



# Can Micronized Sulfur in Urea Reduce Ammoniacal Nitrogen Volatilization and Improve Maize Grain Yield?

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## Abstract

Micronized sulfur (S) in urea may reduce nitrogen (N) loss by ammoniacal N ( $\text{NH}_3\text{-N}$ ) volatilization and provide a better use for S from oil refineries, thereby improving plant nutrition by providing N and S. The objective of this study was to evaluate the use of urea micronized with S (urea+S) to mitigate  $\text{NH}_3\text{-N}$  volatilization and the efficiency of the urea+S as source of N and S for maize (*Zea mays* L.). Three field experiments were implemented, with maize grown in coarse-, medium-, and fine-textured soils and the following treatments: urea, ammonium nitrate, ammonium sulfate, urea+S enhanced with 13% elemental S (urea+S<sub>A</sub>), urea+S with 4% elemental S and 9% S in sulfate form (urea+S<sub>B</sub>), and a control without N application. The leaf N concentrations increased similarly for all the N sources. The leaf S concentrations were greater when the ammonium sulfate and urea+S were applied. The use of micronized S does not decrease the  $\text{NH}_3\text{-N}$  volatilization from urea side-dress applied to maize. However, in comparison with ammonium sulfate, the urea+S are a viable alternative for supplying N and S to maize because of their greater operational efficiencies and due to their high N concentrations.

**Keywords** Nitrogen sources · Ammonia · Alternative sulfur source · No-till

## 1 Introduction

Urea is the main nitrogen (N) source for agriculture and is used commercially worldwide (Trenkel 2010). When urea is applied on the soil surface without being incorporated, it is hydrolyzed to ammonia and can be lost to the atmosphere through ammoniacal N ( $\text{NH}_3\text{-N}$ ) volatilization (Azeem et al. 2014). In acidic soil, depending on the soil conditions during surface application, N losses can exceed 70% of the applied N (Lara Cabezas et al. 1997). According to Yamada and Abdalla (2000), most N losses occur due to the volatilization of  $\text{NH}_3$ . The volatilization of  $\text{NH}_3\text{-N}$  is the result of alkalization close to the urea granules during their hydrolysis (Raun and Johnson 1999). In turn, the hydrolysis of urea is the result of the action of urease, which is an extracellular enzyme produced by microorganisms or originating from plant residues

(Frankenberger and Tabatabai 1982). According to Overrein and Moe (1967), the pH may increase from 6.5 to 8.8 adjacent to urea granules. This increase in pH is proportional to a decrease in  $\text{H}^+$  concentration, which impedes the conversion of ammonia ( $\text{NH}_3$ ) into ammonium ( $\text{NH}_4^+$ ) and favors  $\text{NH}_3\text{-N}$  volatilization (Overrein and Moe 1967). Under no-till conditions, the soil surfaces covered with straw provide an environment favorable for the intensification of the microbial  $\text{NH}_3$  volatilization process (Rochette et al. 2009).

Preventing N losses is essential to increase the efficiency of N fertilization, which in turn depends on several factors, including soil texture, previously grown crops, climatic conditions, N source, N application rate, and N application method (Al-Kanani et al. 1991; Cantarella 2007; Rodrigues and Kiehl 1986). The methods that have been investigated to mitigate  $\text{NH}_3\text{-N}$  loss through the use of urea in agriculture include pre-treatment with urea granules with polymers that have different principles of action, urease and nitrification inhibitors (Alfaro et al. 2018; Cantarella et al. 2008), rock dusts, organic compounds (Jadon et al. 2018), micronutrients (Grohs et al. 2011), and sulfur (S) (Nascimento et al. 2013; Trenkel 2010). Among the possible alternatives, the use of S to reduce N losses through urea has been observed to significantly reduce

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$\text{NH}_3\text{-N}$  volatilization (Nascimento et al. 2013; Rech et al. 2017). The acidifying effect of elemental S oxidation in soil may neutralize alkalization during urea hydrolysis, minimizing N loss through  $\text{NH}_3\text{-N}$  volatilization (Trenkel 2010). Other N sources have been used to avoid N loss through  $\text{NH}_3\text{-N}$  volatilization, such as ammonium sulfate and ammonium nitrate (Cantarella 1998). However, while urea contains 45% N and ammonium nitrate contains 34% N, ammonium sulfate contains only 20% N and 22–24% S. The low N concentration in ammonium nitrate and ammonium sulfate results in a greater application and transport cost per unit of N applied (Franco and Saraiva Neto 2007).

In addition to the advantage of reducing  $\text{NH}_3\text{-N}$  volatilization, N sources containing S provide a nutrient that is limiting for agricultural production across more than 100 million ha worldwide (Bettany and Stewart 1982). Soils deficient in S are increasingly being reported due to the replacement of soil amendments containing S with soil amendments containing little or no S, such as urea and triple superphosphate (Boswell and Friesen 1993). The reduction in S soil stocks from crop uptake and loss of S through leaching and erosion is also a reason that S is a limiting factor (Kim et al. 2013). Additionally, the application of S together with N yields has not only agronomic advantages but also ecological advantages because it can provide a suitable use for the excess of S from oil refineries as a result of recent environmental regulations in many countries that require oil refineries to reduce the amount of S in fuel (Babich and Moulijn 2003).

The objectives of this study were to verify whether  $\text{NH}_3\text{-N}$  volatilization decreases when urea micronized with S (urea+S) is used rather than conventional nitrogen fertilizers and to evaluate the efficiency of N and S sources in terms of plant nutrition, yield components, and grain yield (GY) for maize grown in three different types of soil.

