

# Long-Term Sulfur Fertilization: Effects on Crops and Residual Effects in a No-Till System of Argentinean Pampas

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*A long-term experiment has been conducted between 2001 and 2008 at Balcarce, Argentina, to determine the effect of sulfur (S) fertilization on S concentration in grains, crop yield, and residual in soil. Two treatments were evaluated: annual S application to crops (15 kg ha<sup>-1</sup>; S1) and a control with no S fertilization (S0). Sulfur fertilization only increased wheat yield (22% of the crops in the experiment). However, S application increased S concentration in grains in wheat, soybean, and maize (56% of the crops). Although, for all years, the S mass balance was positive for S1 and negative for S0, no differences in soil S extracted as sulfate (S-SO<sub>4</sub><sup>-2</sup>) content previous to the crop sown were determined. The absence of differences in S accumulation in aboveground vegetative biomass and grain of the maize used as a check also suggest that long-term S fertilization did not affect the soil S availability for crops.*

**Keywords** Long-term fertilization, no-tillage, residual, S sulfur

## Introduction

In developed countries, sulfur (S) deficiency has become widespread during recent years, mainly because of the reduction in the S concentration of industrial gases emissions and changes in the composition of commercial fertilizers toward lower S contents (Scherer 2001). In countries with low industrial activity, like Argentina, crop S deficiency has emerged, but the causes are different. Particularly in the southeastern Buenos Aires Province, some fields have been characterized as S deficient as a result of (i) soil organic matter (SOM) depletion due to the intensive tillage during the past decades (Studdert and Echeverría 2000), (ii) the current adoption of no-tillage (NT) systems that reduce S mineralization (Lupwayi et al. 2004), and (iii) the increase in crop requirement derived from their enhanced yield potential. For these conditions Reussi Calvo, Echeverría, and Sainz Rozas (2008) reported up to 37% of yield increases in response to S fertilization in wheat (*Triticum aestivum* L.) and Pagani et al. (2009) determined up to 11% more grain production in maize (*Zea mays* L.). As a consequence, farmers adopted S fertilization,

Received 5 September 2011; accepted 14 December 2011.

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commonly in annual applications of gypsum [ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 18.5% S and 20% calcium (Ca)] at sowing. The applied rates are empirical (between 10 and 20 kg S  $\text{ha}^{-1}$ ) because of the lack of reliable methodology to quantify plant-available S in soils (Echeverría 2006). This practice has been successful to ensure adequate S provision to crops but does not consider long-term implications for the soil.

One aspect to be considered to improve fertilization strategies is that S application can have residual effects. Residual S can occur mainly in two different ways: as sulfate ( $\text{SO}_4^{-2}$ ) adsorption by the soil and by the immobilization of S in organic forms. Adsorption is relevant in evolved soils, with low pH and positive net charge, and it takes place especially in subsoil layers (Robarge and Johnson 1992). In contrast, soils from temperate regions have net negative charge (Brady and Weil 2008) and  $\text{SO}_4^{-2}$  adsorption is not considered an important mechanism. As a consequence, in these soils  $\text{SO}_4^{-2}$  is prone to being leached with percolating rainwater. For this reason, S immobilization by microorganisms is a relevant process of S accumulation in these conditions (Castellano and Dick 1990).

Several field studies were performed in the Argentinean Pampas to evaluate the direct effect of annual S fertilization on crop production (Gutiérrez Boem et al. 2004; Salvagiotti and Miralles 2008; Reussi Calvo, Echeverría, and Sainz Rozas 2008; Pagani et al. 2009). However, there is a lack of information about the long-term effect of S application on crops and the residuality of this nutrient in soil. Therefore, García et al. (2010) observed a greater S extracted as sulfate (S- $\text{SO}_4^{-2}$ ) content at 0 to 60 cm deep in S-fertilized treatments after 5 years of annual gypsum applications in the northern Argentinean Pampas. Along the same line, Echeverría et al. (2011) reported for a wheat/soybean [*Glycine max* (L) Merr.] double crop (commonly used in the area) that 66% of the S applied to wheat as gypsum was recovered as S- $\text{SO}_4^{-2}$  in the 0- to 60-cm soil layer when soybean was sown. This residual S- $\text{SO}_4^{-2}$  may remain soluble in the soil after fertilization, if leaching does not occur, or be immobilized by microorganisms and later mineralized.

