tr>
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<td>0.25</td>
<td>764</td>
<td>5 (7)</td>
<td>593</td>
</tr>
</tbody>
</table>

† d(grain) diameter of the fertilizer granule; d_ES, elemental S particle diameter; f_ES, mass fraction of elemental S in the granule; d_eff, effective diameter (i.e., diameter of elemental S mixed through soil predicted to oxidize at the same rate as the cogranulated elemental S).

‡ Values in parentheses are SD.
treatments (Table 1). A very good agreement between observed and fitted values was obtained (Supplemental Fig. S3), indicating that the cubic model describes well the oxidation behavior of cogranulated ES. A Michaelis–Menten equation was used to take into account the effect of immobilization on the release of sulfate. The estimated parameter values were 0.37 mg SO$_4$–S kg$^{-1}$ d$^{-1}$ for $I_{\text{max}}$ and 0.19 mg kg$^{-1}$ for $K_m$. When fitting the oxidation parameters to the leaching curves without taking into account immobilization, the estimated value of $d_{\text{eff}}$ was similar for the treatments with fast oxidation (with $d_{\text{eff}} < 140$ μm) but up to 50% larger for the treatments with slow oxidation, illustrating that ES oxidation may be considerably underestimated when based on sulfate measurements alone (Zhao et al., 2015).

The experimentally derived effective diameters ranged from 50 to 600 μm (Table 1). As already concluded from the leaching curves, the rate of oxidation decreased (and effective diameter hence increased) with increasing ES content of the fertilizer and increasing granule size, whereas ES particle size only had an effect at the lower ES contents (20 or 50 g ES kg$^{-1}$).

### Observed vs. Predicted Effective Diameters

The value of $d_{\text{eff}}$ for each fertilizer was predicted from the fertilizer composition according to Eq. [4] if $I_{\text{ES}} d_{\text{gran}}/d_{\text{ES}} \geq 1.11$ (Case B) or according to Eq. [5] if $I_{\text{ES}} d_{\text{gran}}/d_{\text{ES}} < 1.11$ (Case A) (Table 1). These predicted values were compared with the experimentally derived values of $d_{\text{eff}}$ (Table 1) and were generally in good agreement (Fig. 5). The model $R^2$ was 0.86, and predicted values were within a factor 2 of the observed values. This can be considered a very good prediction given that the model was derived on theoretical grounds and no parameter fitting was involved.

However, at the lower ES contents, the effective diameter was generally underpredicted (Fig. 5), and hence the rate of oxidation was overpredicted (Supplemental Fig. S3). These were the treatments in which Case A was valid or approached, indicating that Eq. [5] underestimates $d_{\text{eff}}$. It was assumed that the ES particles will oxidize at the same rate as ES particles mixed through soil in Case A. We hypothesize that the presence of insoluble impurities in the base MAP slowed down the oxidation in this case. These fertilizer impurities present in the insoluble residue...
Increasing ES content and increasing granule size were found to decrease the ES oxidation rate in most cases, whereas ES particle size only affected the oxidation rate at low ES content and small granule size (Table 1). At low ES content, all ES particles are soil exposed (Fig. 2, Case A), explaining the effect of particle size on oxidation rate, whereas at high ES content, the area covered by the ES particles exceeds the granule surface area, in which case the particles act as a single aggregate, and the size of the individual ES particles becomes irrelevant (Fig. 2B).

A sensitivity analysis was performed to explore in more detail how fertilizer composition is expected to affect the oxidation rate. Figure 6 gives the predicted effective diameters as a function of ES content for different granule and ES particle sizes. The kink in the curves corresponds to the transition of Case A to Case B (Fig. 2). At low ES content, adding more ES to the granule has no effect on the surface area per ES particle, and the (relative) oxidation rate hence remains constant. Once the ES content reaches the point where the ES particles cover the whole granule surface, adding more ES to the granule does not further increase the effective surface area. Hence, the surface per unit mass of ES decreases, result-
ing in an increase in the effective diameter and a decrease in the oxidation rate.

This analysis implies that no effect of ES particle size on oxidation rate is to be expected if Case B is valid, which would usually be the case for commercial products. An effect of decreasing granule size is expected when Case B is valid but not when Case A is valid (Fig. 2). For most of our experimental treatments, the condition for Case B was satisfied, explaining why decreasing granule size generally decreased the effective diameter and hence increased the oxidation rate (Table 1). Only the treatments with the lowest ES content (20 g kg$^{-1}$) and large ES particle size (60 μm) showed the same oxidation rate for both granule sizes ($d_{	ext{eff}}$ around 80 μm) (Table 1), which is also in agreement with the theoretical consideration because the condition for Case A was satisfied.

**Application to Commercial Products**

The model was derived ab initio, without any fitting of parameters, and was validated using laboratory-produced granules, which allowed varying each parameter ($f_{\text{ES}}, d_{\text{gran}}, d_{\text{ES}}$) independently within realistic ranges.