## 2 Materials and Methods

### 2.1 Characterization of the Experimental Sites

Field experiments with maize crops grown under no-till farming were conducted at three sites with sandy loam (coarse-textured soil), sandy clay loam (medium-textured soil), and clay (fine-textured soil) soil (Table 1). The coarse-, medium-, and fine-textured soils at the experimental sites were classified as Typic Hapludox, Rhodic Hapludox, and Typic Rhodudalf (Soil Survey Staff, 2014), respectively. The experiment conducted in a coarse-textured soil was located at latitude 22°77'S and longitude 48°57'W in São Manuel, São Paulo State, Brazil. At Botucatu, the experiments were conducted in medium- and fine-textured soils. The site with the medium-textured soil was located at latitude 22°83'S and longitude 48°42'W, and the site with the fine-textured soil was located

at latitude 22°84'S and longitude 48°42'W. All experimental sites were located at altitudes of approximately 800 m.

The climate is humid mesothermal and is considered Cwa according to the Köppen classification with mean annual rainfalls of approximately 1450 mm and mean temperatures of 24 °C during the warmest month and 13 °C during the coldest month (Miranda et al. 2015). The temperature and rainfall data for the period of this study were collected from meteorological stations located in São Manuel and Botucatu (Fig. 1).

### 2.2 Conducting the Experiments

For the initial chemical characterization of the experimental sites, the soil was sampled at two depths, 0–0.20 and 0.20–0.40 m (Table 2). The soil pH was determined in a 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> suspension (1:2.5 soil/solution), and the phosphorus (P) and exchangeable calcium (Ca), magnesium (Mg), and potassium (K) concentrations were determined after extraction with ion exchange resin (Raij et al. 1986). The cation exchange capacity (CEC) and base saturation (BS) values were calculated using the exchangeable bases, and the total acidity (H + Al) was determined at pH 7.0 with calcium acetate, according to Raij et al. (2001). The soil organic matter (SOM) concentration was determined according to Nelson and Sommers (1996).

Each plot consisted of six rows that were 10 m long and 0.45 m apart. Maize was sown at the end of October 2014 beneath millet [*Pennisetum americanum* (L.) K. Schum.] straw in a no-till system. A simple maize hybrid (DKB 390 PRO) was used. In addition to the side-dressing treatments, 24 kg ha<sup>-1</sup> N as urea, 37 kg ha<sup>-1</sup> P as triple superphosphate, and 40 kg ha<sup>-1</sup> K as potassium chloride were applied just below and to the side of the seed furrow.

The treatments consisted of the application of different sources of N and/or S, to compare conventional N sources to urea micronized with S (urea+S), in a concentration of 13% elemental S (urea+S<sub>A</sub>), and with 4% elemental S and 9% S in sulfate form (urea+S<sub>B</sub>). The treatments are summarized in Table 3. Fertilizer treatments were manually side-dressed in a uniform line next to the maize row at a rate of 180 kg ha<sup>-1</sup> N when maize plants reached the V8 growth stage (Ritchie and Hanway 1986).

### 2.3 N Loss through $\text{NH}_3\text{-N}$ Volatilization

The loss of N through  $\text{NH}_3\text{-N}$  volatilization was evaluated using a semi-open static chamber developed by Nömmik (1973), adapted by Lara Cabezas and Trivelin (1990), and calibrated by Lara Cabezas et al. (1999) for estimating actual losses under field conditions. Collection chambers were constructed from clear and flexible polyvinyl chloride tubing that measured 145.6 mm in diameter and 400 mm in height. The chambers were fitted onto rigid polyvinyl chloride bases that

**Table 1** Characterization of soil physical properties according to particle size (sand, clay, and silt) at two soil depths (0–0.20 and 0.20–0.40 m) from the experimental site in São Manuel and two experimental sites in Botucatu, São Paulo State, Brazil

Depth m	Sand	Clay g kg <sup>-1</sup>	Silt	Soil textural class
São Manuel				
0–0.20	849	118	33	Sandy loam
0.20–0.40	812	158	30	Sandy loam
Botucatu				
0–0.20	706	249	45	Sandy clay loam
0.20–0.40	640	316	45	Sandy clay loam
Botucatu				
0–0.20	127	721	153	Clay
0.20–0.40	115	732	154	Clay

measured 152.8 mm in diameter and 100 mm in height and were inserted into the soil to a depth of 30 mm. The bases were installed in the fields before the application of the N sources, which were weighed in accordance with the base areas of the collector chambers. Instead of a single base for each collector chamber, which was the original method, three bases were used in each experimental unit. Because the chambers for collecting NH<sub>3</sub>-N protect the soil from rain inside the bases, the chambers were switched from base to base in a rotation scheme after each rainfall event and at each experimental site, thereby enabling the collection of more representative samples. Immediately after the application of the N sources, the collector chambers were installed and fitted onto the previously installed bases. Supports were fitted over the tubes, and protective caps were attached to the tubes to allow air but not rain to enter the system.

Two 20-mm-thick polyurethane foam sponge discs (density of 0.028 g cm<sup>-3</sup>) were placed in each collector chamber. The first foam disc was placed at a height of 0.15 m above the ground to capture the NH<sub>3</sub>-N volatilized from the soil, and the second disc was placed at a height of 0.30 m to capture NH<sub>3</sub>-N from the atmosphere, thereby preventing contamination of the lower foam disc. The foam discs were soaked with 20 mL of glycerol-phosphoric acid (5% v/v H<sub>3</sub>PO<sub>4</sub> and 4% v/v glycerol) (Nõmmik 1973). The amount of solution applied to the foam discs was sufficient to soak them without causing dripping.

The foam discs were placed in each collector chamber immediately after the application of N and were replaced at 1, 2, 4, 6, 8, 10, 14, 18, 22, 30, and 40 days after side-dressing. Therefore, the NH<sub>3</sub>-N volatilization data correspond to the total NH<sub>3</sub>-N volatilized in the period between sampling times. The three sites were always sampled in the morning and on the same day.

