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Article

Sulfur Uptake from Fertilizer Fortified with Sulfate and Elemental S in Three Contrasting Climatic Zones

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Abstract: Field trials with labeled fertilizers can be used to provide information on fertilizer efficiency, residual value, and nutrient fate. We assessed the uptake from elemental S (ES) and sulfate S (SO_4-S) in S-fortified monoammonium phosphate fertilizers by various crops at three sites in Argentina, Brazil, and Canada. The S sources were labeled with ^{34}S, and the ^{34}S abundance in the plant tissue was analyzed at an early stage and at maturity over two consecutive years. At the sites in Argentina and Canada, the recovery of ES in the crop was smaller than that of SO_4-S in the first year, while the opposite was true in the second year. At the Brazilian site, the recovery of ES was similar to that of SO_4-S in the first year, but higher in the second year. In the Argentina and Canada sites, the cumulative recovery of SO_4-S was >65% and that of ES was 20–25%. In the Brazilian site, the cumulative recovery of SO_4-S was 9% and that of ES 16%. The higher recovery of ES than of SO_4-S in the Brazilian site was attributed to leaching of added SO_4-S and relatively fast oxidation of ES due to the warm climate. These results suggest that ES may be more suitable than SO_4-S as a fertilizer S source in warm humid climates, while inclusion of SO_4-S in the fertilizer is recommended in colder climates as slow oxidation limits the initial availability of ES.

Keywords: fertilizer efficiency; sulfur; stable isotope

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1. Introduction

Sulfur is an essential element for all crops. Sulfur deficiency has become more common, due to decreased atmospheric inputs, increasing yields, and a shift to high-analysis fertilizers with no or little S. As a result, S fertilization has become more important [1]. Commonly used S fertilizer sources contain either SO_4-S (e.g., ammonium sulfate, $(NH_4)_2SO_4$; gypsum, $CaSO_4{\cdot}2H_2O$) or elemental S (ES). Sulfate is readily available to plants, but is vulnerable to leaching because of its weak adsorption in most soils [2]. Several studies have confirmed considerable leaching of fertilizer SO_4-S [3,4], but field data are scarce. Kirchmann et al. [5] carried out mass balance calculations for a long-term field experiment (35 years of continuous crop cultivation) in central Sweden (humid continental climate, precipitation of 660 mm year^{-1}) and estimated that 88% of S added as ammonium sulfate, at a cumulative rate of 3200 kg S ha^{-1}, was leached from the soil. Friesen [6] carried out a field trial in Togo (tropical climate, precipitation of 1500 mm year^{-1}) using ^{35}S-labeled single superphosphate (SSP). Soil sampling indicated that 44% of applied SO_4-S had leached below 90 cm depth by the end of the cropping season.

Elemental S needs to be oxidized to become available to plants. Oxidation of ES is a biological process that is highly temperature-dependent [7] and generally proceeds faster with increasing soil pH and organic matter content [8]. Most studies on ES oxidation have been carried out using ES particles mixed throughout soil. The oxidation rate of these particles increases with decreasing particle size and hence larger specific surface area [7–9]. However, ES in commercial fertilizers is typically applied as sulfur-bentonite pastilles or co-granulated with macronutrients in compound fertilizers (NPK). These co-granulated ES particles oxidize more slowly than the same particles mixed through the soil, due to a decrease in the surface area in contact with soil [10,11].

There are few peer-reviewed field studies assessing the fate of fertilizer S and the plant availability of S-fortified macronutrient fertilizers, despite the commercial importance of these fertilizers [12]. Sawyer et al. [13] conducted three field trials comparing ammonium sulfate to S-fortified P fertilizers (with half of the S as SO_4-S and half as ES). There was no difference in yield or ain plant S concentration between the sulfate fertilizer and the S-fortified fertilizers, but in only one of the trials was there a yield response to the S application. It is difficult to predict S response in the field, since organic S mineralization is an important contributor to the S supply to plants [14]. The extent of organic S mineralization during a growing season depends on many factors and cannot be accurately predicted.

The use of isotopic tracers does not rely on a yield response, but allows direct measurement of the amount of fertilizer that is taken up by the plant [15]. Few studies have used isotopic tracers for assessing the fate of fertilizer S. Goh and Gregg [16] studied the fate of ^{35}S-labeled gypsum ($CaSO_4{\cdot}{}_2H_2O$) in nine pasture sites in New Zealand. They found that 15 to 40% of the applied SO_4-S was converted to organic S within 75 days or less and that >30% of applied S was leached from the topsoil within 2 months of application at five of the nine sites. Friesen [6] compared the contribution of SSP and ES-fortified triple superphosphate (TSP) in a field trial in Togo using ^{35}S-labeled fertilizers, concluding that the ES-fortified TSP was equally effective as SSP in the first year, but had greater residual effectiveness due to less leaching. Sanborn et al. [17] used S fertilizers at natural abundance levels but with distinct signatures from regional background S isotope ratios to estimate the contribution of these fertilizers to S uptake by pine (*Pinus contorta*) from isotope analysis of the leaves. They found that, on average, 41 to 55% of S in the leaves was derived from fertilizer K_2SO_4 compared to 11 to 21% for surface-applied ES pellets. This approach, based on natural abundance, can only be used if there is a substantial difference in sulfur isotopic ratios between fertilizer S and soil S. Furthermore, isotope fractionation during transformations by soil and plant uptake processes may result in underestimates of the fertilizer recovery, as has been found to be the case for ^{15}N [18]. Degryse et al. [19] used an enriched stable isotope (^{34}S) tracing technique to compare fall and spring application of an S-fortified monoammonium phosphate (MAP with 5% ES and 5% SO_4-S) fertilizer in a field trial in Champaign (IL, USA) over two seasons. Timing of application strongly affected the contribution of fertilizer SO_4-S to plant uptake (12% when spring-applied vs. 5% when fall-applied in the first year), but had little effect on the contribution of fertilizer ES (12−14%).

