Long-term fate of fertilizer sulfate- and elemental S in co-granulated fertilizers

Fien Degryse · **Roslyn Baird** · **Ivan Andelkovic** · **Michael J. McLaughlin**

Abstract In previous studies, we assessed sulfur (S) uptake by crops from elemental S (ES) and sulfate-S (SO_4-S) in S-fortified monoammonium phosphate fertilizers over two years. The recovery by the crop ranged from 16 to 28% for ES and from 9 to 86% for SO_4-S. Here, we used a model which takes into account organic S cycling, SO_4-S leaching and ES oxidation to explain the observed recoveries. Higher recoveries of ES than SO_4-S in two of the four sites could be explained by partial leaching of SO_4-S and relatively fast oxidation of ES, due to a warm climate and high S-oxidizing soils. The same model was used for longer-term (5-year) predictions, and a sensitivity analysis was carried out. The size of the labile soil S pool and total S uptake strongly affected the recovery of both SO_4-S and ES. Predicted recoveries after 5 years were over threefold higher for a small than for a large labile organic S pool and for a high-uptake than for a low-uptake scenario. Leaching mainly affected SO_4-S, with predicted recoveries halved under a high-leaching scenario. Slow oxidation resulted in recoveries in the first year being fourfold lower for ES than for SO_4-S or even lower in case of a long lag-time.

However, it is predicted that total recoveries of ES will eventually reach those of SO_4-S or exceed them if there is SO_4-S leaching. Our model demonstrates that long-term trials are needed to evaluate the true effectiveness of a slow-release fertilizer source such as ES.

Keywords Elemental sulfur · Sulfate · Fertilizer recovery · Model

Introduction

Sulfur is an essential element for plant growth. Historically, inputs through rainfall or as a component of fertilizers were sufficient to meet the plant demand and, as a result, relatively little research has been devoted to S as a plant nutrient compared to phosphorus, which is taken up by plants in similar amounts. However, sulfur deficiency has become more common since the 1980s due to reduced atmospheric deposition, increasing yields and a reduction in use of S-containing fertilizers such as single superphosphate (Scherer 2001). As a result, the demand for S fertilizers has increased (Ceccotti 1996) and will likely continue to increase.

The most commonly used S fertilizers are either sulfate-S (SO_4-S) or elemental S (ES) based. Sulfate-S is immediately available to plants, but is prone to

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leaching. In high rainfall environments, leaching is a major loss (Eriksen and Askegaard 2000). Elemental S does not leach, and is 100% S, thus reducing the cost of transport and application compared to SO_4-S. However, it needs to be oxidized to sulfate in order to be available for plant uptake. Surface-based oxidation rates generally range between 10 and 80 μg cm^{-2} day^{-1} at 25 °C and tend to increase with pH and organic matter content (Zhao et al. 2015). Small ES particles oxidize quickly because of their high surface area (Germida and Janzen 1993), but they are not suitable for practical use due to dust and explosion hazards. Commercial products usually consist of ES cogranulated with macronutrient fertilizers or ES:bentonite pastilles, and are much slower to oxidize (Chien et al. 2011). Degryse et al. (2016b) showed that the oxidation rate of ES cogranulated with monoammonium phosphate (MAP) was inversely proportional to the ES content and to the granule size, which could be mathematically explained based on the surface area of ES particles in contact with soil.

The use of stable isotopes allows tracing how much of the nutrient in the plant is derived from fertilizer and how much of the fertilizer is taken up by the crop. This technique has been widely used for nitrogen, but very few field studies using isotopically labeled S fertilizers have been carried out in agro-ecosystems (Chalk et al. 2017). Degryse et al. (2018) carried out a field trial in Champaign (IL, US) with ^{34}S-labeled fertilizers to assess the uptake of S from MAP fertilizer cogranulated with ES and SO_4-S when applied in fall or in spring. For ES, the recovery in the crop over 2 years was similar for both application times (∼ 25%). For SO_4-S, the recovery was considerably higher for the spring-applied fertilizer (23%) than for the fall-applied fertilizer (10%). A simple model was developed, which showed that the recoveries could be explained based on leaching of applied SO_4-S, oxidation of ES and cycling of organic S. Similar field trials were carried out on three other sites in Argentina, Brazil and Canada (Degryse et al. 2020). The recoveries varied strongly between sites, S source and year. While recoveries declined in the year after application for SO_4-S, they generally increased for ES.

In this study, we further refined the previously developed model and applied it to all four sites. The same model was used to model long-term (5 year) recoveries of fertilizer SO_4-S and ES, and a sensitivity analysis was carried out to assess how the various parameters affected the recoveries of fertilizer S by crops. The aim of this modelling exercise is to obtain better insight into the factors determining the fate of fertilizer S in soil–plant systems.

Materials and methods

Data set

The results of four field trials were used in the modeling (Table 1). In all field trials, the recovery of S from MicroEssentials (MES) fertilizers was determined over two years using ^{34}S-labeled fertilizers. These fertilizers were MAP-based fertilizers, cogranulated with SO_4-S (as ammonium sulfate) and ES. The ES particles in the MES fertilizers had a mass-based median diameter around 50 μm (Degryse et al. 2016a). The fertilizers varied in their ES and SO_4-S content depending on which was the most commonly used MES fertilizer for each location: the SO_4-S + ES content of the fertilizers was 5 + 5% (Argentina and US), 2 + 7% (Brazil) or 7.5 + 7.5% (Canada). In the field trials carried out in Argentina, Brazil and Canada, MES fertilizer was applied at the start of the first crop. In the field trial in the US, the MES fertilizer was applied either in fall or in spring before the first crop. The crops were harvested at an early stage or at maturity and all aboveground material was removed. Full details of the experimental trials are provided elsewhere (Degryse et al. 2018, 2020).

Determination of ES oxidation rate

The ES oxidation rate was measured in soil (0–10 cm) sampled at the field sites using a column oxidation method, in which columns are incubated and leached at regular time intervals to remove sulfate produced by ES oxidation during the incubation period (Degryse et al. 2016a). In short, 10 mg of ES (Sigma, sized between 20 and 63 μm with a mass-based median diameter of 35 μm) was mixed through 50 g of soil. The soil was packed into a column (60-ml syringe) and saturated bottom to top. The soil was immediately leached (top to bottom) with 50 ml of water and then incubated at 25 °C. The columns were leached with 40 ml of water every week for the first couple of weeks and then biweekly. The S concentration in the leachates was determined with inductively coupled

Table 1 Recoveries of fertilizer S (% of added S) in the harvested material in year 1 and year 2 and cumulative recoveries over both years for the four field trials considered in this study (Degryse et al. 2020, 2018)

S source	Argentina	Brazil[a]	Canada	USA	
				Fall	Spring
SO4-S					
Year 1	77.6	6.8 (4.3 + 2.5)	59.1	6.8	18.2
Year 2	8.1	2.5 (1.2 + 1.3)	6.5	2.7	4.4
Yr 1 + Yr2	85.7	9.3	65.7	9.6	22.5
ES					
Year 1	12.3	8.3 (4.2 + 4.0)	5.8	18.4	21.5
Year 2	13.4	7.7 (3.5 + 4.2)	13.4	5.3	6.4
Yr 1 + Yr 2	25.7	15.9	19.2	23.7	27.9

The fertilizer S was added as MAP cogranulated with SO_4-S (2–7.5%) or ES (5–7.5%)

[a]Two crops (soybean/maize) were grown in 1 year—the values in brackets give the recovery for each crop separately

plasma-optical emission spectrometry (ICP-OES). The oxidation rate of ES was estimated from the S recovery:

$$\%ES_{oxid} = (S_{leached} - S_{soil})/ES_{applied} \times 100 \qquad (1)$$

where $ES_{applied}$ is the amount of ES applied (mg), $S_{leached}$ is the cumulative amount of S recovered in the leachates (mg) and S_{soil} the cumulative amount of soil-derived S leached, which was determined from a control treatment without added ES. The surface-based oxidation rate was estimated from the experimentally determined by fitting the cubic equation proposed by Watkinson to the data using least-square regression (Watkinson and Blair 1993).