The ammonium phosphate was removed from the foam discs by successively washing them with 300 mL of a 1 mol L<sup>-1</sup> KCl solution. Then, a 50-mL aliquot was steam distilled, and 10 mL of 10 mol L<sup>-1</sup> NaOH was added to each sample. The distillate was collected in a solution of H<sub>3</sub>BO<sub>3</sub> + indicator. The ammonium phosphate concentration was

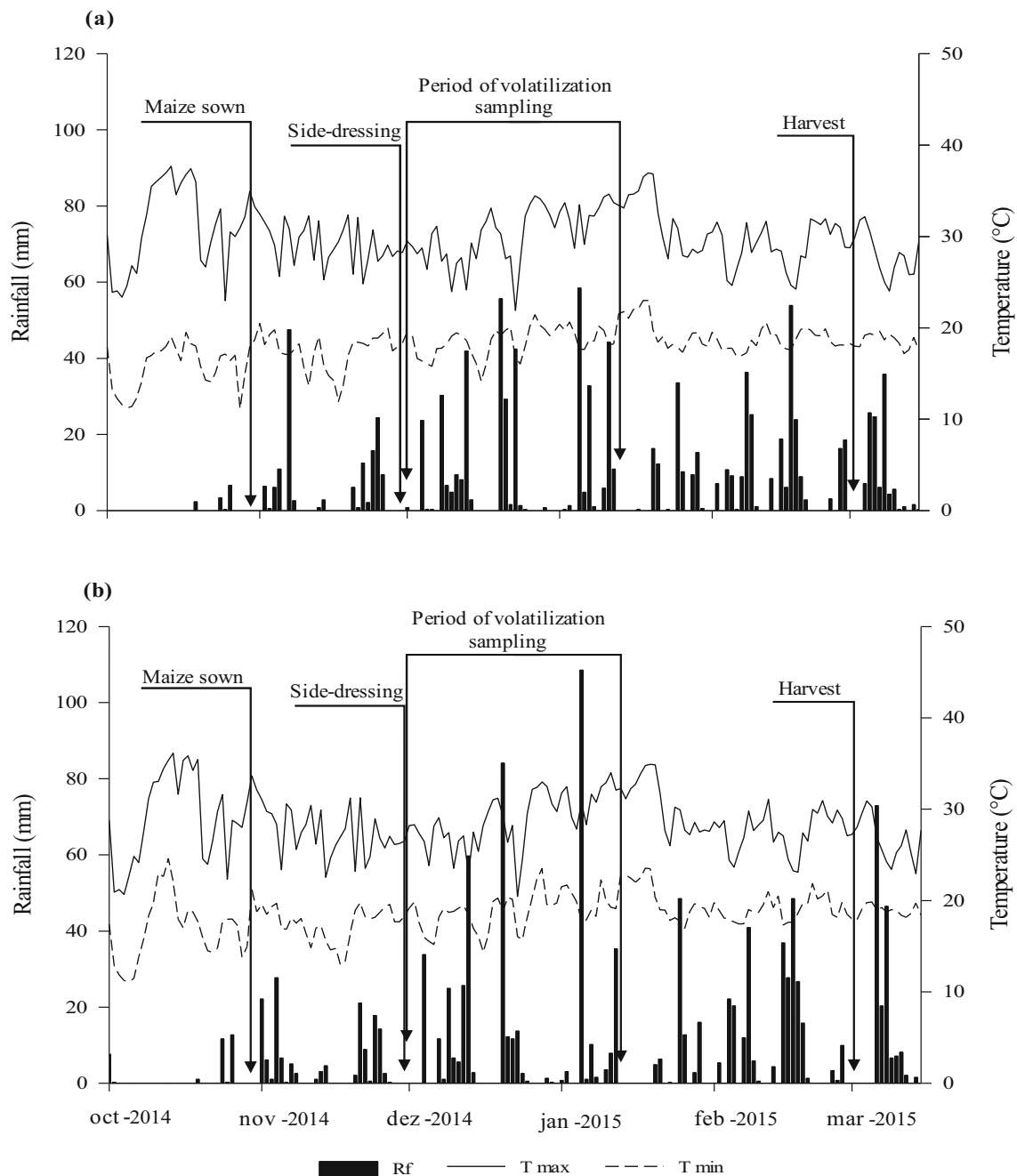
determined by colorimetry according to the method described by Qiu et al. (1987). The amount of NH<sub>3</sub>-N determined in each sampling corresponded to the NH<sub>3</sub>-N volatilized according to the area of the chamber base (0.0166 m<sup>2</sup>), and was converted to NH<sub>3</sub>-N volatilized per hectare. The total NH<sub>3</sub>-N volatilized after 40 days of N application was obtained by the sum of each sampling.

## 2.4 Maize Crop Measurements

The central third of the leaf from the base of the ear was collected from 10 plants per plot at the VT growth stage for foliar diagnosis (Raij et al. 1997). All samples were dried in a forced-air oven at 60 °C and then ground in an electric Wiley mill. The tissue concentrations of N and S were determined following digestion with H<sub>2</sub>SO<sub>4</sub> and nitro-perchloric acid solution, respectively (Malavolta et al. 1997). The concentrations of N and S in the extracted solutions were determined using the semi-micro Kjeldahl method and atomic absorption spectrophotometry, respectively, following the methods described by Malavolta et al. (1997).