As recently pointed out in a review paper on the use of ^{34}S in agroecosystems, there have been few studies using labeled SO_4-S or ES fertilizers in the field, and hence little information on the efficiency, residual value, or leaching risk of these fertilizers [20]. Climatic conditions are expected to have a large effect on the fate of SO_4-S and ES fertilizers, as the oxidation of ES is highly temperature-dependent and the leaching of SO_4-S depends on the precipitation excess. In this study, we used stable isotope tracing to compare the contribution of SO_4-S and ES in S-fortified MAP fertilizers to crop uptake in three sites with vastly different climates. The aim of the study was to determine the direct contribution and residual value of SO_4-S and ES to crop uptake under different climatic conditions.

2. Materials and Methods

2.1. Trial Overview

Three field trials, in Argentina, Brazil, and Canada, were conducted over 2 years to assess how much S in the plant was derived from S-fortified MAP fertilizer. Table 1 gives an overview of the locations, climate, and soil properties, and Table 2 summarizes the fertilizer rates, crops, and sowing and harvest dates. The fertilizers used were MicroEssentials (MES; The Mosaic Company, Tampa FL), which consist of MAP co-granulated with ammonium sulfate and ES. The fertilizers varied in their ES and SO_4-S content, depending on which is the most common MES fertilizer for each location (Table 1). The labeled fertilizers were made in the laboratory as described below.

Table 1. Overview of location, climate, and soil properties of the three sites.

	Argentina	**Brazil**	**Canada**
Location	Lujan, Buenos Aires	Itiquira, Mato Grosso	Indian Head, Saskatchewan
Coordinates	34°46″ S, 59°37″ W	17°09″ S, 54°45″ W	50°32″ N, 103°40″ W
Climate [1]	Humid subtropical	Tropical	Humid continental
Soil [2]	Typic Argiudoll	Typic Hapludox	Udic Boroll
pH (water)	6.4	5.8	8.1
SO_4-S (mg kg^{-1}) [3]	4.2	5.8	4.0
Organic C (%) [4]	1.4	2.0	2.5
CEC ($cmol_c$ kg^{-1}) [5]	19	10	13
CaCO3 (%) [6]	0	0	1.7
Clay (%) [7]	20.0	65.8	46.9
Texture	Silt loam	Clay	Clay

[1] Climate classification according to Köppen et al. [21]; [2] USDA-NRCS [22]; [3] extraction with 0.01 mol L^{-1} Ca(H2PO4) 2 [23]; [4] dry combustion method [24]; [5] cation exchange capacity determined through extraction with 1 mol $L–^{1}$ NH_4OAc [25]; [6] pressure calcimeter method [26]; [7] pipette method [27].

Table 2. Overview of fertilizer type, S rate, and sowing date of the different crops.

Site	**Fertilizer [1] (%SO_4-S/%ES)**	**S Rate (kg ha^{-1})**	**Crop**	**Sowing Date**
Argentina	MES10 (5/5)	20	Corn	11 November 2011
			Soybean	20 November 2012
Brazil	MES9 (2/7)	28	Soybean	2 December 2011
			Corn	23 March 2012
			Soybean	27 November 2012
			Corn	5 March 2013
Canada	MES15 (7.5/7.5)	32	Canola	6 June 2012
			Wheat	1 June 2013

[1] The fertilizers are MicroEssentials fertilizers, which are monoammonium phosphate-based fertilizers fortified with ammonium sulfate and elemental sulfur (percentage of SO_4-S and ES indicated in brackets after the fertilizer name).

Two types of labeled plots were included in each field trial. In four plots, the SO_4-S was enriched with a stable isotope (^{34}S), and in four other plots, the ES was enriched with ^{34}S. The fertilizers were applied as broadcast application (by hand) at the start of the first growing season. Plants were collected at two growth stages (at an early stage and at maturity); all aboveground material biomass was removed. The ^{34}S atom % in the plant was determined to quantify the contribution of fertilizer SO_4-S and ES to S uptake (Figure 1). The uptake of S by crops from the labeled fertilizer was also determined in the second year after application in the same plots to assess the residual value of the fertilizer. No attempt was made to measure ^{34}S atom % in the soil, since it was unlikely this would have resulted in useful data given the low rate of S applied compared to background soil S and the inherent heterogeneity of granular fertilizer applications.