Cogranulated fertilizers oxidize more slowly than ES particles mixed through soil, due to agglomeration of ES in the fertilizer residue. This can be expressed using the "effective diameter", i.e. the diameter of ES particles mixed through soil that would oxidize at the same rate as (co-)granulated ES. The effective diameter (d_{eff}) has been shown to correspond to:

$$d_{eff} = d_{gran}.f_{ES} \qquad (2)$$

where d_{gran} is the diameter of the fertilizer granule and f_{ES} the fraction of ES in the fertilizer (Degryse et al. 2016b).

In the field modelling (see below), we did not use the cubic equation but a first-order equation to describe the oxidation, as it is easier to implement. Moreover, we have found that the first-order equation generally describes the oxidation of cogranulated

fertilizers slightly better than the cubic equation. The cubic and first-order equation produce almost identical results up to about 70% oxidation, after which the cubic equation predicts slightly faster oxidation (Degryse et al. 2016a). As shown by Degryse et al. (2016a), the first-order oxidation rate constant can be calculated from the surface-based oxidation rate and the effective diameter as follows:

$$k_{oxid} = 0.03k_s/d_{eff} \qquad (3)$$

where k_{oxid} is the first-order rate constant (day^{-1}) and k_s is the surface based oxidation rate ($\mu g\ cm^{-2}$ day^{-1}) (Table 2).

Modeling of field data

The uptake of fertilizer S by the crops was modelled with a simple-box model, taking into account the various processes that affect the fate of fertilizer S. The goal of this modeling exercise was to derive an estimate for the oxidation rate of ES under field conditions and to obtain better insight into the factors that drive fertilizer S uptake by plants. The model takes into account oxidation of ES, turnover of S into the organic S pool, leaching of sulfate, and plant uptake (see Fig. 1). Numerical calculations were carried out which kept track of the original source of S (soil, fertilizer SO_4-S or ES) in each pool. Atmospheric S deposition was not accounted for, as its contribution was unknown and would have been small compared to the added fertilizer S. The model is very
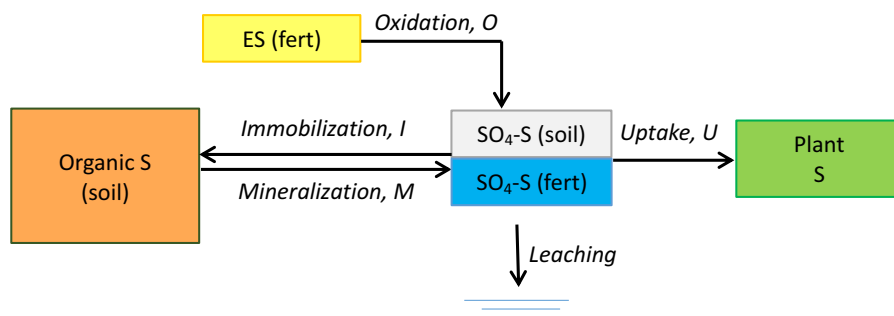
Fig. 1 Schematic illustrating the various processes that were taken into account to model the contribution of fertilizer SO_4-S or elemental S (ES) to the uptake of S by the plants. The plants take up S from the SO_4-S pool. The applied fertilizer ES is converted to SO_4-S through oxidation. Immobilization results in conversion of SO_4-S to organic S, whereas mineralization of organic S results in the release of SO_4-S. Leaching may result in removal of SO_4-S from the root zone (Taken from Degryse et al. 2018)

similar to the one described by Degryse et al. (2018), but two modifications were made: the calculations were carried out on a soil area basis instead of soil mass basis and the mineralization was described with a first-order reaction (Eq. 8) instead of a constant mineralization rate. Furthermore, while previously the oxidation rate constant was fitted to the observed field data, here we derived the oxidation rate based on the results of an independent laboratory experiment. As a result, there were only three adjustable parameters (the leached sulfate fraction, the labile organic S pool and the mineralization rate constant), which were optimized by fitting them to the observed field data as described below.

The oxidation was described as a first-order reaction, with a temperature-dependent rate constant (assuming a Q10 value of 3.4 corresponding to a 13% increase in oxidation rate for each °C increase in temperature; Germida and Janzen 1993):

$$O = k_{\text{oxid}(T)} \times ES \qquad (4)$$

$$k_{\text{oxid}(T)} = k_{\text{oxid}(25)} \times 1.13^{(T-25)} \qquad (5)$$

where O is the oxidation rate (kg S ha^{-1} day^{-1}), ES the amount of elemental S (kg S ha^{-1}) and $k_{\text{oxid}(T)}$ and $k_{\text{oxid}(25)}$ are the rate constants (day^{-1}) at temperature T and 25 °C, respectively. The daily soil temperature was calculated based on the minimum and maximum monthly temperatures, using an equation modified from Chapman (1997) in order to cover both the northern and southern hemispheres:

$$T = \left[(T_{\text{July}} - T_{\text{Jan}}) \times 1.03 \times \cos\left(2\pi \frac{t_0 + t - 213}{365} \right) \right.$$
$$\left. + T_{\text{Jan}} + T_{\text{July}]} \middle/ \right.$$
$$\qquad (6)$$

with T_{Jan} the average January temperature, T_{July} the average July temperature, t_0 the start date (time of fertilizer application, ordinal date) and t the time in days since the application. Using the 11-d running average air temperature (Zheng et al. 1993) instead had negligible effect on the predictions (details not shown).

The immobilization of sulfate into labile organic S (LOS) and the mineralization of LOS to sulfate were assumed to be first-order reactions:

$$I = k_{\text{immob}}.SO_4\text{-S} \qquad (7)$$

$$M = k_{\text{min}}.LOS \qquad (8)$$

where I and M (kg S ha^{-1} day^{-1}) are the immobilization and mineralization rates, k_{immob} and k_{min} are first-order rate constants (day^{-1}) and SO_4-S and LOS are the amounts of SO_4-S and LOS in the root zone (kg S ha^{-1}). As in our previous study (Degryse et al. 2018), the immobilization rate constant, k_{immob}, was fixed at 0.02 day^{-1}, based on results from Fuller et al. (1986) and Vermeiren et al. (2018), while the mineralization rate constant was fitted. The temperature dependence of these processes has not been studied in detail, though recent work in which field data of forest ecosystems were simulated suggested Q10 values between 2.2 and 2.8 (Dolschak and Berger 2020). We

found that including a Q10 of 2.5 had hardly any effect on the other parameter estimates or the predicted long-term fate of fertilizer, so no temperature dependence was included.

Leaching of applied sulfate was considered only to occur shortly after application. While this is a simplification, most leaching of added sulfate is indeed expected to occur early in the season, when (i) there is little water use by the crop and hence more water moving through the soil profile and (ii) the added sulfate has not been converted to organic S yet. Leaching was implemented in the model by correcting the added rate of fertilizer SO_4 (fertSO_4-S$_{added}$) as follows:

$$\text{fertSO}_4\text{-S}_{ini} = \text{fertSO}_4\text{-S}_{added}(1 - f_{leach}) \qquad (9)$$

where f_{leach} is the fraction of added S leached from the root zone and fertSO_4-S$_{ini}$ is the initial rate of fertilizer-derived SO_4-S in the rootzone.

A sigmoidal curve was used to describe the uptake of S by plants:

$$U_t = \frac{a}{1 + (b/t)^c} \qquad (10)$$

where U_t is the total amount of S taken up by the plant (kg S ha^{-1}) as a function of time t (d) and a, b, c are parameters adjusted to fit the observed uptake at the early growth stage and at maturity. The use of a sigmoidal uptake curve is supported by field experimental data (Bender et al. 2013). As plants take up S from the SO_4-S pool, the contribution of each source (fertilizer SO_4-S, ES or soil) to the plant uptake at any given time step was assumed to be proportional to the fraction of S derived from that source in the SO_4-S pool.