Maize was harvested in March 2015, and the following yield components were determined: final plant population (PP, number of plants extrapolated to the number of plants/ha), number of ears per plant (NEP, number of ears/total number of plants), number of grains per ear (NGE, number of grains in 10 ears), and 100-grain weight (W100, average of eight samples of 100 grains). Grain yield (GY), as the yield component, was determined by manually harvesting the plants from 8-m sections of two central rows. The water content of the grains was determined by oven drying the grains at 105 ± 3 °C for 24 h, and yields were calculated in kg ha<sup>-1</sup> based on a moisture content of 130 g kg<sup>-1</sup>. The N-use efficiency (NUE) was calculated according to the equation proposed by Fageria and Baligar (2005):  $NUE = \text{kg ha}^{-1} \text{ yield increase relative to the control} / \text{kg ha}^{-1} \text{ N applied}$ .

Grain samples were ground in an electric Wiley mill to determine their N and S concentrations, as described in Malavolta et al. (1997), and the total accumulated N and S



**Fig. 1** Rainfall (Rf), maximum temperatures (Tmax), and minimum temperatures (Tmin) recorded during the experimental periods in **a** São Manuel and **b** Botucatu, São Paulo State, Brazil

contents of the grain were determined by multiplying the N and S concentrations by the GY.

## 2.5 Statistical Analysis

Each experimental site was established using a randomized complete block design with four replicates. The data from each experimental site were analyzed separately and subjected to analysis of variance at 5% probability, and the means were compared using Fisher's least significant difference (LSD) test

at 5% probability. All of the statistical analyses were performed using SISVAR 5.3 (Ferreira 2010).

## 3 Results

### 3.1 NH<sub>3</sub>-N Volatilization

At all sites and for all treatments, 90% of the NH<sub>3</sub>-N was volatilized during the first 10 days of the 40-day period after

**Table 2** Chemical characterization of soil at two depths (0–0.20 and 0.20–0.40 m) from the coarse-textured soil in São Manuel and the medium- and fine-textured soils in Botucatu, São Paulo State, Brazil

Depth m	pH <sup>a</sup>	SOM <sup>b</sup> g kg <sup>-1</sup>	P mg kg <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup> -S	H + A <sup>c</sup>	K	Ca cmol <sub>c</sub> kg <sup>-1</sup>	Mg	CEC <sup>d</sup>	BS <sup>e</sup> %
Coarse-textured soil										
0–0.20	5.1	12	25	6	2.1	0.08	1.8	0.5	4.5	53
0.20–0.40	4.9	9	13	6	2.1	0.06	1.5	0.3	4.0	47
Medium-textured soil										
0–0.20	4.5	21	26	7	4.1	0.08	1.9	0.8	7.0	41
0.20–0.40	4.3	16	13	8	4.7	0.09	1.7	0.8	7.3	35
Fine-textured soil										
0–0.20	4.5	21	11	35	5.7	0.06	1.9	0.9	8.8	35
0.20–0.40	4.5	18	6	38	5.0	0.12	2.3	0.7	8.1	39

<sup>a</sup> Soil pH measured in calcium chloride solution

<sup>b</sup> Soil organic matter

<sup>c</sup> Potential acidity

<sup>d</sup> Cation exchange capacity

<sup>e</sup> Base saturation

side-dressing (Fig. 2). In the coarse-textured soil, the highest rates of NH<sub>3</sub>-N occurred until 4 days after N application, resulting in an average total volatilization of 26% of each N source between 1 and 4 days after N application. Between the fourth and sixth days after N application, volatilization was significantly reduced, particularly in the plots that received ammonium nitrate, ammonium sulfate, and urea+S<sub>A</sub>. This reduction in volatilization occurred due to the rainfall (23.6 mm) that occurred between the third and fourth collection dates (Fig. 2a). The last NH<sub>3</sub>-N volatilization peak occurred 8 days after the application of urea+S<sub>A</sub>. However, 10 days after N application, the volatilization decreased for all of the treatments except the urea treatment, possibly due to the occurrence of heavy rainfall (50 mm of rainfall occurred between the fifth and sixth collections) (Fig. 2a).

NH<sub>3</sub>-N volatilization also increased for up to 4 days after N application in the medium- (Fig. 2b) and fine-textured soils (Fig. 2c), with NH<sub>3</sub>-N volatilization peaking in the urea+S<sub>B</sub> and common urea treatments, respectively. Because 33.8 mm of rainfall

occurred from 4 to 6 days after N application, NH<sub>3</sub>-N volatilization decreased in both experiments, especially under the urea alone and urea+S<sub>B</sub> treatments. Although this rainfall occurred before the third collection (4 days after application), the amount of N volatilized increased at the third collection due to the warm and dry conditions that began several days before the treatment application and persisted for much of the period between the second and third collections. While the treatments with urea and urea+S<sub>B</sub> decreased NH<sub>3</sub>-N volatilization by 6 days after N application, the NH<sub>3</sub>-N volatilization remained high after the application of urea+S<sub>A</sub> and only decreased 6 to 8 days after N application in both the medium- and fine-textured soils.

In the coarse-textured soil, the sources that resulted in the greatest NH<sub>3</sub>-N volatilization 40 days after N application were urea+S<sub>A</sub> and urea+S<sub>B</sub>, with total respective NH<sub>3</sub>-N volatilization values of approximately 2.6 and 2.7 kg ha<sup>-1</sup> greater than the volatilization observed after urea application (Fig. 3). In the medium-textured soil, urea+S<sub>B</sub> resulted in the greatest total volatilization, followed by urea+S<sub>A</sub>, with 3.04 kg ha<sup>-1</sup>