Sulfur concentration in grains was proposed as an index to evaluate S status in crops (Hitsuda, Sfredo, and Klepker 2004). Although it is useless to ameliorate the S status in the evaluated crop, it allows determination of deficiency areas to improve fertilization in subsequent crops. In Australia, Randall, Spencer, and Freney (1981) determined field S-deficient zones based on the S concentration and nitrogen (N) / S ratio in wheat grains. Similarly, Reussi Calvo, Echeverría, and Sainz Rozas (2011) observed that total S and N/S in grains could be utilized to diagnostic S deficiencies of wheat in soils of the Argentinean Pampas. In long-term experiments, these indexes could be useful to evaluate the soil S status after continuous fertilizer applications.

Crop S uptake can be used as an indicator of residuality of S inorganic forms and can also be used to measure the increase in soil S availability caused by net mineralization (Eriksen et al. 1995). Eriksen and Mortensen (1999) evaluated soil S status of long-term experiments using oilseed rape (*Brassica napus*, L.) and determined that annual application of inorganic fertilizers caused no differences in the S uptake.

The aims of this study were to evaluate the long-term effect of S fertilization on (i) crop yield and S concentration in grain and (ii) the residual effect as S- $\text{SO}_4^{-2}$  and its consequence in maize S status.

## Materials and Methods

### Soil Characteristics

The study was conducted between 2001 and 2008 in a long-term crop rotation experiment at the Instituto Nacional de Tecnología Agropecuaria (INTA), at Balcarce, Argentina (37°

**Table 1**

Selected soil characteristics for the experimental site at the beginning of the experiment

Depth (cm)	Clay (%)	Silt (%)	Sand (%)	SOC (g kg <sup>-1</sup> )	pH	P Bray (mg kg <sup>-1</sup> )	N-NO <sub>3</sub> <sup>-</sup> (kg ha <sup>-1</sup> )
0 to 20	23	36	41	25.4	5.53	28.7	30.3
20 to 40							12.7
40 to 60							6.8

45' S and 58° 18' W, 138 m above sea level). The soil of the experimental site is a complex of Mar del Plata series (fine, mixed, thermic Typic Argiudoll) and Balcarce series (fine, mixed, thermic Petrocalcic Paleudoll) with less than 2% slope (no erosion). The petrocalcic horizon of the Balcarce series soil is below 0.7 m. Soil selected properties at the beginning of the experiment are shown in Table 1. Prior to the establishment of the experiment, the site had been under agriculture rotation with conventional tillage that included moldboard plowing, disking, and field cultivation with the least tillage operations necessary to get an appropriate seedbed.

### Experiment Design

Two treatments were established: annual S application to crops (15 kg ha<sup>-1</sup>; S1) and a control with no S fertilization (S0). Treatment S1 was defined as the rate commonly used by farmers and was broadcast applied as gypsum prior to sowing. The experimental design was randomized complete blocks with four repetitions. The experimental unit dimensions were 12 × 5 m.

The typical rotation cycle in the southern Buenos Aires Province is maize, soybean, and wheat/soybean double crop. For maize and soybean, the optimal sowing dates are during October and November respectively, and the harvest period starts during April–May for both crops. Wheat is planted in June–July and harvested at the end of December. Double-cropped soybean is sown immediately after wheat harvest and harvested during May. Crop sequence during the first rotation cycle was maize (sown in 2001), soybean (2002), and wheat/soybean double crop (2003); the second cycle was integrated by wheat/soybean double crop (2004), maize (2005), and soybean (2006). In 2007 wheat/soybean double crop was sown, corresponding to the third rotation cycle. Wheat sown in 2007 suffered frost damage at flowering and, given its negligible grain yield, was not harvested.

High potential varieties and hybrids, widely used in the zone were used. The numbers of plants established per m<sup>2</sup> were 8, 25, 300, and 35 for maize, soybean, wheat, and late sown soybean respectively. Crops were sown under the NT system in optimal dates for the zone and were kept free of weeds, pests, and diseases. To avoid deficiencies, soybean and maize were fertilized with 20 kg of phosphorus (P) ha<sup>-1</sup> and the wheat/soybean double crop was fertilized with 30 kg P ha<sup>-1</sup> as triple superphosphate (0–46–0). Wheat and maize were also fertilized with 140 kg of N ha<sup>-1</sup>, although maize in 2005 received 176 kg N ha<sup>-1</sup>. Nitrogen was applied as urea (46–0–0). Soybean was inoculated before sowing with *Bradyrhizobium japonicum*. Phosphorus was applied at sowing, whereas N was applied at Zadoks 22 (Zadoks, Chang, and Konzak 1974) in wheat and V6 (Ritchie and Hanway 1982) in maize. All fertilizers were applied at broadcast, in surface and with full coverage.