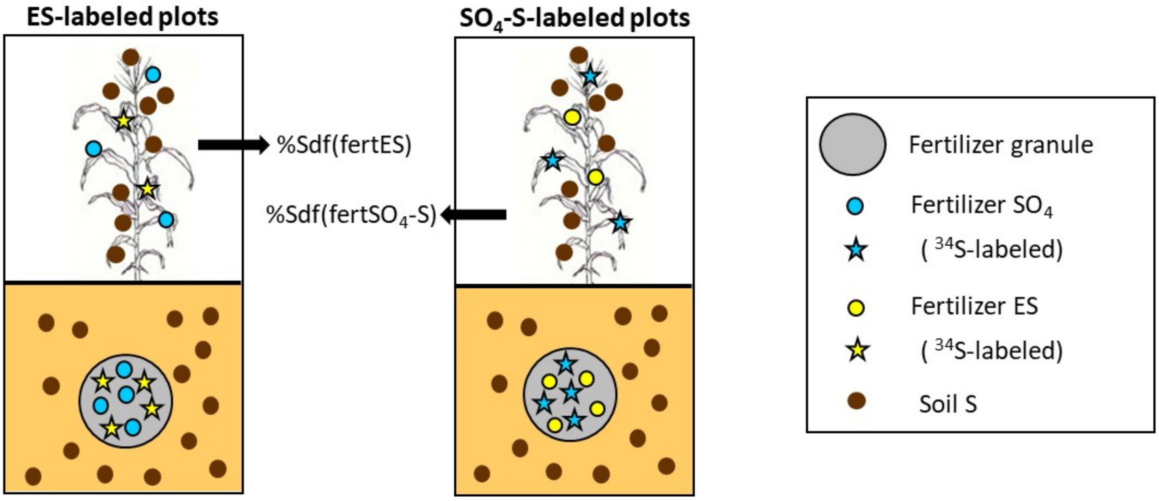

Figure 1. Method principle: the plots were fertilized with S-fortified monoammonium phosphate (MAP) fertilizers. In four plots, the elemental S (ES) in the fertilizer was labeled with ^{34}S and in four other plots, the SO_4-S was labeled with ^{34}S. The percentage of plant S derived from fertilizer ES (%Sdf(fertES)) or from fertilizer sulfate (%Sdf(fertSO_4-S)) was calculated from the ^{34}S atom % excess in the plants on the ES-labeled and SO_4-S-labeled plots, respectively (modified from [19]).

The labeled plots were grouped together to avoid inter-plot interference. Both blocks of labeled plots (ES- and SO_4-S-labeled) were bordered by two plots with unlabeled MES fertilizer and a control plot with MAP fertilizer on each side. The plots were small, as described in detail below, and all three experimental sites were uniform, without any slope or change in soil type. ANOVA analysis indicated that there was no effect of block (labeled ES vs. SO_4-S) on yield or plant tissue concentrations (B, Ca, Cu, Fe, K, Mg, Mn, P, S, Zn), confirming site homogeneity and justifying the grouping of plots per treatment. A *t*-test analysis indicated no significant difference in the plant ^{34}S abundance between the two center and the two outer plots of each block, indicating that the microplots were sufficiently large to avoid interference from the neighboring plots.

2.2. *Fertilizer Labeling*

The labeled fertilizer granules were produced from powdered fertilizer-grade MAP, ammonium sulfate ($(NH_4)_2SO_4$) and ES (Sigma-Aldrich) in ratios to obtain the same composition as commercial MES9 (2% SO_4-S, 7% ES), MES10 (5% SO_4-S, 5% ES), or MES15 (7.5% SO_4-S, 7.5% ES). The S in $(NH_4)_2SO_4$ or ES was enriched with ^{34}S (20%) using $(NH_4)_4\ {}^{34}SO_4$ (converted from $Na_2\ {}^{34}SO_4$, Novachem Pty Ltd.) or elemental ^{34}S (Novachem Pty Ltd.), respectively. Care was taken to ensure the ES had the same particle size distribution as in the commercial products (median diameter around 40 μm). The powder mixture was granulated in a laboratory drum and the granules were screened between 2.00 and 3.35 mm, similar to commercial fertilizer granules. More detail about the fertilizer manufacturing process can be found elsewhere [19].

2.3. *Field Trials*

2.3.1. Argentina

The site was located in Lujan, Buenos Aires (Table 1). The average annual precipitation is 1000 mm. Weather data for the experimental period are shown in Figure 2A. The plots were 1 × 0.76 m in size. The MES10 fertilizer was added at a rate of 15.24 g plot^{-1}, corresponding to 20 kg S ha^{-1}, at the time of sowing of the first crop. The MAP fertilizer in the four control plots was added at 11.69 g plot^{-1} (35 kg P ha^{-1}) to supply the same amount of P as the MES10 fertilizer. Additional urea was added in both years as required.