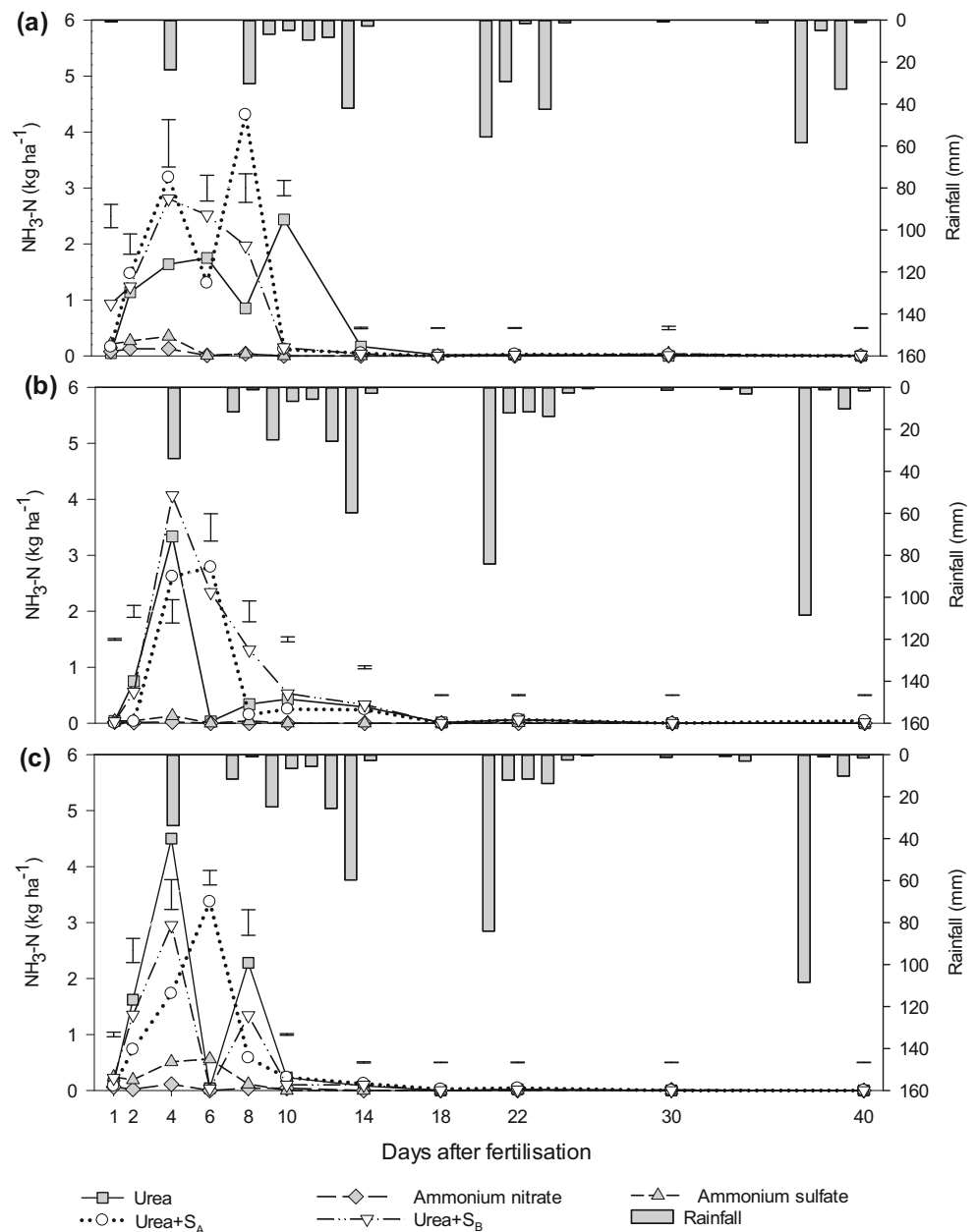
**Table 3** Concentrations of nitrogen (N) and sulfur (S), rate of fertilizer application, and the rates of nutrient application for each nutrient according to each treatment

Treatment	Concentration of nutrients		Rate of fertilizer	Rate of each nutrient	
	N %	S		N kg ha <sup>-1</sup>	S
Control	–	–	–	–	–
Urea	45	–	400	180	–
Ammonium nitrate	34	–	529	180	–
Ammonium sulfate	20	24	900	180	216
Urea+S <sub>A</sub> <sup>a</sup>	40	13 <sup>a</sup>	450	180	58.5
Urea+S <sub>B</sub> <sup>b</sup>	37	13 <sup>b</sup>	487	180	63.2

<sup>a</sup> Urea micronized with 13% elemental S

<sup>b</sup> Urea micronized with 4% elemental S and 9% S in sulfate form

**Fig. 2** Rainfall and ammoniacal nitrogen ( $\text{NH}_3\text{-N}$ ) volatilization, as affected by side-dressing nitrogen sources, in coarse-textured soil (a) in São Manuel and medium- (b) and fine-textured soil (c) in Botucatu, São Paulo State, Brazil. Least significant differences ( $p \leq 0.05$ ) are presented as error bars



less  $\text{NH}_3\text{-N}$  volatilization than that for urea+ $\text{S}_B$ . The application of urea resulted in approximately  $3.94 \text{ kg ha}^{-1}$  less  $\text{NH}_3\text{-N}$  volatilization than that for urea+ $\text{S}_B$ . In the fine-textured soil, the application of urea resulted in more total volatilization than that for urea+S.