### ***Plant Determinations***

At physiological maturity, defined as Zadoks 90 for wheat (Zadoks, Chang, and Konzak 1974), R6 for maize (Ritchie and Hanway 1982), and R8 for soybean (Fehr and Caviness 1977), crops were harvested, collecting material from a surface of 8 m<sup>2</sup> per plot.

In 2008, maize was cultivated without S fertilization to prove residual effects of previous applications. Maize grain yield was determined as described for previous crops. Total aboveground vegetative biomass (AVB) production was calculated as the difference of total aboveground biomass minus grains. It was measured considering 10 plants per plot selected at random. Grain and AVB samples were oven dried at 65 °C until a constant weight was reached and then weighed and ground (1-mm mesh) to determine total N and S.

Plant and grain S content was determined by dry combustion at 1350 °C and S thermoconductivity detection with TruSpec S analyzer (LECO 2011). Grain N concentration was determined by dry combustion at 950 °C and N thermoconductivity detection with a TruSpec CN analyzer (LECO 2011).

Crop evapotranspiration (ET) was determined as the product of potential evapotranspiration (ET<sub>0</sub>) and crop coefficient (K<sub>c</sub>). The ET<sub>0</sub> was calculated according to Penman (1948), and the K<sub>c</sub> (ET/ET<sub>0</sub>) values were those reported for the region by Della Maggiora, Gardiol, and Irigoyen (2000). The water-holding upper and lower limits used for the calculation of relative plant-available soil water (PAW) were those reported for the zone for Travasso and Suero (1994). Actual ET was assumed to be equal to ET<sub>0</sub> when PAW >0.4 and to decline linearly with PAW between 0 and 0.5 (Sadras and Milroy 1996). Water excess was calculated as the water above the water-holding upper limit. Rainfall and ET<sub>0</sub> data was obtained from INTA's weather station, sited 500 m from the experimental site.

### ***Soil Determinations***

Composite soil samples (5 subsamples per plot) were taken at depths of 0 to 20, 20 to 40, and 40 to 60 cm. For the wheat/soybean double crop, soil sampling was realized only when wheat was sown. Samples were dried at 30 °C and ground to pass a 2-mm sieve. Recognizable crop residues and roots retained on the 2-mm sieve were eliminated. Soluble and adsorbed S as sulfate (S-SO<sub>4</sub><sup>-2</sup>) was extracted with Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> (Islam and Bhuiyan 1998) and then determined by turbidimetry through barium chloride (BaCl<sub>2</sub>) and Tween 80 as a stabilizer (Johnson 1987). It was not possible to sample the soil prior to wheat sowing in 2007, so none of the determinations could be performed.

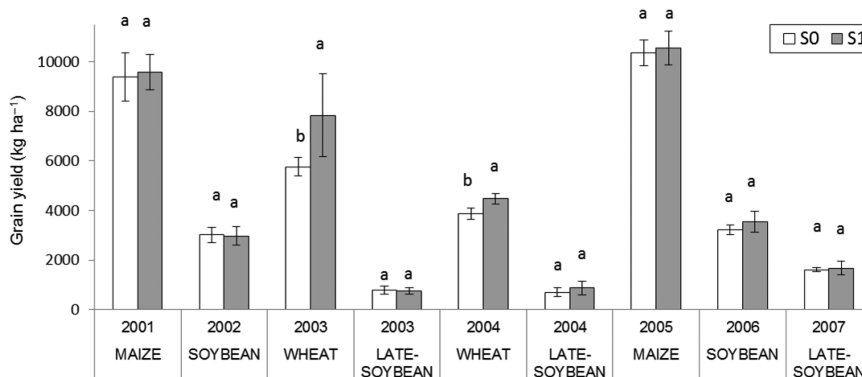
### ***Statistical Analyses***

Treatment effects were evaluated by analysis of variance (ANOVA) using the Statistical Analysis System (SAS Institute 1985), and all the effects were treated as fixed (PROC GLM, Littell, Freund, and Spector 1991). When F statistic for treatments was significant, least significant difference (LSD) at the 0.05 level was calculated.