Differential equations were formulated as described previously (Degryse et al. 2018) and solved numerically in Microsoft Excel using a 1-day time step. The initial soil SO_4-S amount was based on a 0–20 cm soil analysis. The fitted parameters were the amount of LOS, the mineralization rate constant k_{min}, and the leached fraction of sulfate f_{leach}. Best-fit parameter values were obtained by least-square regression of measured versus predicted percentage of plant S derived from fertilizer (%Sdff). For the site in Canada, also a lag-time for the oxidation was fitted (Degryse et al. 2016b), because the negligible contribution of fertilizer ES to the uptake at the early growth stage in the first year could not be explained without a

lag-period and because no convergence was obtained without including a lag-time. It is noteworthy that Chapman (1989) observed an increase in the lag period of ES oxidation with decreasing temperature. This might explain why a lag-time had to be inferred for the site in Canada, but not for the other sites.

Long term prediction and sensitivity analysis

The model described above was slightly adjusted to make predictions over the longer term (5 years) and assess how the outcome was affected by changing a single parameter value.

As before, the plant uptake of S, U (kg S ha^{-1}) was described with a sigmoidal curve:

$$U_t = \frac{1.51 \cdot U_{max}}{1 + (80/t)^3} \qquad (11)$$

where U_{max} is the maximal (not nutrient limited) S uptake at the end of the growth season, assumed to be 100 days. Constant values were used in Eq. 11 for the parameters b and c from Eq. 10 (80 and 3 respectively, which was in the range of the values fitted to the observed uptakes), as a change in these values had insignificant effects on the outcome. However, to take into account that the S supply (from fertilizer or soil mineralization) may become insufficient over time to meet the plant demand, the equation was modified as follows:

$$\frac{\Delta U}{\Delta t} = 0 \ \text{if} \ U_t - U_{t-1} > (SO_4\text{-S})_{t-1} \qquad (12)$$

In other words, if the amount of SO_4-S in the root zone (kg S ha^{-1}) at a given time was smaller than the amount of S that would be taken up by plants during the next time step according to Eq. 7, the actual uptake for that time step was set to 0. This is a simplification, but because sulfate is a freely diffusible anion with little sorption in most soils (Curtin and Syers 1990), it is acceptable to assume that the whole quantity in the root zone can potentially be accessed by plant roots in a short period of time.

At the end of each growth period, the relative uptake (RU) was calculated as:

$$RU = \frac{U_{100}}{U_{max}} \qquad (13)$$

where U_{100} is the actual uptake at the end of the 100-d growth period. Thus, a value for $RU < 1$ indicated that the S supply was insufficient to meet the plant demand over the whole growth period. Ignoring luxury uptake, a linear relationship exists between yield and uptake, so in the simplified framework of this model, the RU also represents the relative yield (yield relative to the yield under optimal S nutrition).

For the long-term prediction, the leaching factor was implemented in a slightly different way. Instead of applying the leaching factor to added fertilizer sulfate, it was applied to the SO_4-S pool at the start of each cropping season (SO_4-S_t):

$$SO_4 - S_t = (1 - f_{leach})SO_4\text{-}S_{t-1} \qquad (14)$$

where SO_4-S_{t-1} is the SO_4-S content in the root zone at the previous time step. This was applied for the whole SO_4-S pool irrespective of the original source (soil, fertilizer SO_4-S or ES).

The predictions were carried out over a 5-year timeframe. To assess how each parameter affected the outcome, a sensitivity analysis was carried out in which each parameter was varied while holding the others constant. The crop cycle was assumed to start at ordinal date 121 (May 1) and last 100 days. The default uptake was 15 kg ha^{-1}, as amounts exported in harvested products generally range between 5 and 30 kg ha^{-1} (Till 2010). Our model only accounted for S uptake in harvested products, i.e. the fate of S in plant residues was not considered. The default fertilizer rate was 20 kg S ha^{-1}, half as SO_4-S and half as ES. Addition of only one S form at 10 kg S ha^{-1} instead had only a small effect on the predicted recovery. For simplicity, the modelling was carried out for a single application at the start of the 5-year period. Reapplication of S would have resulted in slightly lower recoveries due to the larger S pool resulting in more dilution of the S added in year 1. The default leaching factor was 0.2. Assuming a root zone depth of 800 mm and negligible retardation of sulfate, this corresponds to a precipitation excess of 160 mm. The default min/max temperatures were 0 and 25 °C (temperate climate). The default oxidation rate at 25 °C was 0.006 day^{-1} (which represents, for instance, a granular fertilizer with 5% ES and surface-based oxidation rate of 35 µg cm^{-2} day^{-1}) and the lag time 0 days. Default values for the labile organic S pool and immobilization rate were

100 kg ha^{-1} and 0.005 day^{-1}, i.e. within the range of the values fitted for the experimental sites (Table 3). In the sensitivity analysis, one parameter was varied within a realistic range (see values in Table 4), while the others were left at the default values.

Predictions for yearly application

The predictions above focus on the long-term recovery of fertilizer S (single application). The same model was used to assess the overall S balance and S availability to plants for scenarios with yearly application. The predictions were carried out for a low-S scenario (50 kg LOS ha^{-1} with low mineralization rate) in which repeated annual applications are more likely as S deficiency is likely to occur in the short term without S input.

The predictions were done for an optimal S uptake (U_{max}) of 15 kg S ha^{-1} for either relatively low ($f_{leach} = 0.2$) or high ($f_{leach} = 0.5$) leaching conditions. A zero-input scenario was included, as well as a low-input scenario in which 5 kg SO_4-S ha^{-1} was added each year. This value was chosen because even without addition of S fertilizers, some S input occurs through atmospheric input and through incidental addition through other fertilizers. For instance, commercial ammonium phosphate fertilizers generally contain around 1.0–1.5% SO_4-S as an impurity (Clay et al. 2012; own unpublished data). In the other scenarios, S was added at a higher rate (≥ 15 kg S ha^{-1}) either as SO_4-S, ES or a 50/50 mixture of both. For ES, both a mid-range oxidation rate ($k_{oxid,25}$ 0.006 day^{-1}, $T_{Jan/July}$ of 0/25 °C) and slow oxidation ($k_{oxid,25}$ 0.003 day^{-1}, $T_{Jan/July}$ of −10/20 °C, t_{lag} 50 days) were considered (Table 5). The fertilizer was added at the start of each growing season. The crop cycle was assumed to start at ordinal date 121 (May 1) and to last 100 days.

Results

Oxidation rate

The time to oxidize 50% of the ES powder (average diameter 35 µm) ranged from 14 days in the Canadian soil to 42 days in the Argentinian soil (Fig. 2). This corresponds to a surface-based oxidation rate (at 25 °C) ranging from 21 to 87 µg cm^{-2} day^{-1}
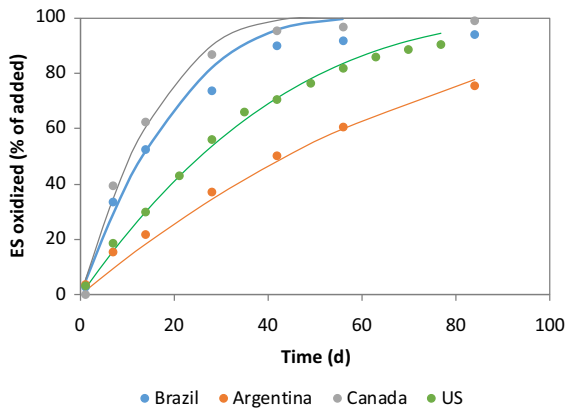
Fig. 2 Percentage of ES (average particle diameter of 35 μm) recovered in the leachates (oxidized) as a function of time in the soils (0–20 cm) sampled at the four field sites. The columns were incubated at 25 °C between leaching events. The lines are the fitted curves using the surface-based oxidation rates given in Table 2

(Table 2), which is within the normal range of literature-reported values (Watkinson 1989; Zhao et al. 2015). Based on the effective diameter of ES in the fertilizers (Eq. 2), the first-order oxidation rate (Eq. 3) was estimated to range between 0.004 and 0.011 day^{-1} (Table 2).