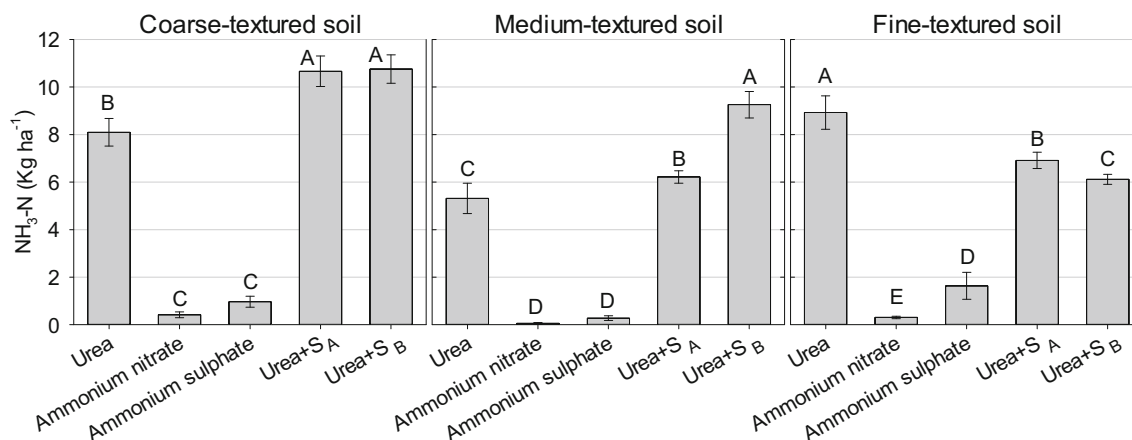
### 3.2 Concentration of N and S in Maize Leaves

Regardless of the N source, N application increased the concentrations of N in the leaves of plants grown in the coarse-textured soil, but no difference was observed among the treatments for the medium-textured soil, not even for the control. The leaf N concentrations increased relative to the control only when urea+ $\text{S}_B$  was applied to the fine-textured soil (Table 4).

In the coarse-textured soil, the leaf S concentrations were greater only when ammonium sulfate and urea+ $\text{S}_A$  were applied (Table 4). In the medium-textured soil, the treatments with ammonium sulfate also resulted in greater S concentrations in the maize leaves, and the application of urea+S resulted in greater S concentrations than those in the control, urea, and ammonium nitrate treatments (Table 4). In the fine-textured soil, the S concentrations in the maize leaves were similar in all the treatments (Table 4).

### 3.3 Maize Yield Components

The final plant population was not affected by any of the treatments, and the average plant population in all



**Fig. 3** Total ammoniacal nitrogen (NH<sub>3</sub>-N) volatilization, as affected by side-dressing nitrogen sources, in coarse-textured soil in São Manuel and medium- and fine-textured soil in Botucatu, São Paulo State, Brazil.

Values in the columns followed by the same letter are not significantly different at  $p \leq 0.05$  according to the Fisher's LSD test. Error bars represent the standard error

experimental sites was 58,160 plants ha<sup>-1</sup>. In the coarse-textured soil, the NEP was lower in the control and ammonium sulfate treatments. The highest NGE was observed when ammonium sulfate was applied, and the lowest NGE was observed in the control treatment. The W100, GY, and NUE were the same in all the treatments in the coarse-textured soil that received a N source side-dressing (Table 5).

The application of common urea and urea+S provided the highest NEP in relation to the other treatments in the medium-textured soil (Table 5). However, the NGE was the highest for the urea+S<sub>A</sub> application, which resulted in consecutively higher GY than the other treatments even when the W100 showed no differences among the treatments (Table 5). The NUE was higher when prototype A was applied than urea, providing 10 kg of grain per kg of N more in comparison with the urea treatment (Table 5).

In the fine-textured soil, the NEP was the same for all the treatments, including the control, whereas the NGE, W100, and GY were lower only in the control treatment. Therefore, there were no differences in GY and NUE regardless of the N sources (Table 5).

### 3.4 Concentrations and Total Accumulation of N and S in Maize Grains

The treatments had no effect on the concentrations of N and S in the maize grains in the coarse- and medium-textured soils (Table 4). In the fine-textured soil, a higher N concentration was measured in response to applications of ammonium sulfate and urea+S. However, there was no effect on the S concentration in the grains (Table 4).

Although the grain N contents were not affected by the treatments, the total accumulation of N in the grains was greater in the treatments than in the control for the coarse- and medium-textured soils. However, no differences in the N accumulated in grains were observed in the fine-textured soil

(Table 4). The total accumulation of S in the grains was greatest for the ammonium sulfate treatment on the coarse-textured soil. The control and ammonium nitrate treatment resulted in the lowest S accumulation in the grains in the medium-textured soil, and no differences were observed in the fine-textured soil, not even in the control (Table 4).

## 4 Discussion

Peaks and valleys in the NH<sub>3</sub>-N volatilization data were observed, possibly in response to the climatic conditions. The movement of N into deeper soil layers can be stimulated by rain, which would reduce volatilization. In contrast, when little or no rainfall occurs, intense hydrolysis of urea occurs via urease, which increases the potential for losses of NH<sub>3</sub>-N. To avoid great losses of NH<sub>3</sub>-N after side-dressing N fertilizer, appropriate irrigation management is recommended among other solutions, such as the incorporation of fertilizer by applying water immediately after the application of N sources that have a high potential for losses through volatilization (e.g., urea) (Wang et al. 2004). When urea is transported into deeper soil layers, gaseous NH<sub>3</sub> molecules migrate from below the soil to the atmosphere. During this process, these molecules may encounter areas of soil with low pH, which results in the transformation of NH<sub>3</sub> into NH<sub>4</sub><sup>+</sup> upon the receipt of a proton. These molecules subsequently remain in the soil solution or are electrostatically adsorbed into negative charges. In addition to dry periods, periods of high temperatures favor increased NH<sub>3</sub>-N loss through volatilization due to an increased NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> ratio in the soil solution, reduced NH<sub>3</sub> solubility, increased urease activity, and increased evaporation rate (Trivelin et al. 1994). Generally, temperatures are milder during and shortly after rainfall events. Therefore, the peaks and valleys observed in the NH<sub>3</sub>-N volatilization data may be

**Table 4** Effect of nitrogen (N) source side-dressing on N and sulfur (S) concentrations in maize leaves and concentration and total accumulations in maize grains in coarse-, medium-, and fine-textured soils