## **Results and Discussion**

### ***Yield Response to S***

Sulfur fertilization increased wheat yield in 2003 and 2004 (Figure 1) but maize and soybean yield did not differ between treatments (Figure 1). This inconsistency in crop yield



**Figure 1.** Crop yields for unfertilized (S0) and sulphur-fertilized (S1) treatments. Vertical bars for each column indicate standard error of the mean. For each year, the same letters indicate statistically equal values between S rates at  $P < 0.05$  using Fisher's protected LSD.

response to S fertilization agrees with previous observations in the region (Echeverría et al. 2011; Reussi Calvo, Echeverría, and Sainz Rozas 2011). Climatic conditions in the zone could partially explain that yield response to S fertilization occurred in wheat but not in maize and soybean. During wheat growth, temperatures in the region do not promote high soil organic-matter (SOM) mineralization rates (Videla et al. 1996). In contrast, for summer crops (soybean and maize), mineralization increases and consequently the S provision to crops could be sufficient to maximize grain yield.

Field-management history was proposed as a qualitative indicator of the probability of crops to respond to S applications. In northern Argentinean Pampas, Ferraris (2002) determined that soybean response to S fertilization increased as the prior period under continuous agriculture was longer. In the present study, soil was under crop rotation for more than 25 years. In addition, up to the beginning of the experiment, tillage consisted of disking and chisel plowing. For this region Studdert, Echeverría, and Casanovas (1997) determined that conventional tillage caused SOM reductions, particularly the labile fraction that largely contributes to nutrient provision by mineralization (Alvarez and Alvarez 2000). Therefore, although the soil presented high SOM contents (Table 1), the previous management may explain the latent S deficiency.

Sulfate content in soils is an indicator of S availability to crops, although some inconsistencies between this test and crops production were reported (Scherer 2001). Jones (1986) suggested that  $10 \text{ mg kg}^{-1} \text{ S-SO}_4^{-2}$  at 0 to 20 cm deep was necessary to attain good crops yields. Additionally, Beaton and Soper (1986) determined a critical  $\text{S-SO}_4^{-2}$  availability of  $36 \text{ kg ha}^{-1}$  at 0 to 60 cm. Prior to wheat sown in 2004, soil  $\text{S-SO}_4^{-2}$  content (Table 2) was lower than the proposed thresholds, and this can explain yield increases due to S application. However, for wheat sown in 2003,  $\text{S-SO}_4^{-2}$  content previous to planting was greater than these critical levels (Table 2), but the observed yields ( $5760$  and  $7846 \text{ kg ha}^{-1}$  for S0 and S1 respectively) were greater than the mean of the region ( $4650 \text{ kg ha}^{-1}$ ) (Calviño and Monzón 2009). The greater yield and crop S demand can explain the response to S application during that year.

Late-sown soybean did not increase yield in response to S fertilization. In northern Argentinean Pampas, late soybean response to S application is commonly determined (Salvagiotti et al. 2004; García et al. 2010) as a consequence of the soil S depletion caused by the uptake of preceding wheat. One possible explanation for the absence of response

**Table 2**  
Soil S-SO<sub>4</sub><sup>-2</sup> (kg ha<sup>-1</sup>) content previous to crop sown in unfertilized (S0)  
and fertilized (S1) treatments

Depth (cm)	Maize 2001		Soybean 2002		Wheat 2003		Wheat 2004		Maize 2005		Soybean 2006		Maize 2008	
	S0	S1	S0	S1	S0	S1	S0	S1	S0	S1	S0	S1	S0	S1
0-20	17.5	17.5	19.6 a	19.7 a	19.5 a	20.4 a	8.7 a	10.8 a	10.1 b	16.3 a	10.6 a	10.9 a	7.6 a	8.2 a
20-40	13.9	13.9	9.0 a	16.9 a	9.1 a	9.7 a	8.8 a	10.1 a	17.0 a	8.0 b	9.2 a	8.5 a	4.9 a	5.3 a
40-60	12.6	12.6	6.7 a	10.6 a	8.0 a	10.7 a	8.9 a	8.4 a	4.8 a	10.2 a	8.1 a	8.0 a	3.0 a	5.2 a
0-60	44.1	44.1	35.3 a	47.2 a	36.6 a	40.7 a	26.4 a	29.2 a	31.9 a	34.5 a	27.9 a	27.4 a	15.5 a	18.7 a

*Note.* For each year and soil depth, the same letters indicate statistically equal values between S rates at  $P < 0.05$  using Fisher's protected LSD.

determined in this experience could be that soybean yield was reduced by the water deficit that occurred from R1 to R6 (23.1 mm) in 2003 and from V5 to harvest (40.2 mm) in 2004.