Modeling of field data

Figure 3 shows the modelled and observed %Sdff and fertilizer S recovery, using the best-fit parameters listed in Table 3. Modelling for the USA field trial results (Fig. 3d, e) was carried out before (Degryse et al 2018), but was repeated here because of some differences in the modelling approach. Here, we used the experimentally determined oxidation rate (Table 2), while the oxidation rate was previously fitted to the field data. The oxidation rate that was

estimated from the field data (0.0046 day^{-1} at 20 °C, corresponding to 0.0085 day^{-1} at 25 °C; Degryse et al 2018) was slightly higher than the experimentally measured value (0.0071 day^{-1}).

Overall, the observed trends in time for %Sdff and fertilizer recoveries could be well described with the theoretical model (Fig. 1). The percentage of plant S derived from fertilizer SO_4 is predicted to decrease in time, due to incorporation of the labeled fertilizer SO_4 into the labile organic S pool. It is predicted that a near-steady-state is reached in the second year, in which the %Sdff equals the ratio of fertilizer SO_4 present in the rootzone (not leached out) to the total amount of labile S. Thus, a larger LOS pool results in less S being derived from fertilizer and lower fertilizer S recovery. The fitted labile organic S pools ranged from 75 kg S ha^{-1} for the Argentina site to 417 kg S ha^{-1} for the Brazilian site.

For fertilizer ES, an increase in the %Sdff over time is initially predicted due to the ongoing oxidation, and this was indeed observed for the Argentinian, Canadian and USA sites. However, at the Brazilian site, the %S derived from fertilizer ES was much higher for the soybean crop at the early growth stage (ca 13%) than for the other sampling occasions (4.0–6.6%).

Due to the high temperatures at the Brazilian site, it is predicted that the ES is nearly fully oxidized (86%) within the first cropping season. As a result, the %S derived from fertilizer ES in the second cropping season shows little change (Fig. 3b). At the other sites, where ES oxidation is still incomplete after one season, the %S derived from fertilizer ES still continues to increase in the second season.

The modeling suggested that little or no leaching of sulfate occurred at the Argentinian and Canadian site. For the Brazilian site, it was estimated that about half of the applied sulfate was leached out of the rootzone.

Table 2 Measured surface-based oxidation rates at 25 °C ($k_{s,25}$) for the four soils and derived first-order oxidation rate constant ($k_{oxid,25}$) based on the effective diameter of the ES in the fertilizer (d_{eff})

	Argentina	Brazil	Canada	USA
$k_{s,25}$ (μg cm^{-2} day^{-1})	21	68	85	36
Fertilizer (% ES)[a]	MES10 (5)	MES9 (7)	MES15 (7.5)	MESZ (5)
d_{eff} (μm)	150	210	225	150
$k_{oxid,25}$ (day^{-1})	0.0042	0.0098	0.0113	0.0071

[a]MicroEssentials (MES) fertilizer used in the field experiment with %ES in the fertilizer in brackets

Fig. 3 Modelled (lines) and measured (symbols) percentage of plant S derived from fertilizer SO_4-S or ES (left) and percentage of fertilizer S recovered in the crop (right) as a function of time (day 0 = seeding in Year 1) for the sites in **a** Argentina, **b** Brazil (insets for more clarity), **c** Canada, and **d**, **e** US (**d**: spring applied; **e**: fall-applied fertilizer). Parameter values used in the model are given in Table 3
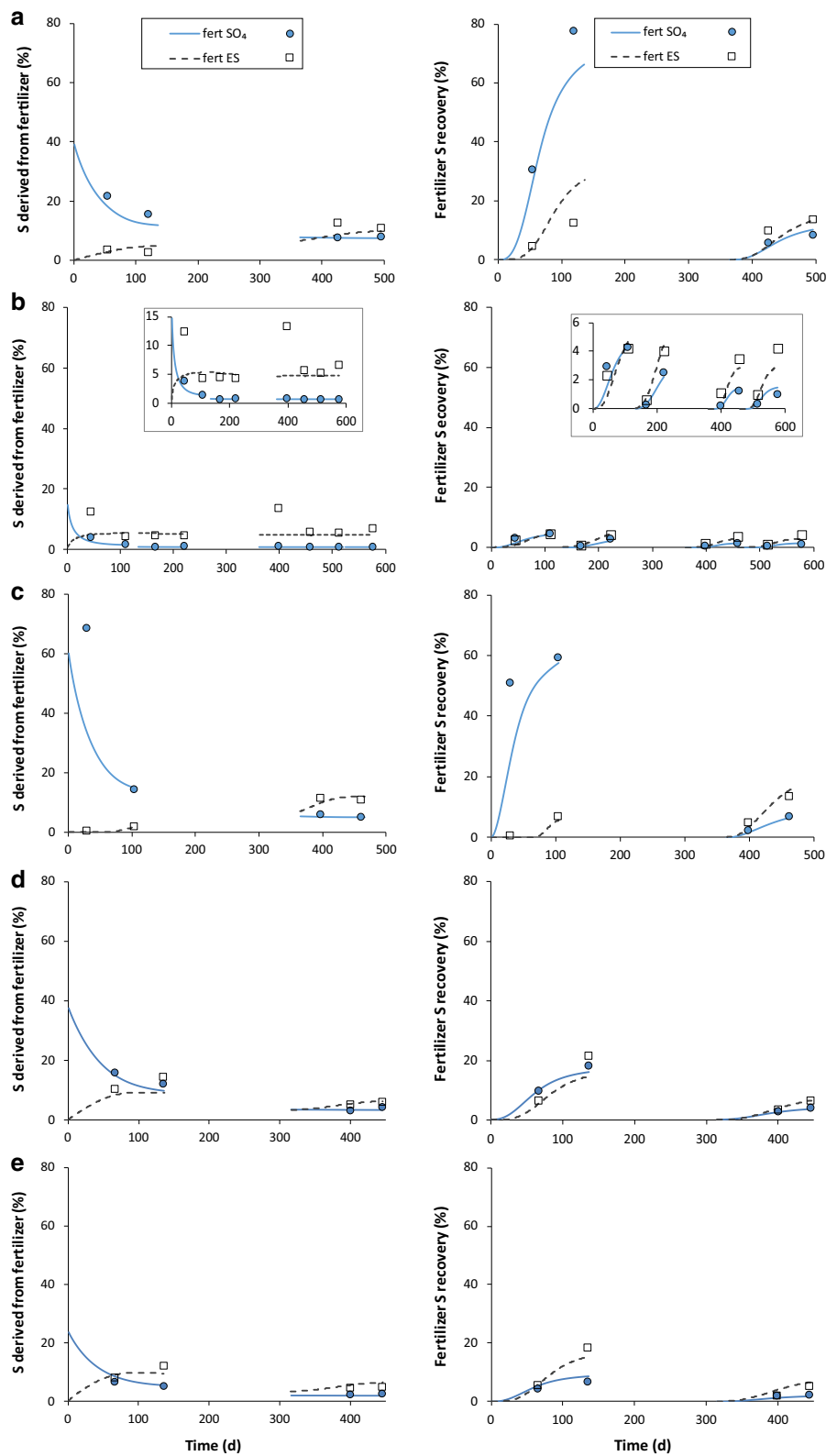
Table 3 Parameter values used for the modelling

Parameter	Argentina	Brazil	Canada	US	Notes
Temperature, T_{Jan}/T_{July} (°C)					
T_{Jan} (°C)	23.8	25.2	−14.8	−4.6	
T_{July} (°C)	10.2	20.8	18.2	23.9	
Uptake U (kg ha^{-1})	Adjusted to correspond to measured uptake				
a[a]	62/17	26/32/14/14	98/34	30/19	
b[a]	80/80	80/100/60/70	80/80	90/80	
c[a]	3.3/2.7	3.0/4.0/5.0/5.0	2.0/2.1	2.7/2.5	
Organic S					
k_{immob} (day^{-1})	0.02	0.02	0.02	0.02	Fixed
k_{min} (day^{-1})	0.0086	0.0070	0.0073	0.0026	Fitted
Labile organic S, LOS (kg ha^{-1})	68	417	113	187	Fitted
ES oxidation					
$k_{oxid(25)}$ (day^{-1})	0.0042	0.0098	0.0113	0.0071	Measured
Lag time (day)	0	0	70	0	Fitted (Canada only)
SO$_4$-S fraction leached, f_{leach}	0	0.47	0.16	0.34 (Spring) 0.66 (Fall)	Fitted

[a]The numbers separated by a slash are values for the consecutive crops during the 2-year period. At the Brazil site, two crops per year were grown

This can be explained by the very high rainfall early in the season (nearly 600 mm rainfall in the first two months; Degryse et al. 2020). Predictions with Hydrus-1D indicated that such a high leaching loss is indeed realistic under these conditions (details not shown). For the US site, it was estimated that 34% of the spring-applied and 66% of the fall applied sulfate leached out of the rootzone. Soil sampling of plots on which sulfate of potash was applied at high rates showed that 50% of spring-applied and 85% of fall-applied sulfate leached below 90 cm, confirming that substantial sulfate leaching indeed occurred (Degryse et al. 2018).