Treatment	Coarse-textured soil		Medium-textured soil		Fine-textured soil	
	N	S	N	S	N	S
Concentration in maize leaves (g kg <sup>-1</sup> )						
Control	15.1b	1.19c	18.8a	1.78c	19.5b	1.70a
Urea	20.3a	1.56b	21.0a	1.84c	21.0ab	1.69a
Ammonium nitrate	21.0a	1.37bc	21.4a	1.72c	20.6ab	1.76a
Ammonium sulfate	22.0a	2.00a	19.3a	2.46a	20.7ab	1.87a
Urea+S <sub>A</sub>	22.0a	1.85a	22.8a	1.96b	19.5b	1.95a
Urea+S <sub>B</sub>	19.9a	1.50b	20.6a	2.02b	23.2a	1.90a
Concentration in maize grains (g kg <sup>-1</sup> )						
Control	15.6a	3.2a	14.1a	1.0a	14.6c	1.5a
Urea	15.0a	3.5a	15.6a	1.3a	15.2bc	1.3a
Ammonium nitrate	15.0a	3.1a	17.1a	1.1a	15.4bc	1.1a
Ammonium sulfate	15.6a	3.5a	15.4a	1.3a	17.8a	1.4a
Urea+S <sub>A</sub>	15.4a	3.2a	15.4a	1.0a	17.0ab	1.1a
Urea+S <sub>B</sub>	14.6a	3.4a	15.8a	1.2a	16.5ab	1.2a
Total accumulated in maize grains (kg ha <sup>-1</sup> )						
Control	73b	5c	126b	9b	96c	11a
Urea	133a	10b	160a	13a	161b	15a
Ammonium nitrate	139a	12ab	191a	12b	160b	11a
Ammonium sulfate	136a	14a	174a	14a	207a	18a
Urea+S <sub>A</sub>	141a	11b	187a	13a	173ab	11a
Urea+S <sub>B</sub>	128a	11b	177a	14a	180ab	18a

Values in the columns followed by the same letter are not significantly different at  $p \leq 0.05$  according to the Fisher's LSD test

strongly related to climatic conditions, especially with the application of conventional or S-treated urea.

The similarity between urea alone and urea+S regarding  $\text{NH}_3\text{-N}$  volatilization may be related to the form of S and its concentration in the urea+S. Urea+S<sub>A</sub> contains only elemental S, urea+S<sub>B</sub> contains only 9% S as sulfate, while ammonium sulfate contains one molecule of sulfate for every two molecules of  $\text{NH}_4^+$  [ $(\text{NH}_4)_2\text{SO}_4^{2-}$ ]. The presence of the sulfate anion leads to an acidic reaction in the soil, and the sulfate acts as an accompanying ion for  $\text{NH}_4^+$ , favoring the vertical displacement of  $\text{NH}_4^+$  in the soil (Lara Cabezas et al. 1997). The presence of S in urea granule was not enough to reduce the  $\text{NH}_3\text{-N}$  volatilization losses in the coarse- and medium-textured soil; however, the higher initial amount of  $\text{SO}_4^{2-}\text{-S}$  in the fine-texture soil may have allowed a bigger interaction between sulfate and  $\text{NH}_4^+$  reducing the volatilization compared with regular urea, once the soil chargers were filled with  $\text{SO}_4^{2-}\text{-S}$  more than the other two sites. Further studies are necessary to verify the ability of higher concentrations of micronized S in sulfate urea granules to prevent  $\text{NH}_3\text{-N}$  loss through volatilization in soils with different  $\text{SO}_4^{2-}\text{-S}$  concentrations.

In the three studied soils, no single N source resulted in a greater total volatilization of N for any of the soil types. These differences occurred due to the characteristics of the soils in

each experiment. According to Bayer and Mielniczuk (1997), an increase in the SOM concentration is related to an increase in the microbial population and CEC. With a larger microbial population, the urease activity is also higher, thus favoring the hydrolysis and consequent loss of  $\text{NH}_3\text{-N}$ . In no-till systems, the presence of plant residues is ideal for increasing the SOM concentration and microbial population, and plant residues decrease the contact of urea with the soil, thereby decreasing the adsorption of  $\text{NH}_4^+$  into the soil and favoring N loss through the volatilization of  $\text{NH}_3\text{-N}$  (Rochette et al. 2009).

Although the experiments in the different textural classes of soil were not statistically designed to have their results compared with one another, the total amount of volatilized  $\text{NH}_3\text{-N}$  did differ according to each N source and soil type. Due to strong interactions between the factors that determine  $\text{NH}_3\text{-N}$  volatilization, it is very difficult to compare the results of experiments in different soil types. It is even more difficult to compare the results obtained in coarse-textured soil with those obtained in the other soils because the distance between the sites results in climatic differences. The climatic differences between the medium- and fine-textured soils were less, which allowed for a fair comparison.