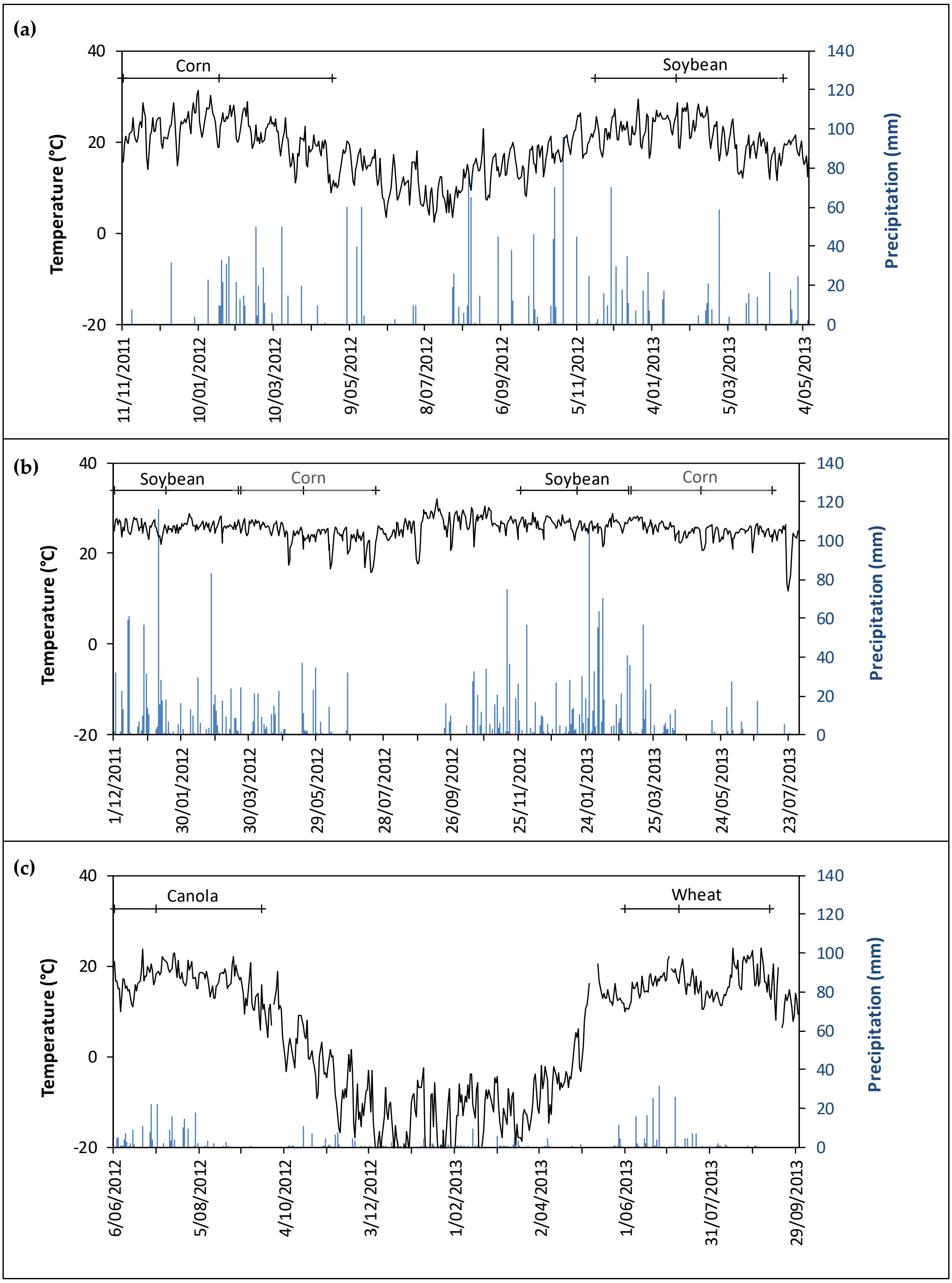

Figure 2. Daily average temperature (black) and precipitation (blue) from the start of the experimental period for the sites in (**a**) Argentina (source: on-site rain gauge, read daily by the farmer), (**b**) Brazil (source: Fundação de Apoio à Pesquisa Agropecuária de Mato Grosso—nearby weather station), and (**c**) Canada (source: http://climate.weather.gc.ca/---nearby weather station). The horizontal lines at the top of the graph indicate the periods of crop growth (with sowing, early-stage harvest, and maturity harvest marked by a vertical dash).

The plants were grown in a single row per plot (row width of 0.76 m). Corn (*Zea mays* L., Agriseed 9009 MG Simple Hybrid.) was grown the first year, using 7 plants plot^{-1} (92,000 plants ha^{-1}), with 3 plants harvested at tasseling (VT) and 2 plants at maturity (R6) [28]. The plants at the edge of the plot were not included in the analyses. Soybean (*Glycine max,* NA 5009 RG, maturity group V) was grown in the second year, using 20 plants plot^{-1} (263,000 plants ha^{-1}), with 8 plants harvested at R1 stage and 8 plants harvested at the R7 stage [29].

2.3.2. Brazil

The experiment was conducted in Itiquira, Mato Grosso (Table 1). The average annual precipitation is 1560 mm, with most rainfall from October to April. Weather data for the experimental period are shown in Figure 2B. The plots were 1 × 0.76 m size. The MES9 fertilizer was added at a rate of 23.7 g plot^{-1} (21 kg S ha^{-1}). The MAP fertilizer in the control plots was added at 21.6 g plot^{-1} (64 kg P ha^{-1}) to supply the same amount of P as the MES9 fertilizer. Additional MAP (150 kg ha^{-1}) and urea (120 kg ha^{-1}) were added to all plots at the start of the corn growth in both years.

The local practice of “double cropping” was followed [30]. In both years, a soybean/corn rotation was grown in the same single-row plots (0.76 m row width). Soybean (TMG 115 RR, maturity group 8.6) was planted in November (16 plants plot^{-1} or 210,000 plants ha^{-1}), with 8 plants harvested at the R1/R2 stage and 8 plants at maturity (R7) [29]. Corn (Penta TL) was planted in March immediately after the soybean harvest, at 6 plants plot^{-1} (79,000 plants ha^{-1}), with 3 plants harvested at tasseling (VT) and 3 plants harvested at maturity (R6) [28].

2.3.3. Canada

The experiment was conducted in Indian Head, Saskatchewan (Table 1). The average annual precipitation is 428 mm, with more precipitation in summer than in winter. Weather data for the experimental period are shown in Figure 2C. The plots were 1 × 0.61 m size. The MES15 fertilizer was added at a rate of 13 g plot^{-1} (32 kg S ha^{-1}). The MAP fertilizer in the control plots was added at 8.25 g plot^{-1} to supply the same amount of P as the MES15 fertilizer (31 kg P ha^{-1}). Urea was side-banded at planting to supply a total of 125 kg N ha^{-1}. Additional P (13 kg ha^{-1}) and N (110 kg ha^{-1}) was added in the second year at seeding as MAP and side-banded urea.

Canola (*Brassica napus* L., InVigor 5440) was planted in the first year using a no-till drill at a plant density of ca. 60 plants m^{-2} with a row width of 23 cm. Aboveground biomass was sampled from two 0.4-m sections of crop row at GS 50 stage [31] and at maturity, with grain separated from the biomass. Wheat (*Triticum aestivum* L., Unity) was seeded in the second year in two rows per plot at a density of 8.2 g plot^{-1} (134 kg ha^{-1}). Aboveground biomass was sampled from two 0.4-m sections of crop row at Feekes 9–10 (early boot) growth stage [32] and at maturity with grain separated from the straw after drying.

