

Performance of Urea-Based Fertilizers Associated With Elemental Sulfur or Polymers on Ammonia Volatilization

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Received: January 13, 2021

Accepted: February 21, 2021

Online Published: March 15, 2021

doi:10.5539/jas.v13n4p73

URL: <https://doi.org/10.5539/jas.v13n4p73>

Abstract

High N-NH₃ losses are expected when conventional urea is applied to the soil surface. In order to reduce it, urea granules could be coated with different materials to decrease fertilizer dissolution rate or to stabilize N-NH₄⁺ by acidification. In this study, we investigated the effect of a polymer-coated urea and powdered S⁰ added to urea, in the presence or absence of a S-oxidizing bacterium (*Acidithiobacillus thiooxidans*), on soil pH, SO₄²⁻ availability, NH₄⁺, and NH₃ volatilization. Applying S⁰ before urea and the inoculation with bacteria have promoted the highest S⁰ oxidation rates. The greater decrease in soil pH occurred when S⁰ was applied before urea at a higher dose, which also decreased NH₃ volatilization by 83% up to 4 days after urea application. However, the decrease in soil pH did not increase the concentration of NH₄⁺, nor did it decrease the accumulated amount of volatilized NH₃ over time. The inoculation of *A. thiooxidans* accelerates S⁰ oxidation process, but it was insufficient to counteract the H⁺ consumption by urea hydrolysis. Therefore, the S⁰ application with urea did not offer chemical protection against NH₃ loss, but a physical barrier in the controlled-release urea had less dissolved urea in soil and reduced NH₃ losses.

Keywords: N-fertilizer, slow-release, urease, S⁰, NH₃ volatilization

1. Introduction

Urea is a solid N-fertilizer with the highest concentration of N (46%) and the lowest cost per unit of nutrient. Nevertheless, N losses by ammonia (NH₃) volatilization decrease its agronomic efficiency. In soil, urea is hydrolyzed to NH₃ and CO₂ (Sigurdarson et al., 2018), and NH₃ can be lost to the atmosphere as a gas. The acidity around the granule application region is a key driver of a lower NH₃ volatilization (Longo & José De Melo, 2005; Viero et al., 2014) because if there is sufficient H⁺ in the medium, the NH₃ is converted to NH₄⁺ (da Costa et al., 2019), which is a more stable N-specie in soil. Hence, the application of acidifying substances together with urea might lower the emission of NH₃ and temporarily keep a higher NH₄⁺ concentration in soil (Trenkel, 2010).

Elemental sulfur (S⁰) is a high-purity S-source (> 98%), and due to this, a small mass of product would be required to satisfy the ideal H⁺ demand for N hydrolysis in urea granules. However, the form of sulfur absorbable by plants is sulfate (SO₄²⁻). Thus, oxidation of S⁰ is mediated by soil microbes, such as bacteria of the genus *Acidithiobacillus*, which produces H₂SO₄ that is readily dissociated in soil solution as SO₄²⁻ and 2H⁺ (Li et al., 2005; Kupka et al., 2009). If we consider the hypothetical reaction CO(NH₂)₂ + S⁰ + 3/2O₂ → 2NH₄⁺ + H₂CO₃ + SO₄²⁻, the oxidation of one mole of S should neutralize the alkalinity produced by one mole of urea; hence, the ideal mass ratio of S/N is 1.145. In controlled-release urea fertilizers, S⁰ is used together with polymers as a coating on urea granules to retard the granule dissolution due to hydrophobic nature of those substances (Wang et al., 2019). However, although the polymer layer improves the granule coating quality, it limits the action of microorganisms in the S⁰ oxidation (Zhao et al., 1996).

Fine particles of S⁰ have faster oxidation in soil because of their high specific surface (Chapman, 1989; Friesen, 1996). However, the application of powdered S⁰ results in losses by wind and poor distribution, and it might irritate the human airway (Boswell & Friesen, 1993). Alternatively, adherent substances are used to protect S⁰ on

urea granules, decreasing the segregation of the mixture and maintaining the large surface of S^0 particles, which is a condition more favorable to S^0 oxidation. Moreover, applying S^0 together with urea, rather than separately, reduces the costs of fertilizer's application. However, there is little information about the effect of this association in the acidity and stability of NH_4^+ in soil. Therefore, the objective of this study was to investigate the performance of urea-based fertilizers associated with S^0 or polymer application in the presence or absence of bacteria *Acidithiobacillus* on the volatilization of NH_3 and stabilization of NH_4^+ in soil.

2. Method

The experiment was conducted using a forced airflow system adapted to capture volatilized NH_3 . Powder elemental sulfur (S^0) was passed through a 320-mesh sieve. We tested the following: urea (45% N) with and without application of powdered elemental sulfur, an early application of S^0 and *Acidithiobacillus thiooxidans*, and commercially controlled-release urea coated with S^0 , polyolefins and ethylene-vinyl acetate copolymers-EVAC (accounted for 3% of coated fertilizers weight and 37% N and 16% S).