The total amount of  $\text{NH}_3\text{-N}$  was low for the ammonium sulfate and ammonium nitrate as expected, but the total volatilization from urea alone and urea+S was also low, resulting



**Table 5** Effect of nitrogen source side-dressing on the number of ears per plant (NEP), number of grains per ear (NGE), 100-grains weight (W100), grain yield (GY), and nitrogen use efficiency (NUE) of maize in coarse-, medium- and fine-textured soils

Treatment	NEP no.	NGE no.	W100 g	GY kg ha <sup>-1</sup>	NUE kg kg <sup>-1a</sup>
Coarse-textured soil					
Control	0.92bc	324d	27b	4690b	–
Urea	1.08a	396c	36a	8834a	23a
Ammonium nitrate	1.05a	455ab	34a	9267a	25a
Ammonium sulfate	0.90c	488a	33a	8824a	22a
Urea+S <sub>A</sub>	1.00ab	457ab	35a	9138a	24a
Urea+S <sub>B</sub>	1.05a	433b	33a	8712a	22a
Medium-textured soil					
Control	0.98b	412c	38a	8914c	–
Urea	1.08a	454b	36a	10,320b	7b
Ammonium nitrate	1.05ab	470b	38a	11,133ab	12ab
Ammonium sulfate	1.05ab	489b	37a	11,226ab	13ab
Urea+S <sub>A</sub>	1.10a	543a	36a	12,131a	17a
Urea+S <sub>B</sub>	1.10a	449b	38a	11,162ab	12ab
Fine-textured soil					
Control	1.02a	383b	30b	6564b	–
Urea	1.00a	504a	36a	10,585a	22a
Ammonium nitrate	1.00a	490a	36a	10,381a	21a
Ammonium sulfate	1.05a	519a	37a	11,616a	28a
Urea+S <sub>A</sub>	1.02a	476a	37a	10,214a	20a
Urea+S <sub>B</sub>	1.02a	528a	34a	10,919a	24a

Values in the columns followed by the same letter are not significantly different at  $p \leq 0.05$  according to the Fisher's LSD test

<sup>a</sup> kg of grains kg nitrogen<sup>-1</sup>

in average less than 5% of the total N side-dress applied. According to Lara Cabezas et al. (1997), N losses can exceed 70% of the applied N from urea, being common to observe losses of 15–30% of the total N applied from urea (Cantarella et al. 2008; Otto et al. 2017; Viero et al. 2014). Once there was a rain only 4 days after N application, the N released from urea was carried into the soil, avoiding high volatilization. Similar results were observed by Nascimento et al. (2013), due to rainfall precipitation few days after urea application in the soil surface. The total NH<sub>3</sub>-N volatilized after the application of urea was greater in the fine-textured soil than in the medium-textured soil. The fine-textured soil had a greater CEC and a similar SOM value than the medium-textured soil based on the initial analysis. However, there was typically more plant residue coverage for the fine-textured soil, which could have resulted in reduced contact of the NH<sub>4</sub><sup>+</sup> with the soil and favored more NH<sub>3</sub>-N volatilization.

In the coarse-textured soil, the ammonium sulfate treatment produced the lowest NEP, but the compensatory effect resulted in a larger NGE. Thus, there was no difference in productivity. Haag et al. (2017) reported that the NGE benefits from the

compensatory effect mainly due to decreased PP. In the medium-textured soil, although there was no difference in the NEP, the urea+S<sub>A</sub> treatment produced the largest NGE, resulting in a higher GY, while urea+S<sub>B</sub> resulted in a small NGE. Soils with high P concentrations after liming favors the movement of sulfate to deeper layers (Rajan 1978), as in the medium-textured soil. The large amount of elemental S in urea+S<sub>A</sub> may have been oxidized and released gradually, while the sulfate from urea+S<sub>B</sub> and ammonium sulfate was probably transported to the deep soil layers. Nevertheless, the oxidation of elemental S is slow, about 20 days to start (Horowitz and Meurer 2006), while the definition phase of maximum number of rows per ear is on V8 growth stage, when the treatments were applied, and the maximum potential of ovule formation is established on V12 (Abendroth et al. 2011).

The greater N concentrations in urea+S resulted in lower transportation costs, improved operational performance, and avoided frequent fertilizer shipments (Franco and Saraiva Neto 2007). Because S is supplied with the applications of urea+S, the S concentrations in the maize leaves were high, and this result was even more pronounced with application of urea+S<sub>A</sub> in the coarse-textured soil, possibly due to the S in its elemental form. In addition, the soils with high P concentrations tended to leach sulfate (Rajan 1978), and the slowly oxidized elemental S results in the advantage of avoiding the loss of S to deep soil layers, favoring S uptake by plants during plant cycles and for the next season crop. It is worth mentioning that the oxidation of elemental S is inversely proportional to the clay content in the soil (Germida and Janzen 1993).

The S deficiency in the medium-textured soil may be fundamental to the differences observed in the yield components and GY. When this deficiency was prevented by the urea+S but not by the urea, the NGE and GY with the urea+S<sub>A</sub> treatment were higher than that with the urea treatment. The fine-textured soil, which had a higher SOM concentration compared with the other soils, had a very high initial concentration of S (Rajj et al. 1997), which may have eliminated the effect of S supply on the leaf S concentrations.

Because S and N are common elements in the composition of many proteins (Dijkshoorn and van Wijk 1967), it is expected that supplying these elements could result in maize grains with a greater nutritional value. In this case, when urea+S was applied to the fine-textured soil, a high concentration and accumulation of N in the grains occurred, which was similar to the effect of ammonium sulfate. Nevertheless, no differences were observed in the N accumulated in the grains from the coarse- and medium-textured soil.

## 5 Conclusions

The micronized sulfur in the urea granule is not able to reduce losses through NH<sub>3</sub>-N volatilization on maize crop top-

dressing and the amount of  $\text{NH}_3\text{-N}$  losses is directly related to characteristic of each soil type. Despite the N losses due to  $\text{NH}_3\text{-N}$  volatilization, the application of urea+S provided adequate N nutrition to the maize plants, resulting in GYs similar to those observed following the application of other N sources with low  $\text{NH}_3\text{-N}$  volatilization, such as ammonium nitrate and ammonium sulfate. The urea+S provided S in a form available to the plants. Maize growing in coarse-textured soils, such as sandy and sandy clay loam soils, appeared to be more responsive to urea+S since the S concentration in these soils was low.

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## Compliance with Ethical Standards

**Conflict of Interest** The authors declare that they have no conflict of interest.

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