### Grain S Concentration

Sulfur fertilization increased grain S concentration in wheat (2004), maize (2005), and soybean (2003, 2004, and 2007) (Table 3). Except for late soybean in 2007, grain N/S showed the same trend (Table 3). The greatest response was determined in late-sown soybean, and this could be a consequence of the low quantity of S that remains in the soil after wheat harvest (Table 3). As stated, S uptake by the previous wheat crop increases the probability of S deficiencies in late soybean. The lack of precipitation reduced soybean yield and prevented yield increases, but the difference in the soil S status was probably expressed in the S concentration in grains (Gooding et al. 2003).

Similarly, Caires et al (2006) reported that the application of gypsum did not affect grain yield in soybean but it improved grain quality through an increase in protein and S contents. For wheat, Zhao, Hawkesford, and McGrant (1999) reported that responses in terms of bread-making quality to S fertilization were more common than responses in terms of grain yield. They also determined that the bread-making parameters correlated closely with grain S concentration and N/S ratio. As a consequence, the differences in S concentration and N/S in grains confirms the latent-S deficiency in the southeastern Argentinean Pampas and indicates that protein quality can be improved with S fertilization.

Sulfur concentration in grains was proposed as good diagnostic methodology to distinguish soils with nutrient deficiencies (Randall, Spencer, and Freney 1981). In Australia, Randall, Spencer, and Freney (1981) found S-deficient sites based on low S concentration and high N/S ratio in wheat grains. In Argentina, there is some evidence that support the use of grains to determine S-deficient sites. Mestelan and Pazos (1998) and Reussi Calvo, Echeverría, and Sainz Rozas (2011) confirmed that S concentration and N/S ratio in wheat grains performed well in the soils of the Buenos Aires Province. However, in soybean, Gutiérrez Boem et al. (2006) and Echeverría et al. (2011) determined no differences

**Table 3**  
Sulfur grain concentration and nitrogen to sulfur ratio (N/S) in unfertilized (S0) and fertilized (S1) treatments

Treatment	Maize	Soybean	Wheat	Late soybean	Wheat	Late soybean	Maize	Soybean	Late soybean
	2001	2002	2003	2003	2004	2004	2005	2006	2007
Sulfur (%)									
S0	0.10 a	0.27 a	0.15 a	0.24 b	0.11 b	0.37 b	0.08 b	0.30 a	0.28 b
S1	0.10 a	0.27 a	0.11 a	0.36 a	0.16 a	0.51 a	0.12 a	0.34 a	0.33 a
N/S									
S0	12.9 a	21.6 a	14.0 a	25.7 b	21.2 b	17.7 b	19.9 b	21.8 a	25.2 a
S1	12.1 a	21.2 a	14.9 a	15.1 a	13.5 a	13.9 a	12.1 a	18.8 a	22.0 a

*Note.* For each crop and variable, the same letters indicate statistically equal values between S rates at  $P < 0.05$  using Fisher's protected LSD.

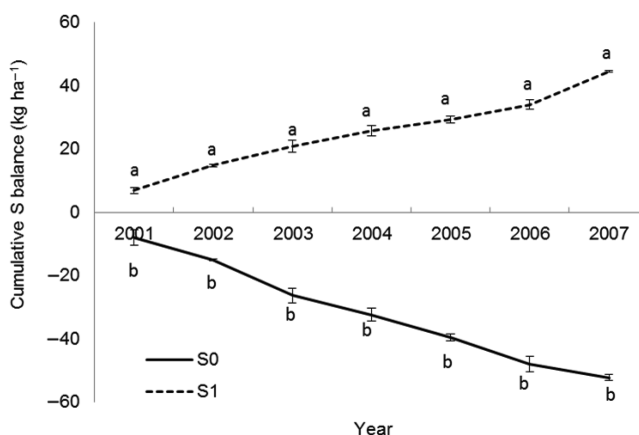
in grain S concentration and N/S ratio among sites with contrasting yield response to S fertilization.

For all soybean crops in the experiment, S concentration in grains was greater (Table 3) than the threshold of 0.23% proposed by Hitsuda, Sfredo, and Klepker (2004) for an adequate crop. In the current experiment, soybean yield did not respond to S fertilization, indicating that this critical level could perform well for the southeastern Argentinean Pampas conditions. However, Gutiérrez Boem et al. (2006) and Echeverría et al. (2011) reported yield responses to S applications when S concentration in grain was more than 0.23%. Based on these determinations, Echeverría et al. (2011) suggests that although more research is necessary, the threshold should be moved to near 0.3%.