For further validation, the model was applied to predict the oxidation rate for commercial fertilizers using the data reported by Degryse et al. (2016), who determined oxidation rates for commercial MAP-based fertilizers with 50 to 75 g ES kg$^{-1}$ and ES-bentonite pastilles with 900 g ES kg$^{-1}$. Note that our model was developed for ES cogranulated with soluble macronutrient fertilizers (e.g., MAP, TSP, urea), but given the low fraction of the insoluble binder component (bentonite) in the pastilles, it was assumed that the model can be applied for these pastilles as well. An additional treatment with small MAP granules ($d_{\text{gran}}$, 1.7 mm), not reported by Degryse et al. (2016), was also included (Supplemental Fig. S4). Predicted and observed oxidation rates agreed reasonably well (Fig. 7) and illustrate the effect of the ES content and of granule size. In general, the oxidation rates were slightly overpredicted for these commercial fertilizers. This could be related to the uncertainties and inaccuracies in both the model and measurements but might also be caused by factors not accounted for by the model. For instance, the presence of fertilizer impurities in commercial fertilizer would result in not only ES but also impurities remaining in the granule cavity, which might reduce the soil-exposed surface of the ES.

No further validation with literature-reported data could be performed because most studies on ES oxidation have focused on ES particles mixed through soil. In the limited number of studies that compared ES oxidation between ES-fortified granular fertilizers and particulate ES, information about granule and ES particle size (used as input in our model) is usually not provided. To our knowledge, only Friesen (1996) studied the effect of cogranulation on ES oxidation in detail. He found that plant
yield and S uptake responses to S-granulated TSP (TSP with 160 g ES kg⁻¹ and with d_{ES} < 150 μm) was inversely proportional to the granule diameter. From the composition of the fertilizer, it can be inferred that Case B would have been valid, in which case the oxidation rate is indeed expected to be inversely proportional to the granule diameter.

Model Limitations

The model assumes that the granule residue has the same surface area in contact with the soil as the original granule. If the granule is surface applied and disperses under rain impact, this would result in faster oxidation than predicted by this model. Also, tillage could potentially break up the granule residue, although this may not necessarily be the case given the small size of the granule residue.

Furthermore, the model does not take into account carrier effects. It is assumed that the soluble macronutrients in the fertilizer diffuse away and that the oxidation of ES will occur at the same rate irrespective of the carrier. However, Friesen (1996) found an approximately 30% greater plant response to cogranulated compound fertilizers (160 g ES kg⁻¹) with phosphate carriers (TSP or DAP) than with urea, suggesting more oxidation occurred with the phosphate carriers, possibly due to stimulated microbial growth in the presence of P, resulting in a higher surface-based oxidation rate. Alternatively, the differences could be related to factors that are accounted for in our model but that were not reported, particularly granule size. The granules were sized between 1.7 and 3.4 mm (i.e., a size range wide enough that considerable variation between the average granule size of the different fertilizers may still have existed and could have caused the differences in oxidation rate). In any case, although a different macronutrient carrier may affect the surface-based oxidation rate, it is expected that the effect of cogranulation, which is related to the reduction in surface area, would still be similar for other soluble macronutrient fertilizers (e.g., DAP, urea).

The model only addresses the effects of cogranulation on ES oxidation rate. It is well known that temperature, water content (Janzen and Bettany, 1987a), and soil properties (Watkinson, 1989; Zhao et al., 2015) also affect oxidation rate. This could be taken into account by modifying the surface-based oxidation rate (k) depending on climatic and soil conditions, but this was outside the scope of this study.

CONCLUSIONS

The model presented in this paper predicts the effective diameter of ES in cogranulated fertilizers based on the fertilizer composition, specifically granule diameter, ES particle diameter, and ES content. This effective diameter corresponds to the diameter of ES particles mixed through soil that would oxidize at the same rate as the granular ES fertilizer and hence allows easy implementation in models developed to predict oxidation of particulate ES under field conditions. Thus, the model may assist in predicting S release from ES-fortified granular fertilizers and in guiding fertilizer recommendations, although validation of the model’s accuracy under field conditions is still required. The model does not describe the variations caused by climatic or soil factors, which have been studied elsewhere.

The model also allows estimation of how changes in granule size, ES particle size, and ES content will affect the oxidation of granular fertilizers and may hence assist in improving fertilizer formulations. For instance, model predictions and experimental observations indicate that a decrease in ES particle size will only increase the oxidation rate at ES contents below a certain threshold value that depends on granule and ES particle size. In most cases, the ES content is above this threshold and the oxidation rate is not affected by ES particle size but increases with decreasing granule size and decreasing ES content.

SUPPLEMENTAL MATERIAL

The supplemental material includes elemental S particle size (Fig. S1), S leaching curves for the ES particles mixed through soil (Fig. S2), observed and modeled S leaching and oxidation curves for the ES-fortified granules (Fig. S3), and observed S leaching and oxidation curves for small or large MES10 granules (Fig. S4).

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REFERENCES