Long term prediction and sensitivity analysis

To assess how various parameters affect the recovery of fertilizer S, we carried out predictions over a 5-year time frame, using the parameters shown in Table 4. Table 6 gives the predicted fate of the fertilizer S under the various scenarios. Note that the % of fertilizer S taken up over the 5-year period corresponds to the cumulative recovery in the plant after 5 years (Fig. 4). Differences between the ES and SO$_4$-S source were most pronounced in the first year. Depending on the scenario, the predicted recovery in the first year ranged from 7 to 35% for SO$_4$-S and from 3 to 21% for ES. It is noteworthy that higher recoveries of SO$_4$-S were observed in the field trials for Argentina and Canada ($\geq$ 59%), due to the high S offtake in the first year ($>$ 50 kg S ha^{-1}), as all aboveground material was removed. For the scenario analysis, we used more typical values of 5–30 kg S ha^{-1}.

In the default scenario, representing a mid-range oxidation in a temperate region, recoveries for SO$_4$-S were double those of ES in the first year, due to incomplete oxidation of ES (39% oxidized at the end of the first cropping season). However, from the second year onwards, recoveries are predicted to be larger for ES than for SO$_4$-S, as more ES is oxidized (73% at end of second cropping season) while leaching losses are larger for SO$_4$-S than ES, resulting in cumulative recoveries of ES to slightly exceed those of SO$_4$-S by the fourth year.

As to be expected, the crop S uptake strongly affected the recovery of fertilizer S (Fig. 4a), with the recoveries in the first year being about proportional to the uptake. Fertilizer rate also affected uptake, with a lower fertilizer rate resulting in higher recovery (Fig. 4b). However, the effect was much less

Table 4 Parameter values used in the sensitivity analysis[a]

Parameter	Default	Alternatives	
		Low	High
Uptake, U_{max} (kg ha^{-1})	15	5	30
Fertilizer rate, SO_4-S/ES (kg ha^{-1})	10/10	5/5	20/20
Leaching factor, f_{leach}	0.2	0	0.5
Labile organic S, LOS (kg ha^{-1})	100	50	300
Mineralization rate constant, k_{min} (day^{-1})	0.005	0.002	0.008
Temperature, T_{Jan}/T_{July} (°C)	0/25	−10/20	22/27
Oxidation rate, $k_{oxid(25)}$ (day^{-1})	0.006	0.003	0.009
Lag time, t_{lag} (day)	0	50	100

[a]The initial soil SO_4-S pool was fixed at 10 kg SO_4-S ha^{-1}

Table 5 Parameters used for the S balance calculations with yearly application

Parameter	Value	
Uptake, U_{max} (kg ha^{-1})	15	
Leaching factor, f_{leach}	0.2 or 0.5	
Soil sulfate-S, SO_4-S (kg ha^{-1})	5	
Labile organic S, LOS (kg ha^{-1})	50	
Mineralization rate constant, k_{min} (day^{-1})	0.002	
ES oxidation scenario[a]	Normal	Slow
Temperature, T_{Jan}/T_{July} (°C)[a]	0/25	−10/20
Oxidation rate, $k_{oxid(25)}$ (day^{-1})[a]	0.006	0.003
Lag time, t_{lag} (day)[a]	0	50

[a]Values chosen to represent mid-range oxidation (temperate climate and soil with average oxidation rate) or slow oxidation (cold climate and soil with slow oxidation due to low pH or organic matter content) for a macronutrient fertilizer cogranulated with 5% ES

pronounced than the effect of uptake, due to the "dilution" of added S into the organic S pool. A lower fertilizer rate resulted in more dilution into the organic S pool, and hence a lower %S being derived from the fertilizer.

The leaching factor strongly affected the recoveries of SO_4-S, but much less so of ES, as the concentration of ES-derived S in the SO_4-S pool remains low due to the gradual release of ES (Fig. 4c). The predictions show that, without any leaching, the contribution of ES is initially lower than that of SO_4-S due to the slow oxidation, but, over time, the cumulative recovery of ES approaches that of SO_4-S. If there is leaching, the cumulative recovery of ES eventually exceeds that of SO_4-S.

Because of slower oxidation of ES at low temperatures, recoveries of ES are lower in colder climates, and it will hence take longer before the cumulative recovery of ES reaches that of SO_4-S (Fig. 4d). The same is true if the soil had an inherently lower oxidation rate (Fig. 4e), as a result of a low content of OM or a low pH. A lag time can result in much lower ES recoveries in the first year, but no effect is expected in subsequent years (Fig. 4f).

The labile organic S pool is expected to have a large effect on the recovery of fertilizer ES, due to the relatively fast turnover of the LOS pool and hence dilution of the added fertilizer S (Fig. 4g). Similarly, a high mineralization rate resulted in lower recoveries as faster turnover of the LOS pool resulted in more dilution of the added S (Fig. 4h).

Predictions for yearly application

Here, we predict overall S balances (Table 7) and relative uptake (Fig. 5) for different scenarios of yearly S application in an initially S-deficient soil. In the case of a zero- low SO_4-S supply (5 kg ha^{-1}year^{-1}), uptake and leaching exceed the input, resulting in a negative S balance. This is more pronounced under high leaching conditions (f_{leach} = 0.5) than under low leaching conditions (f_{leach} = 0.2) and hence the relative uptake (uptake relative to the uptake under optimal S supply, as argued above, representative of the relative yield) decreases more quickly under the high leaching scenario.

If fertilizer SO_4-S is added at the same yearly rate as the S uptake under optimal supply (15 kg ha^{-1} year^{-1}), the relative uptake still decreases over time as leaching of S results in a

Table 6 Effect of change in parameter values (see Table 4) on the predicted fate of fertilizer SO_4-S and ES five years after application. The values show the percentage of added S taken up in harvested material, leached below the rootzone, incorporated in the soil S pool, or still present as ES (unoxidized)

Scenario		SO_4-S (% of added)			ES (% of added)			
		Uptake	Leached	Soil	Uptake	Leached	Soil	ES
Default		52	27	21	59	9	30	2
Uptake	Low	19	30	51	19	11	67	2
	High	70	24	6	84	5	9	2
Fertilizer rate	Low	56	27	17	64	8	26	2
	High	46	28	26	51	9	37	2
Leaching	Low	63	0	37	56	0	42	2
	High	33	60	7	62	19	17	2
Temperature	Low	53	27	20	51	6	27	15
	High	52	27	21	60	10	29	0
Oxidation rate	Low	53	27	20	50	7	28	15
	High	52	27	21	61	9	29	0
Lag time	Low	52	27	20	57	9	32	3
	High	53	27	20	55	8	33	4
LOS	Low	67	25	8	80	6	12	2
	High	23	30	47	22	11	64	2
Mineralization	Low	52	23	25	65	4	29	2
	High	51	30	19	57	12	29	2

negative S balance. In contrast, when adding ES at the same rate, (near) maximal uptake is achieved over the 5-year time frame if the ES oxidizes relatively quickly, as less S is lost from the root zone. However, in the case of relatively slow ES oxidation, the relative uptake is initially less than for SO_4-S at the same rate. In contrast with SO_4-S, the relative uptake stagnates and then increases for the slow-oxidizing ES as ES accumulates in the soil, and hence surpasses the uptake in the scenario with yearly SO_4-S application by the third year under high leaching conditions. However, in the low leaching scenario, where relatively little SO_4-S is lost by leaching, it takes > 5 years to achieve the same uptake with the slow-oxidizing ES as with SO_4-S, as the majority (62%) of added ES is still predicted to be unoxidized over the five-year timeframe.