For wheat, S concentrations were less than the threshold of 0.15% proposed by Gyori (2005) and confirmed by Reussi Calvo, Echeverría, and Sainz Rozas (2011) for the southeastern Argentinean Pampas (Table 3). These results demonstrate the accuracy of the diagnostic tool. Additionally, Reussi Calvo, Echeverría, and Sainz Rozas (2011) also proposed the threshold of 13.3:1 for the N/S ratio to discriminate S-deficient zones. Both wheat crops (2003 and 2004) had N/S ratios greater than this value, indicating that the index could be also used to diagnose the S status of wheat.

### Soil $S-SO_4^{-2}$ Content

Sulfur-fertilized plots showed a positive S balance in contrast to unfertilized treatments, where annual S exportation in grains produced a negative balance (Figure 2). Consequently, in 2008 the difference in cumulative S balance between treatments was  $96.7 \text{ kg ha}^{-1}$  (Figure 2). For six long-term experiments located in the northern Argentinean Pampas, García et al. (2010) reported greater differences between treatments in S mass balances for the same crop rotation after 10 years ( $220.6 \text{ kg S ha}^{-1}$ ). The difference with respect to the current experiment can be explained by the longer period under study, the greater S rates applied (between  $17$  and  $25 \text{ kg S ha}^{-1}$ ), and the greater crop S exportation in unfertilized treatments due to greater crop yield.



**Figure 2.** Cumulative sulfur balance for unfertilized (S0) and fertilized (S1) treatments in the 2001–2007 period. Vertical bars for each point indicate standard error of the mean. For each year, the same letters indicate statistically equal values between S rates at  $P < 0.05$  using Fisher's protected LSD.



Mass balance is a valuable management tool, but it has some deficiencies, such as the inability to estimate internal flows and the fact that it considers only nutrient amounts but ignores availability (Öborn et al. 2003). For mobile nutrients, such as S, the most important consideration is that mass balance does not take into account the possible losses. However, it gives the opportunity to estimate the potential of S increases or depletions in soils.

Soil S-SO<sub>4</sub><sup>-2</sup> contents at 0 to 60 cm deep did not differ between treatments (Table 2). This indicates that residual S-SO<sub>4</sub><sup>-2</sup> was not only influenced by the remaining S after crop harvest but also depends on other mechanisms. In contrast, García et al. (2010) determined residual S-SO<sub>4</sub><sup>-2</sup> in the long-term experiments of northern Pampas. After 10 years of S fertilization soil S-SO<sub>4</sub><sup>-2</sup> contents at 0 to 60 cm were 45.0 and 35.0 kg S ha<sup>-1</sup> for fertilized and unfertilized treatments respectively. They also determined that the differences between treatments was slight compared with differences in cumulative S mass balance (220.6 kg S ha<sup>-1</sup>) and argued that S immobilization and losses, could explain the low residuality.

Sulfate lixiviation is the main process that limits residuality in soils with low anion exchange capacity and udic moisture regime (Scherer 2001), as in southeastern Buenos Aires Province. For an organic crop rotation on a sandy soil in Denmark, Eriksen and Askegaard (2000) determined a strong relationship ( $r^2$  0.99) between the average annual drainage and S-SO<sub>4</sub><sup>-2</sup> leaching. No studies of SO<sub>4</sub><sup>-2</sup> leaching were performed in Argentinean Pampas, but for NO<sub>3</sub><sup>-</sup>, an anion with characteristics similar to SO<sub>4</sub><sup>-2</sup>, Sainz Rozas, Echeverría, and Barbier (2004) reported that leaching was the main N loss process that occurs during maize growth period in the region. For the same zone, Aparicio, Costa, and Zamora (2008) reported that the amount of nitrate (NO<sub>3</sub><sup>-</sup>) leached was associated with the rainfall quantity.

Leaching takes place when the water moving vertical downward in the soil profile is greater than plant transpiration, soil evaporation, and the amount of water necessary for soil saturation (Scherer 2001). As a consequence, water excess could be useful to explain the soil SO<sub>4</sub><sup>-2</sup> variations caused by leaching (Eriksen and Askegaard 2000). Except for late-sown soybean of 2004, water excess was determined in all crops (Table 4). In addition, precipitations during fallow, when evapotranspiration was negligible, were also important and caused water excess (Table 4). This fraction of total water that is not retained in soil pores promotes S-SO<sub>4</sub><sup>-2</sup> leaching with negative implications for the agronomic S-use efficiency and the environment.