2.4. Plant Analysis

The plant material was dried at 60° C (Argentina, Brazil) or 35° C (Canada). Dry matter weight was recorded. Dried samples from each plot were bulked and mixed thoroughly. The samples were analyzed for total composition and ^{34}S abundance as described previously [19], with ^{34}S analysis carried out by Isolytix Ltd. using elemental analysis–isotope ratio mass spectrometry (EA-IRMS). Reference samples (IA R061, BaSO4, and NBS-1577Bbovine liver) were included with each run, as well as a gravimetrically prepared ^{34}S-enriched $(NH_4)_2SO_4$ sample.

The percentage of plant S derived from fertilizer SO_4-S or fertilizer ES was calculated from the ^{34}S atom % excess in the plant relative to that in the respective S source:

$$\%\text{Sdff}\ (\text{SO}_4-\text{S}) = \frac{^{34}\text{S atom\% excess in plant}}{^{34}\text{S atom\% excess of fertilizer SO}_4-\text{S}} \times 100, \tag{1}$$

$$\%\text{Sdff}(\text{ES}) = \frac{^{34}\text{S atom\% excess in plant}}{^{34}\text{S atom\% excess of fertilizer ES}} \times 100 \tag{2}$$

The recovery of fertilizer SO_4-S or ES by the crop was calculated as the amount of fertilizer-derived SO_4-S or ES taken up by the plant (i.e., total S uptake multiplied by %Sdff(SO_4-S or ES)/100) divided by the amount of fertilizer SO_4-S or ES applied to the soil. The cumulative recovery was calculated by summing the recovery at the relevant sampling time and the recoveries at maturity in the preceding crops.

2.5. Statistical Aanalysis

Statistical analysis was carried out with IBM SPSS (Version 25). An independent-samples *t*-test was used to compare the yield between the MAP ($n = 4$) and the labeled MES ($n = 8$) treatments and to compare the recovery of fertilizer SO_4-S ($n = 4$) and ES ($n = 4$) at each harvest.

3. Results

3.1. Crop Yield, S Concentrations in Plant Tissue, and Total S Uptake

At the Argentinian site, visual differences in corn growth between the MAP and MES10 treatments were apparent early in the season, as was also reflected in the lower biomass yield for the MAP treatment at the early harvest (Table 3). The S tissue concentrations in the corn at early stage (R1) were indeed low (1.2 g kg^{-1} in the MAP treatment). Optimal concentrations in the whole shoot at early stage have been reported to be 1.5–1.9 g kg^{-1} [33]. By the maturity harvest, there was no longer a significant difference in total biomass or grain yield between the MAP and MES10 treatments. The lack of deficiency later in the season may be related to mineralization of organic S and/or root proliferation resulting in increased access to labile S. Soybean grown in the second year showed no significant differences in biomass yield between the MAP and MES10 treatments at either stage. The S concentrations in soybean grain were 2.8 g kg^{-1}, above the reported critical level of around 2.3 g kg^{-1} for the grain at maturity [34].

At the Brazilian site, there was no difference in biomass yield between the MAP and MES9 treatments. Additionally, the S concentrations or S uptake were not significantly different between the MAP and MES9 treatment (Table 3). The S concentrations in corn at early harvest were very low, which may be related to depletion of soil S levels during the preceding soybean crop and/or fast growth rate resulting in nutrient dilution.

Table 3. Dry matter yield, S concentration, and total S uptake by the aboveground biomass sampled at an early stage or at maturity. Where determined separately, results for stover and grain are shown in brackets (stover/grain).

			Dry Matter Yield (Mg ha^{-1})			S in Plant (g kg^{-1})			S Uptake (kg ha^{-1})		
Site	**Crop**	**Stage**	**MAP**	**MES**	**Sign.[1]**	**MAP**	**MES**	**Sign.[1]**	**MAP**	**MES**	**Sign.[1]**
Argentina	Corn	Early	9.2	10.0	*	1.20	1.43	*	11.1	14.2	***
		Maturity	37.0 (22.9/14.1)	40.2 (26.5/13.8)	ns	1.30	1.33	ns	47.6	51.5	ns
	Soybean	Early	4.8	4.6	ns	1.54	1.69	ns	7.2	7.7	ns
		Maturity	9.4 (5.8/3.6)	7.7 (4.9/2.8)	ns	1.44 (0.63/2.78)	1.53 (0.80/2.80)	ns	13.5 (3.6/9.9)	11.9 (4.0/7.9)	ns
Brazil	Soybean	Early	1.6	1.9	ns	2.32	2.23	ns	3.8	4.1	ns
		Maturity	12.7	12.4	ns	1.47	1.57	ns	18.8	19.6	ns
	Corn	Early	5.5	4.9	ns	0.53	0.53	ns	2.9	2.6	ns
		Maturity	15.2	17.2	ns	1.35	1.34	ns	19.4	22.1	ns
	Soybean	Early	0.75	0.77	ns	1.95	1.96	ns	1.4	1.5	ns
		Maturity	6.6	6.9	ns	1.96	1.90	ns	13.1	13.0	ns
	Corn	Early	3.5	3.1	ns	0.94	1.08	ns	3.3	3.4	ns
		Maturity	12.0	12.8	ns	1.10	1.06	ns	12.9	13.4	ns
Canada	Canola	Early	1.1	1.4	*	3.36	8.37	***	3.6	11.8	***
		Maturity	11.7 (7.4/4.3)	12.5 (7.9/4.6)	ns	5.00 (5.88/3.48)	5.64 (6.33/3.55)	ns	58.2 (42.6/15.1)	68.5 (52.7/16.2)	ns
	Wheat	Early	2.2	2.3	ns	2.37	2.65	*	5.2	6.1	*
		Maturity	20.1 (14.5/5.6)	19.9 (14.4/5.5)	ns	1.03 (0.75/1.78)	1.08 (0.85/1.67)	ns	20.8 (10.9/9.9)	21.4 (12.2/9.1)	ns

[1] Statistical significance of difference between MAP and MicroEssentials (MES): * $p < 0.05$, *** $p < 0.001$; ns: not significant.