To compensate for leaching or incomplete oxidation, more S may need to be added than taken off by the crop to reach optimal S supply. Predictions were made with yearly S additions at 18 kg ha^{-1} year for the low leaching scenario and 26 kg ha^{-1} year for the high leaching scenario, either as SO_4-S, slow-oxidizing ES or a 50/50 mixture. In the SO_4-S-only scenario, the balance was still negative due to leaching (Table 7), resulting in a decrease in the relative uptake over time,

particularly in the high leaching scenario. In the scenario with slow-oxidizing ES, the relative uptake increased over time, but the initial values were < 90%, due to the low S reserves and slow oxidation, and they remained below 90% over the 5-year timeframe at the lower rate (18 kg ha^{-1} year^{-1}). With the 50/50 mixture, the initial values were higher than for the slow-oxidizing ES, but there was no decline over time as for the SO_4-S only case.

Discussion

Differences in climatic and soil conditions explain the variation in observed recoveries

The fertilizer recoveries varied strongly between sites, crops/seasons and S source (Table 1). A model taking into account the relevant processes was used to rationalize the observed results. The model assumes the root zone is homogeneous and simplifies the processes affecting the fate of fertilizer S, and caution is therefore warranted when interpreting the results. Notwithstanding these limitations, the modeling gives useful insights into the factors that control the
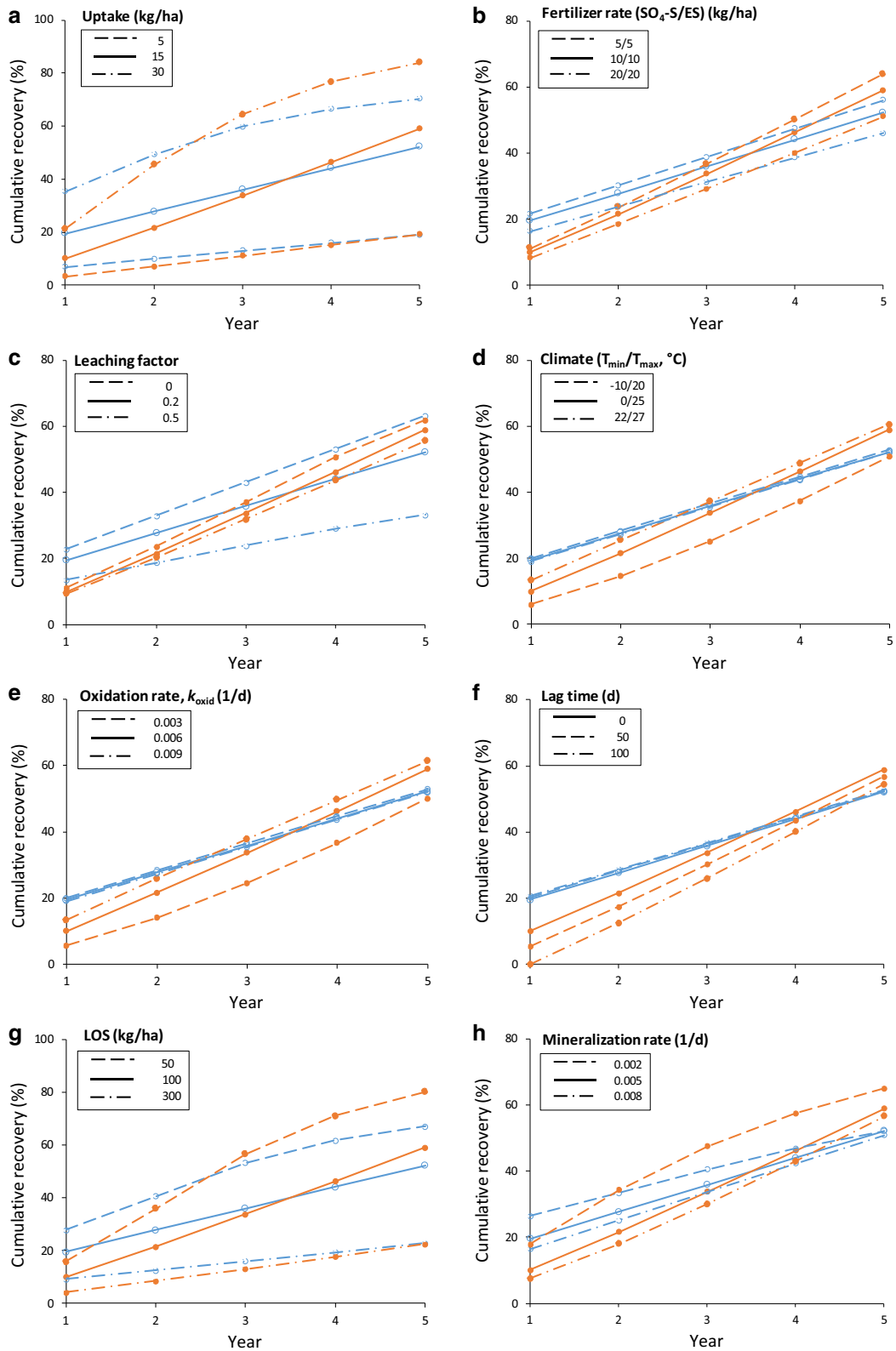
◄ **Fig. 4** Effect of parameter values (sensitivity analysis) on the predicted cumulative recovery of added fertilizer SO_4-S (blue, open symbols) or ES (orange, closed symbols) over a period of 5 years for the default scenario (full line = default scenario). Parameter values for the various scenarios are listed in Table 4. (Color figure online)

contribution and recovery of fertilizer S under field conditions.

The percentage of plant S derived from fertilizer SO_4-S could be explained based on early leaching of added SO_4-S and dilution into the labile soil S pool. The recovery of fertilizer S in plants is affected by the same processes, but also depends on the plant S uptake relative to the fertilizer rate. The labile soil S pool includes both the indigenous soil SO_4-S, in which the dilution is immediate, and the LOS pool. The cycling of organic S is a slow process, explaining the gradual decrease in %S derived from fertilizer SO_4-S, until a near steady-state is reached (Fig. 3). The lower recoveries of fertilizer SO_4-S in the Brazil site than in the other sites can be attributed to a combination of factors according to the model: leaching of added SO_4-S prior to incorporation in organic matter, the large LOS pool resulting in more dilution of added SO_4-S, and the lower S uptake. We speculate that the large

LOS pool is related to higher sub-surface organic matter concentrations in the Oxisol at the Brazilian site. Furthermore, a larger subsoil reserve of inorganic S may also have contributed to larger dilution of the fertilizer S.

The estimated fraction of fertilizer SO_4-S leached was not only high for the Brazilian site (0.47) but also for the US site in the case of a fall application (0.66). Several other studies have indicated that leaching may result in considerable loss of fertilizer-sulfate, especially when fall-applied, but also when spring-applied if there is high rainfall shortly after application (Degryse et al. 2018; Goh and Gregg 1982; Rhue and Kamprath 1973), as was the case for the Brazilian site (Degryse et al. 2020).