Immobilization in organic fractions is the other sink of soil SO<sub>4</sub><sup>-2</sup>. Castellano and Dick (1990) reported that the initial response to excess S-SO<sub>4</sub><sup>-2</sup> caused by gypsum application was the storage of S as ester sulfate. After that, a large portion of this ester sulfate was redistributed to the C-bonded and residual-S pools. Then, organic S was mineralized back to SO<sub>4</sub><sup>-2</sup>. These authors proposed that this mechanism restricts S losses and, through mineralization, increases SO<sub>4</sub><sup>-2</sup> availability to crops. However, Knights et al. (2000) and Yang et al. (2007) reported that in long-term plots, S immobilization was only observed when SOM level increased. In the Askov long-term experiment initiated in 1894, SOM and organic S increased as a result of manure and mineral fertilizer applications. Conversely, when the immobilization did not occur, SO<sub>4</sub><sup>-2</sup> lixiviation was determined (Knights et al. 2000).

### ***Sulfur Concentration, Absorption, and Yield in Unfertilized Maize***

Maize sown in 2008 in unfertilized plots that had previously received S application for 7 years had similar S concentrations in AVB to those plots that were never fertilized. In contrast, S concentration in grain was greater in maize grown in historically S-fertilized

**Table 4**  
Rainfall, crop evapotranspiration (ET), and water excess  
for each crop and fallow

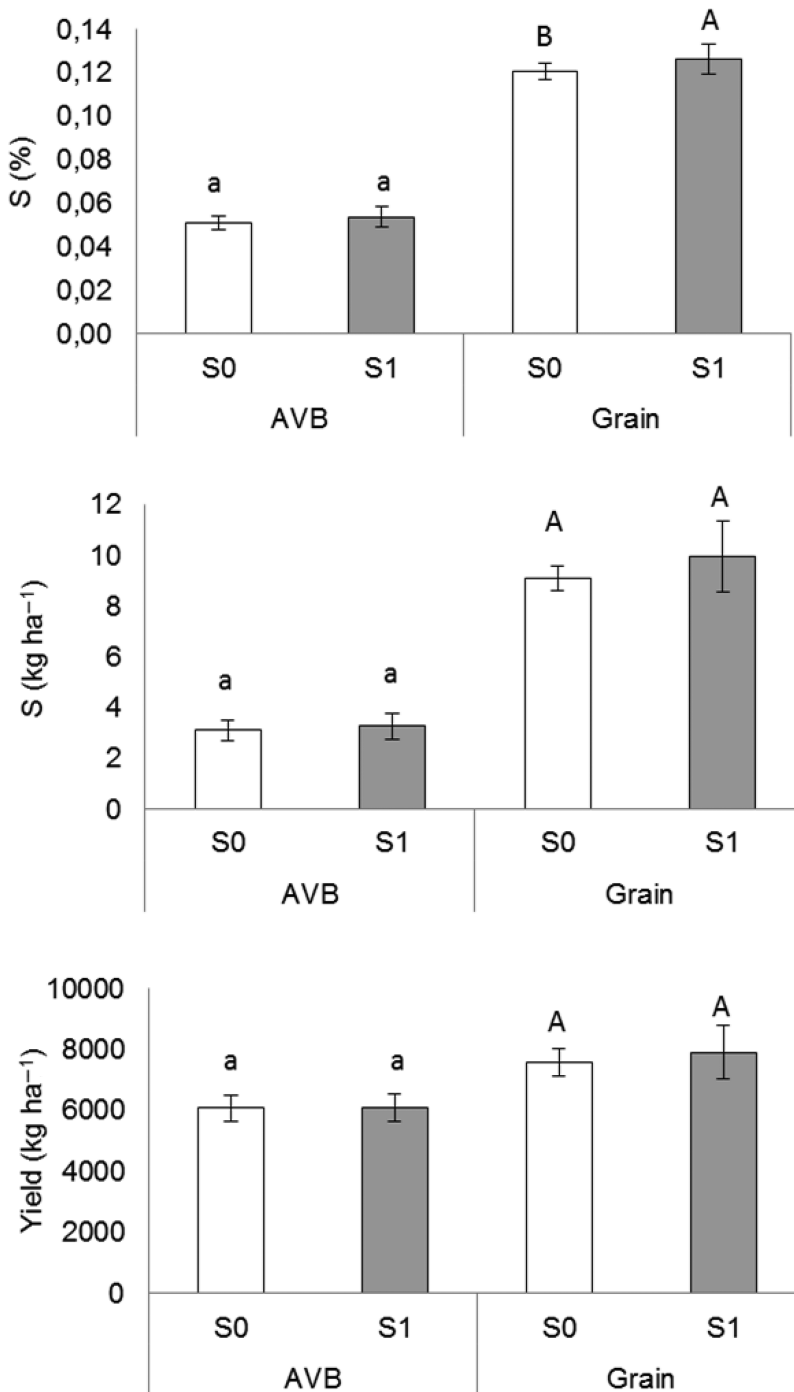
Crop / fallow	Precipitation (mm)	ET (mm)	Water excess (mm)
Maize 2001	844.1	446.5	340.0
Fallow	856.2	0	856.2
Soybean 2002	586.1	458.2	147.1
Fallow	129.0	0	109.8
Wheat 2003	558.1	358.7	199.4
Late soybean 2003	332.0	253.3	80.9
Fallow	31.1	0	28.9
Wheat 2004	424.5	306.4	199.1
Late soybean 2004	215.3	241.7	0
Fallow	371.6	0	264.3
Soybean 2005	489.5	345.2	226.3
Fallow	222.5	0	140.5
Maize 2006	520.7	411.1	109.6
Fallow	333.1	0	333.1
Wheat 2007	941.0	600.1	419.9
Soybean 2007	559.0	267.0	252.2
Fallow	249.8	0	170.8