At the Canadian site, the biomass yield was significantly greater for the MES15 treatment than for the MAP treatment in the canola crop at the early growth stage. However, no significant differences in total biomass or grain yield were observed at maturity. The tissue S concentrations in canola were indeed below reported critical levels at early growth stages (around 3.5 g kg^{-1}) for the MAP treatment, while they were above the reported critical level in mature grain (3.3 g kg^{-1}) [33]. Wheat grown in the second year showed no significant differences in biomass yield between the MAP and MES15 treatments at either stage. The tissue S concentrations in wheat were significantly greater for the MES15 than the MAP treatment at the early growth stage, while there was no significant difference at maturity. At both stages, the concentrations were above reported critical levels (1.5 g kg^{-1} at early stage and 1.2 g kg^{-1} in grain) [33].

The total S uptake in aboveground material at maturity depended on the location, crop, and growing season, and ranged from around 13 kg ha^{-1} (for soybean in Argentina, and soybean and corn in Brazil in the second year) to 69 kg ha^{-1} for the canola crop (Table 3).

3.2. Fertilizer S Uptake and Recovery

Figure 3 shows the percentage of plant S that was derived from fertilizer ES or SO_4-S. The trends over time were similar for the Argentina and Canada sites. In the first year, the contribution of SO_4-S to the plant uptake was much greater than that of ES. At maturity, about 15% of S in the plant was derived from fertilizer SO_4-S, compared to only about 2% from ES. In the second year, however, the contribution of ES increased while the contribution of SO_4-S decreased, and the contribution of ES exceeded that of SO_4-S. The cumulative recovery in the harvested material at the end of the second year was 66−86% for SO_4-S compared to 19−25% for ES (Table 4).

For the Brazilian site, the contribution of SO_4-S to the plant uptake decreased from 1.4% at maturity in the first crop to 0.6–0.7% in the second crop and stayed constant thereafter (Figure 3). The contribution of ES was greater than that of SO_4-S at all sampling occasions. In the first year, around 4% of plant S was derived from fertilizer S in the mature corn and soybean crops, compared to 6−7% in the second year. In both years, a greater contribution of fertilizer ES (12–13%) was observed for the soybean at early stage. The greater contribution of ES than of SO_4-S can be partially attributed to the higher ES content of the MES9 fertilizer (7% ES and 2% SO_4-S). However, the fertilizer recoveries, which take into account these different application rates, were also greater for ES than for SO_4-S in the second year, indicating that other factors played a role (Table 4). The cumulative recovery of fertilizer-applied S in the harvested material at the end of the second year was 9% for SO_4-S compared to 16% for ES.

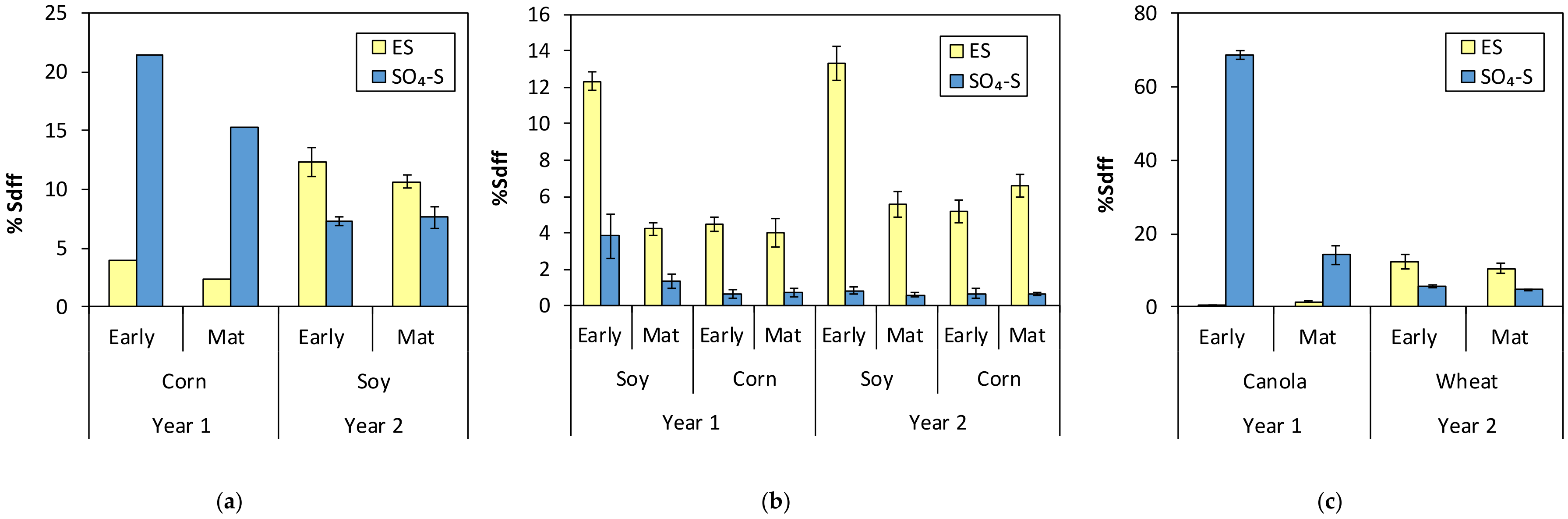

Figure 3. Percentage of S in the plant derived from fertilizer SO_4-S or ES at the different harvests for the sites in (**a**) Argentina, (**b**) Brazil, and (**c**) Canada. Error bars are standard errors of four replicates. (No error bars for Argentina—year 1 because replicates were pooled prior to analysis).