Fertilizer ES is much less prone to leaching, because the slow ES oxidation results in a gradual release of sulfate and high concentrations of ES-derived sulfate are hence avoided. Moreover, most oxidation is expected to occur during times when there is little water movement through the soil profile because of high water use by the crop, since ES oxidation and plant growth are favored by the same environmental conditions (high temperature, sufficient moisture). The slow oxidation of ES explains why the %S derived from fertilizer ES is generally

Table 7 Overall S balance for the scenarios with yearly application, using the parameters given in Table 5

	Input (kg ha^{-1})	Uptake	Leaching	Balance
Low leaching (f_{leach} = 0.2)				
0	0	37	5	−41
5 SO$_4$-S	25	48	10	−33
15 SO$_4$-S	75	68	21	−13
15 ES	75	75	6	−6
15 ES(slow)	75	62	5	7
18 SO$_4$-S + ES(slow) (50/50)	90	68	15	8
18 SO$_4$-S	90	72	24	−6
18 ES(slow)	90	62	5	23
High leaching (f_{leach} = 0.5)				
0	0	32	11	−43
5 SO$_4$-S	25	40	24	−39
15 SO$_4$-S	75	53	50	−28
15 ES	75	73	14	−12
15 ES (slow)	75	54	12	9
26 SO$_4$-S + ES(slow) (50/50)	130	70	46	13
26 SO$_4$-S	130	66	79	−15
26 ES(slow)	130	68	14	49

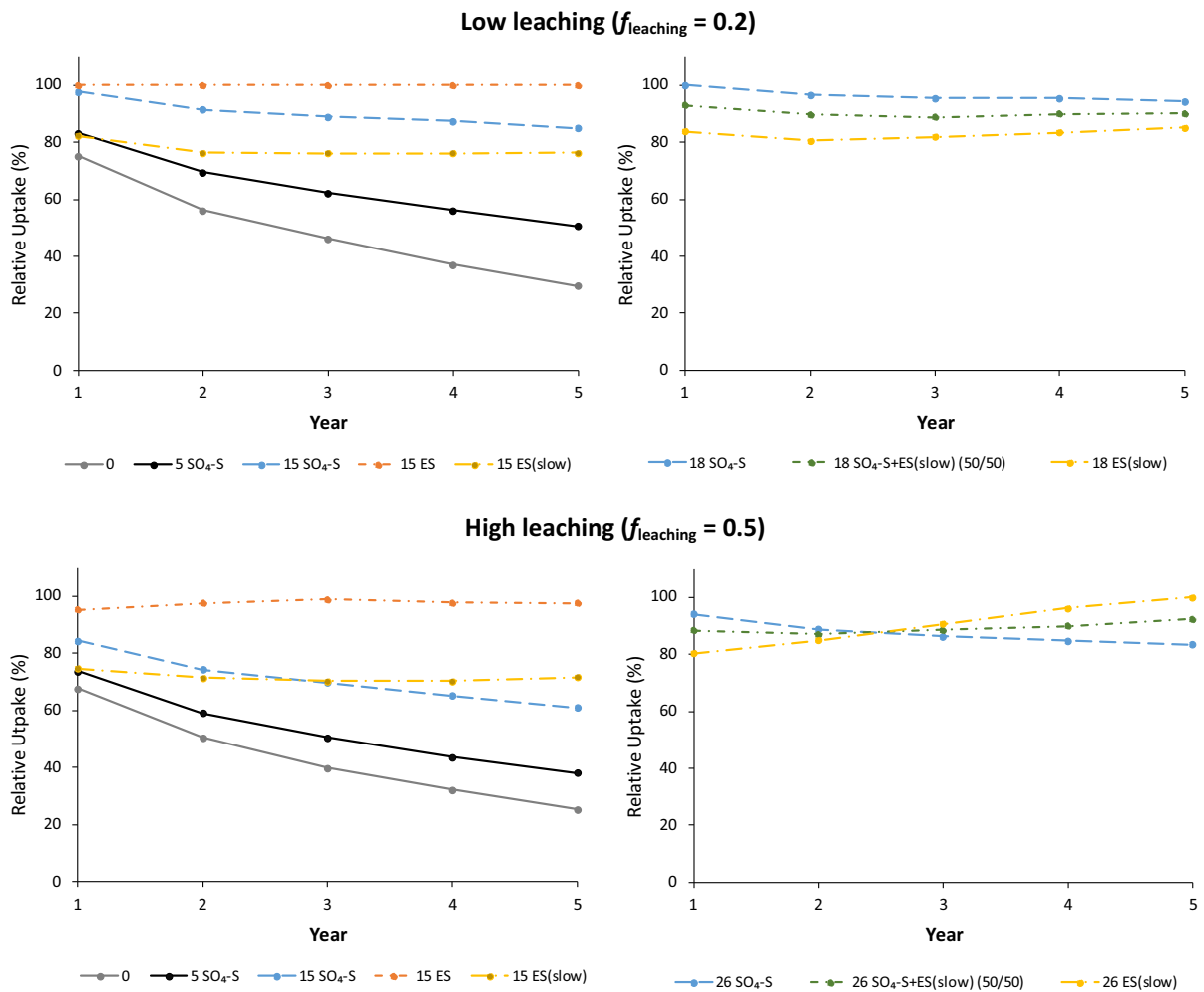## Low leaching ($f_{leaching}$ = 0.2)

High leaching ($f_{leaching}$ = 0.5)

Fig. 5 Predicted relative uptake as a function of time for yearly applications of fertilizer SO$_4$-S or ES (values in kg ha^{-1} in legends) in a soil with low S status for a low leaching or high leaching scenario (parameter values listed in Table 5). Relative uptake values < 100% point to suboptimal S supply

smaller for the first crop than for succeeding crops. The model described most observations well, with the exception of the fertilizer ES contribution at the early (R1/R2) stage of the soy crops in the Brazilian site. As argued before (Degryse et al. 2020), we hypothesize this is related to the shallow rooting of soybean at this early stage. Most likely, these shallow roots would take up relatively more S derived from ES than deep roots which take up more S from the less fertilizer-enriched subsoil. For the fertilizer SO$_4$-S, the rooting depth likely had less effect because of the higher mobility of added SO$_4$-S.

Long term recoveries of ES are expected to equal or exceed those of SO$_4$-S

Long-term (5 year) predictions of fertilizer S recovery in the harvested material were made for various scenarios. While recoveries in the second year declined for SO$_4$-S (range 3–13%), they generally increased for ES (range 4 − 24%). The predicted cumulative recovery after 5 years ranged from 17 to 70% for SO$_4$-S and from 19 to 84% for ES. Sulfur uptake and LOS had the biggest effect on the predicted recoveries (Table 6): more S uptake resulted in a higher recovery in the plant, while higher LOS concentrations resulted in more dilution of the added

S into the soil S pool and hence lower recoveries. The leaching factor had a large effect on the recovery of SO_4-S, but only a small effect on the recovery of ES. Oxidation rate and temperature had large effects on the initial recovery of ES, but less effects on the cumulative recovery after 5 years. As evident from the scenario analysis, cumulative recoveries of ES are expected to reach the values of SO_4-S if there is no S leaching or exceed them if there is S leaching. For instance, Friesen (1991) found that ES-fortified TSP was generally as effective as sulfate sources in the first cropping season and showed a higher residual effect in high-rainfall environments in West-Africa.

It follows from the above that when comparing a soluble fertilizer source to a slow-release source, trials covering only a single season do not allow for a meaningful comparison. In most soils under temperate climate, only 20–50% of ES is expected to be oxidized in the first year for co-granulated fertilizers containing 5–10% ES, while the unoxidized ES will continue to supply plant-available S in successive years. Assuming a constant yearly application, the amount of ES oxidizing in the nth year after the start of the application relative to the added ES rate (f_{oxid}) would be:

$$f_{oxid} = \sum_{i=1}^{n} (1-a) . a^{(i-1)} = 1 - a^n \qquad (15)$$

where a represents the fraction of ES not oxidized in the first year of application. For instance, if 35% ES gets oxidized in the first year ($a = 0.65$), the amount of ES oxidizing in the second year equals 58% of the yearly rate (35% from the current year and 23% from the previous year). Eventually, the yearly SO_4-S supply resulting from ES oxidation adds up to the added S rate, since $\lim_{n \to \infty}(1 - a^n) = 1$ (with $a < 1$). The quicker the oxidation, the faster the yearly SO_4-S supply will approach the added ES rate. Similar reasoning has been applied when considering the agronomic benefits of manure (Schröder 2005) or strongly sorbed nutrients such as phosphorus (Johnston et al. 2014). For instance, while the recovery of fertilizer-applied phosphorus is usually low in the first year, balance considerations demonstrate that the overall efficiency is high due to the residual effect of fertilizer P.