plots (Figure 3). However, S absorption and grain yield did not differ between treatments (Figure 3).

The amount of  $S-SO_4^{-2}$  prior to maize sowing was similar between treatments (Table 2), and this could partially explain the similar values determined in S concentration and accumulation in AVB and grain (Figure 3). Eriksen et al. (1995) proposed that S uptake by plants increased as the soil S mineralization increased. Based on this assumption, the results obtained in the current experiment indicate that the net mineralization of the previous S-fertilized treatments was similar to that in the unfertilized treatment. Similarly, Eriksen and Mortensen (1999) evaluated the soil S status of the Askov long-term experiments using oilseed rape S uptake to determine if the residual effect of annual application of inorganic NPK fertilizers (S was applied in superphosphate; 13% S) contributes to the S supply for plants. They determined that fertilization for more than 100 years increased SOM and soil organic S, but no differences in S uptake by oilseed rape were observed. They concluded that S mineralization was similar between treatments within the growing season of the crop and hypothesized that the residual S effect from long-term annual applications of mineral fertilizers did not increase significantly the level of plant-available soil S compared with unfertilized plots.

## Summary and Conclusions

For the southeastern Argentinean Pampas, a region with latent S deficiencies, the results obtained show that S fertilization with empirical rates ( $15 \text{ kg S ha}^{-1}$ ) increased the yield only in wheat (22% of the crops in the experience). In addition, S concentration in grains was greater in S-fertilized treatments in 56% of the crops. These results confirm



**Figure 3.** Sulfur concentration (upper left), absorbed S (upper right), and yield (bottom) in above-ground vegetative biomass (AVB) and grain for unfertilized maize sown in plots that do not receive (S0) and do receive S fertilization (S1) during 2001 to 2008. Vertical bars for each column indicate standard error of the mean. The same letters indicate statistically equal values between S rates at  $P < 0.05$  using Fisher's protected LSD. Lowercase and capital letters denote AVB and grain, respectively.

deficiencies in the region and indicate that an adequate S fertilization strategy could be necessary to improve yield and grain quality.

Although S mass balance was positive with S addition, no soil  $\text{S-SO}_4^{-2}$  residual effects were found at the depth sampled in this study. Water excess during both times of cropping and fallow supports the hypothesis of leaching as a main cause of  $\text{SO}_4^{-2}$  loss. The absence of differences in S accumulation in maize also suggest that long-term S fertilization did not affect the soil S availability for crops.

Future research will focus on the definition of diagnostic tools to replace empirical S fertilization for a program that includes the diagnostic of soil and/or plant S status.

## Acknowledgments

This study was supported by the INTA Project AERN 295561, the FCA-UNMP AGR319/10, and FONCYT-PICT 2007-446.

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