Table 4. The percentage of fertilizer ES or SO_4-S recovered in the aboveground plant material at each stage (in the given crop or cumulatively over the consecutive crops). Values in parentheses are standard errors of the mean (four replicates).

			S Recovery (%)			**Cumulative S Recovery (%)**		
Site	**Crop**	**Stage**	**SO_4-S**	**ES**	**Sign.[2]**	**SO_4-S**	**ES**	**Sign.[2]**
Argentina	Corn [1]	Early	30.4	4.4		30.4	4.4	
		Maturity	77.6	12.3		77.6	12.3	
	Soybean	Early	5.7 (1.2)	9.6 (2.4)	ns	83.3	21.9	
		Maturity	8.1 (1.0)	13.4 (0.7)	**	85.7	25.7	
Brazil	Soybean	Early	2.9 (1.0)	2.3 (0.2)	ns	2.9 (1.0)	2.3 (0.2)	ns
		Maturity	4.3 (0.9)	4.2 (0.7)	ns	4.3 (0.9)	4.2 (0.7)	ns
	Corn	Early	0.2 (0.1)	0.6 (0.1)	*	4.5 (0.9)	4.8 (0.7)	ns
		Maturity	2.5 (0.9)	4.0 (0.9)	ns	6.8 (1.3)	8.3 (1.1)	ns
	Soybean	Early	0.2 (0.0)	1.1 (0.1)	***	7.0 (1.3)	9.4 (1.1)	ns
		Maturity	1.2 (0.2)	3.5 (0.4)	**	8.0 (1.3)	11.8 (1.2)	ns
	Corn	Early	0.3 (0.1)	1.0 (0.2)	*	8.3 (1.3)	12.8 (1.2)	*
		Maturity	1.3 (0.4)	4.2 (0.2)	***	9.3 (1.3)	15.9 (1.2)	*
Canada	Canola	Early	50.7 (0.8)	0.2 (0.1)	***	50.7 (0.8)	0.2 (0.1)	***
		Maturity	59.1 (2.2)	5.8 (0.9)	***	59.1 (2.2)	5.8 (0.9)	***
	Wheat	Early	2.1 (0.2)	4.5 (0.6)	**	61.2 (2.2)	10.3 (1.0)	***
		Maturity	6.5 (0.5)	13.4 (2.6)	*	65.7 (2.3)	19.2 (2.7)	***

[1] The plant material was accidentally pooled per treatment before analysis, and hence no true replicate measurements could be carried out (only analytical replicates, for which the standard errors were very small). [2] Statistical significance of difference between fertilizer SO_4-S and ES: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$; ns: not significant.

4. Discussion

The percentage of S in the plant derived from fertilizer S and the fertilizer recoveries varied greatly between sites, crops/seasons, and S source. For the Argentina and Canada sites, recoveries of SO_4-S were considerably greater than those of ES in the first season and slightly less in the second season. For the Brazilian sites, recoveries of ES were similar to those of SO_4-S in the first year and higher in the second year (Table 4). By the end of the second season, cumulative recoveries of added S were > 65% for SO_4-S and around 20–25% for ES in the Argentina and Canada sites. In contrast, the cumulative recovery of added S for the Brazil site was less for SO_4-S (9%) than for ES (16%).

The main processes driving the fate of added SO_4-S are organic S cycling, leaching, and crop uptake [19]. In all three sites, the percentage of plant S derived from fertilizer SO_4-S strongly decreased in the first year but showed little change in the second year (Figure 3). This decrease can be explained by dilution of added SO_4-S into the labile soil S pool [35]. The labile soil S pool includes both the indigenous soil SO_4-S, in which the dilution is immediate, and the labile organic sulfur pool. The cycling of organic S is a slow process, explaining the decrease in %S derived from fertilizer SO_4-S, until a near steady-state is reached. Similar observations have been made for N, with average recoveries of ^{15}N-labeled fertilizers decreasing from around 40% in the year of application to around 1% in the third year after application [36].

The SO_4-S recovery in the year of application was much smaller for the Brazil site (5%) than for the Argentina and the Canada sites (> 50%). Faster immobilization of added SO_4-S into the soil organic pool may partly explain this difference, however, leaching of SO_4-S likely also contributed to the lower recovery for the Brazilian site. Leaching losses of fertilizer-applied SO_4-S are most likely to occur with fall-applied fertilizer or when there is intense rainfall in the first months after application [16]. Over winter or early in the season, there is little water use by the crop and hence most water percolates through the soil profile. Nearly 600 mm of rain fell at the Brazilian site in the first 2 months after fertilizer application (Figure 2). Simulations with the software package Hydrus-1D [37] indicated that high leaching losses (> 50%) may occur under these conditions (details not shown). Several other studies have indicated that leaching may result in considerable loss of fertilizer SO_4-S, especially when fall-applied, but also when spring-applied if there is high rainfall shortly after application [16,19,38].

In contrast with SO_4-S, the percentage of plant S derived from ES and ES recoveries were smaller (Argentina and Canada) or similar (Brazil) in the first year compared to the second year. Elemental S is hydrophobic and does not leach, but only becomes available to plants upon oxidation to SO_4-S. Most oxidation is expected to occur during the growing season 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 conditions (warm temperature and adequate soil moisture). The use of ES can therefore greatly reduce leaching losses in high rainfall environments [3,4,39] and hence result in a higher supply of plant-available S later in the season when the demand is high for many crops. For instance, it has been found that more than half of the S uptake by modern corn hybrids occur after flowering (VT/R1) [40]. However, this slow oxidation may result in initial low availability of plant-available S. The rate of oxidation depends on climatic conditions (mainly temperature) and on soil and fertilizer properties. Given the higher temperature at the Brazilian site than at the Canadian site, it is likely that oxidation was considerably faster at the Brazilian site.