The scenario analysis clearly illustrate that fertilizer recoveries need to be interpreted with caution. A

low recovery may be related to leaching, which is a true loss, but it may also be due to incomplete oxidation (in case of ES) or due to incorporation of fertilizer S into the organic pool, in which case the unrecovered S is still available for consecutive crops. As argued before for N, the plant responds in the same way to the labelled fertilizer N (or S) as to an equivalent amount of soil N (or S) that was exchanged with fertilizer N (or S) through mineralization/immobilization (Harmsen and Moraghan 1988). Hence, while stable isotope tracing gives useful insights in the nutrient dynamics, the fertilizer recoveries obtained with this method are not necessarily a good indicator of the true effectiveness.

To further illustrate how SO_4-S and ES compare as fertilizer sources depending on leaching conditions, we used the model to predict the soil S balance and relative uptake over a 5-year timeframe with yearly applications of S fertilizer for a soil with low S status (Fig. 5 and Table 7). With SO_4-S added at the same rate as the (non-limited) S uptake by the crop, leaching resulted in a negative S balance and depletion of the soil S reserves, resulting in S limitation for crop growth over time, particularly under high leaching conditions. Addition of ES resulted in a less negative (fast oxidation) or positive (slow oxidation) balance due to less leaching. However, S limitations for the plant uptake ($RU < 100\%$) occurred for the slow oxidation scenario, as the slow oxidation resulted in not enough S becoming plant-available. Addition of both S forms (as a 50/50 mixture) can help to provide both immediately plant-available S and reduce the risk of leaching. However, under high leaching conditions, S losses are unavoidable and need to be compensated with extra fertilizer to avoid a negative S balance in soils with low S reserves.

Labile organic S represents a large pool of potentially plant-available S

The field observations indicated that, even in the year of fertilizer S application, > 70% of the plant S was derived from the soil. The important role of LOS in plant nutrition explains why extractable sulfate or other soil S tests generally fail as indicators of plant-available S (Castellano and Dick 1991; Jones 1986; Kim et al. 2013). Even extracts that include part of the organic S are unlikely to give a good indication across a range of soil types (Vermeiren et al. 2018). A mass

balance approach, considering S inputs and outputs to avoid soil S depletion, in combination with plant testing may hence be more reliable than soil testing in order to ensure sufficient S supply to crops.

The modeling results indicated labile organic S pools ranging from 75 to 417 kg S ha^{-1}. With organic C stocks generally ranging between 30 and 200 Mg C ha^{-1} in the top 1 m of agricultural soils, we estimate that total organic S roughly ranges from 300 to 2000 kg S ha^{-1} based on a C:S ratio of 100 (Stevenson and Cole 1999). This suggests that roughly 20% of organic S is in a 'labile' form, consistent with estimates of ^{35}S isotope dilution experiments on a wide range of soils (range 4–−25%; Vermeiren et al. 2018). The mineralization of LOS explains why there were no yield effects of fertilizer S application at maturity at any of the sites. However, in three of the four sites, the LOS could theoretically be depleted by a high-demand crop in a couple of seasons without any S input, pointing to the need for S fertilization to sustain the soil S status. Recent studies have indeed indicated that in various regions, soil organic S pools are being depleted due to low inputs, and that even though current responses to S fertilization are often limited to soils with low organic matter contents, it is likely that responses to S fertilization will become more widespread in the future (David et al. 2016; Elkin et al. 2016; Kost et al. 2008).

Model limitations and further development

The conceptual model described here presents a first attempt at rationalizing S fertilizer recoveries taking into account the relevant processes. The model successfully described the observed recoveries of fertilizer SO$_4$-S and (cogranulated) ES at four sites, based on experimentally determined oxidation rates, fitted organic S kinetics and SO$_4$-S leaching rate. It gives a better understanding of the factors determining the recovery of fertilizer S, and shows that even though ES recoveries are usually lower than SO$_4$-S recoveries in the first year, over time the cumulative recoveries are expected to equal those of SO$_4$-S or exceed them if S leaching occurs.

While the model gives useful insight into the factors determining the fate of fertilizer S, further development is needed for it to be useful as a management tool. No independent model validation was included due to lack of data and the model

included many simplifications. For instance, the rootzone was considered to be a single layer, i.e. vertical heterogeneity was neglected. Leaching was implemented using a single yearly leaching fraction at the start of the season, since most leaching occurs shortly after fertilizer application, in early spring or also during winter in case of fall application (Nelson and Uhland 1955). Nevertheless, more accurate predictions could be obtained by incorporating daily leaching into the model using a water flow model that predicts drainage over time. We took a very simple approach to describing the organic S dynamics, using first-order reactions for mineralization and immobilization, and assumed there was no effect of temperature on mineralization to avoid over-parameterization. However, mineralization is likely to increase with increasing temperature (Tabatabai and Al-Khafaji 1980). Also other factors, e.g. soil moisture status, would likely affect mineralization. Moreover, only one pool with a single rate constant was considered in the modelling. However, it is unlikely that a single rate constant can adequately describe the biodegradation kinetics of organic S, given that the mineralization mechanisms involve various substrates, biochemical pathways and microbial communities (Eriksen 2009). The plant uptake was modelled based on the uptake required to support maximal growth, without considering luxury uptake. Furthermore, we only considered net offtake by the plant, i.e. no attempt was made to describe the fate of S in plant residues. Thus, it was implicitly assumed that the dynamics of residue-S are identical to those of labile soil S. More research, both at field scale and in the laboratory, is needed to get a better understanding of the dynamics of both soil organic S and plant residues and the effect of management practices.

The use of elemental S as a source of fertilizer S can assist in reducing leaching losses, which is a major loss pathway of S from soil systems. Several studies in the literature have given recommendations for ES particle sizes based on climatic conditions in order to match S supply with plant demand (Blair et al. 1993; Watkinson and Lee 1994). However, these studies have been carried out using dry-screened ES, which is not commercially available in most countries. There are fungicides in the form of a wettable sulfur powder, but their use as fertilizer is likely cost-prohibitive. Most commercially available ES fertilizers consist of ES cogranulated with binders (e.g., bentonite) or with

macronutrient fertilizers. The use of the "effective diameter" of ES particles, which can be calculated based on the composition and physical characteristics of the fertilizer, allows approaching co-granulated ES in the same way as powdered ES. However, further refinement and validation of our model is needed in order to optimally tailor S fertilization to crop needs.

Simulation models have been used to improve crop N management practices (Shaffer 2002). Sulfur shows many similarities with N and further development of the S model could be useful to optimize S management strategies. This could potentially be done by developing new modules within existing models, such as APSIM (McCown et al. 1996) or CropSyst (Stöckle et al. 2003). However, more long-term field data on S uptake by crops, ideally in combination with soil analysis at different depths, will be required to validate such models. Furthermore, organic S dynamics and interactions with C and N are not fully understood yet. Without doubt, modelling organic S dynamics under field conditions will be a challenging task. Even for N, which has been studied extensively, improvements are still required (Salo et al. 2016; Smith et al. 2020).

Conclusions

Previous trials with stable isotopes showed that fertilizer S recoveries of S-fortified macronutrient fertilizers differed strongly between sites, crops and S source (ES or SO_4-S). A model taking into account the organic S cycling, leaching of SO_4-S and slow oxidation of ES explained these differences. A sensitivity analysis showed that crop S offtake, the size of the labile organic S pool and the extent of S leaching are the main factors determining long-term recoveries of fertilizer S. While slow oxidation results in initially low recoveries of fertilizer ES, the recoveries eventually approach or exceed those of SO_4-S, as ES continues to supply plant-available S in subsequent years and is less prone to leaching. Our results show that, while stable isotope tracing gives useful information on the fate of fertilizer S, the fertilizer recoveries obtained with this 'direct method' are not the best measure of fertilizer effectiveness, particularly with short-term trials, because unrecovered S may still be available for future crops.

The model presented here provided more insight about the factors determining the fate of fertilizer S

and demonstrated the benefit of a slow-release S source in high rainfall environments. However, further development would be required to use it as a tool for site-specific nutrient management. The dynamics of soil organic S, which is a major contributor to S uptake, are still poorly understood.

Declarations

Conflict of interest The authors declare no conflict of interest. The Mosaic company was only involved in field site selection, but had no editorial input into the content of this article.

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