The ES oxidation rate was not determined in this study, but an estimate was made on the basis of literature data. Reported surface-based oxidation rates at 25° C generally range from around 20–75 μg S cm^{-2} d^{-1}. For instance, ES oxidation rates at 25° C ranged from 18 to 52 μg S cm^{-2} d^{-1} in 10 Australian cropping soils (excluding an acid sandy soil) [8]; from 48 to 76 μg S cm^{-2} d^{-1} in 5 New Zealand soil groups [41]; and from 40 to 52 μg S cm^{-2} d^{-1} in 3 soils from Canada, the USA, and Brazil [11]. Co-granulated ES oxidizes more slowly than ES particles of the same size mixed through soil, due to a reduction in the effective surface area. The "effective diameter" of MES fertilizers is around 200 μm, i.e., the ES in MES fertilizers oxidizes at the same rate as ES particles with a diameter of 200 μm mixed throughout the soil [42]. The average temperature in the first cropping season was 17 °C for the

Canadian site and 26 °C for the Brazilian site (Figure 2). Using the cubic equation of Watkinson and Blair [43] and a temperature coefficient (Q10 value) of 3.7 [19], we predicted 24% of ES in MES to be oxidized after 100 days at 17 °C compared to 65% at 26 °C, assuming a mid-range ES oxidation rate of 50 $\mu g\ cm^{-2}\ d^{-1}$. This calculation illustrates the high temperature dependence of ES oxidation and indicates that a large fraction of the ES would likely have been oxidized during the first crop at the Brazilian site, while only a minor fraction was likely oxidized in the first year at the Canadian site.

The slow oxidation of ES explains why the %S derived from fertilizer ES was smaller in the first year than in the second year for the Argentinian and Canadian sites. This difference was much less pronounced for the Brazilian site, where oxidation was likely faster. A total of 4% of S was derived from ES in the soybean and corn crops at maturity in the first year, compared to ca. 6% in the second year. Interestingly, considerably more S was derived from ES for the early stage soybean crop (≈13%). We hypothesize this was 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 high mobility of added SO_4-S and the high rainfall shortly after application, resulting in a more homogeneous distribution of SO_4-S throughout the soil profile. This hypothesis is supported by the soil profile data for SSP and ES-fortified TSP in a high-rainfall environment, which showed a strong enrichment of ES-derived S in the top layer (<15 cm) compared to a more even distribution for the SO_4-S in the SSP treatment [6].

The term "fertilizer recovery" has been used in various ways, depending on the method of determination. Different methods yield different results, as has been discussed in detail for N fertilizers [44,45]. Using isotopic tracers allows for the determination of exactly how much of the labeled fertilizer is taken up by the crop. However, the labeled fertilizer N is partly replaced by unlabeled soil N because of organic N turnover, a process referred to as pool substitution. As a result, the fertilizer recovery determined with isotopic tracers is usually less than estimated from the difference in uptake between fertilized plots vs. control plots [46]. While less explored, the same concepts hold for fertilizer S. Various processes contribute to incomplete recovery of the isotope, and they have different implications for the long-term fate of the added S. Leaching is a true loss mechanism, but S immobilized in organic matter and unoxidized ES are both potentially available for crop uptake in later seasons. Long-term field trials over consecutive years allow assessments to be made of the residual value of the fertilizer and hence give a more realistic picture of the true effectiveness of the fertilizer compared to single-season studies [47]. Since all ES oxidizes to SO_4-S with time, it is to be expected that the cumulative recovery of ES would eventually approach that of SO_4-S if there is little SO_4-S leaching. When there is a risk of leaching, e.g., in high-rainfall regions and/or with fall applications, ES sources may become more effective over time than SO_4-S sources, as they are less affected by leaching. This was observed for the Brazilian site, for which the cumulative recovery of ES was greater than that of SO_4-S in the second year. Similar observations were made in high-rainfall environments in West Africa, where ES-fortified TSP was generally as effective as SO_4-S sources in the first cropping season, but had a greater residual effect due to less leaching [6].

5. Conclusions

The cumulative recoveries of fertilizer S in harvested plant material varied strongly depending on S source, soil, and climatic conditions. Low contribution of fertilizer S to crop uptake was likely caused by dilution of S in the labile S pool, leaching shortly after application (for SO_4-S) and slow oxidation (for ES). At the sites in Argentina and Canada, the recovery of SO_4-S in the crop was greater than that of ES in the first year after application, while the opposite was true in the second year. At the Brazilian site, the recovery of ES was similar to that of SO_4-S in the first year and greater in the second year. The higher recovery of ES than that of SO_4-S for the Brazilian site was likely due to relatively fast oxidation of ES and leaching of added SO_4-S. Thus, the use of ES rather than SO_4-S as S source may result in less fertilizer S loss in high-rainfall environments. However, if there is severe S deficiency, ES oxidation may be too slow to supply sufficient S in the first season after application, particularly for early growth in colder climates. Depending on climatic conditions and fertilization history, ES or SO_4-S may be preferable as the fertilizer S source. Alternatively, a fertilizer containing both forms of S can be used to reduce leaching risks but still provide immediately plant-available S.

Sulfur deficiency has become more common in recent decades and may become even more prevalent in the future. To achieve optimal yields, S inputs should match the plant's needs as well as any losses. Nitrogen management tools have been developed that simultaneously consider turnover into the organic pool, crop uptake, weather conditions, and agronomic practices in order to improve site-specific fertilizer recommendations. Such tools would also be of great use for S, but more research needs to be carried out on the dynamics of S utilization in long-term field trials in order to develop and calibrate such models.

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