The soil used was a Ustox Oxisol, sieved through a 1 mm sieve, containing 190 g kg^{-1} of clay, 40 g kg^{-1} of silt, 770 g kg^{-1} of sand, 160 g kg^{-1} of maximum water retention, 12 g kg^{-1} of organic matter, 12.7 mg dm^{-3} of S and $4.8 \text{ cmolc dm}^{-3}$ of cation exchange capacity and pH 5.6.

The 12 treatments are described in Table 1. Eight treatments were obtained from the combination of two S^0 doses (0.86 and 2.29 g dm^{-3}) in powder form ($< 0.053 \text{ mm}$), early S^0 application (12 d), or S^0 -urea joint application and the presence or absence of *A. thiooxidans*. Two treatments corresponded to a commercial controlled-release urea in the presence or absence of *A. thiooxidans*. In addition, two other treatments corresponding to the application of only urea and one control, without the application of S^0 . The N dose was 2 g kg^{-1} , corresponding to an S/N ratio equal to 0.43 and 1.15 for the S^0 doses 0.86 and 2.29 g kg^{-1} , respectively. Elemental sulfur and urea were applied at 0.5 cm soil depth as well as $140 \mu\text{L}$ of a suspension containing 109 mL^{-1} cells of *A. thiooxidans*. Soil samples were collected immediately before N-urea application and 4, 9, 15, and 19 d after that. A completely randomized experimental design was used. Sixty experimental units were obtained from the combination of the 12 treatments (Table 1) with the five sampling times, and we had three replications per experimental unit.

Table 1. Description of treatments

Treatments	$S^0 \text{ (g dm}^{-3}\text{)}$	TI ‡
Control	0	Control
Urea	0	U
Urea + early S^0 application †	0.86	U + S^0_e
Urea + early S^0 + <i>A. thiooxidans</i> †	0.86	U + S^0_{ei}
Urea + S^0	0.86	U + S^0
Urea + S^0 + <i>A. thiooxidans</i>	0.86	U + S^0_i
Controlled release urea	0.86	CRU
Controlled release urea + <i>A. thiooxidans</i>	0.86	CRU _i
Urea + early S^0 application †	2.29	U + S^0_e
Urea + early S^0 † + <i>A. thiooxidans</i>	2.29	U + S^0_{ei}
Urea + S^0	2.29	U + S^0
Urea + S^0 + <i>A. thiooxidans</i>	2.29	U + S^0_i

The experimental units consisted of Falcon tubes (50 mL) containing 45 cm^3 of soil. Five tubes of the same treatment were grouped and put into the volatilization chambers. Soil moisture was maintained between 85 and 100% of the water retention capacity of the soil, by monitoring the weight of experimental units; room temperature was $25 \pm 2 \text{ }^\circ\text{C}$.

The volatilization chambers were closed glass pots with approximately 1.5 L of internal volume. They were connected to an air inlet tube ($6.25 \text{ cm}^3 \text{ min}^{-1}$) and an air outlet pipe connected to Erlenmeyer flasks (125 mL) containing 25 mL of boric acid (20 g L^{-1}) and methyl red and bromocresol green as a color indicator for collecting NH_3 (g). To avoid potential contamination with NH_3 from the atmosphere, the airflow inlet system was filtered through a phosphoric acid solution (pH < 3.6).

Ammonia collected in the boric acid solution was titrated with $\text{HCl } 0.005 \text{ mol L}^{-1}$. Volatilization chambers were quickly opened to collect one tube at each time of incubation for soil analyses. After the experiment, soil samples

were air-dried for pH and electrical conductivity determination in a soil suspension:water (ratio 1:2.5), $\text{NH}_4^+\text{-N}$ (Kempers & Zweers, 1986), $\text{NO}_3\text{-N}$ (Cataldo et al., 1975), and $\text{SO}_4^{2-}\text{-S}$ (Hoeft et al., 1973).

The results were submitted to analysis of variance and the treatments were compared within each time by the Tukey test at 5% of probability. We calculated the Pearson linear correlation coefficients for the variables NH_4^+ , pH, SO_4^{2-} , accumulated NH_3 , and rate of NH_3 volatilization using the software R version 3.2.0. We adjusted equations through linear and nonlinear models for accumulated NH_3 using the *Stats* package of the software R.

3. Results

3.1 NH_3 -Volatilization

There were contrasting differences between treatments in terms of NH_3 volatilization (Table 2, Figure 1). In fact, the accumulated of N- NH_3 volatilization for up to 19 d corresponded to 65% of the total N applied as urea, 56% for urea combined with the application of powdered S^0 , regardless of the application time or dose of S^0 , and 3% for the controlled-release urea. On average, NH_3 volatilization was 95% lower for the controlled-release urea than conventional urea.

Table 2. Adjustment of sigmoidal and linear equations for the percentage of accumulated $\text{NH}_3\text{-N}$ (g) as a function of incubation time (t).

Treatment	Dose of S^0 (g dm^{-3})	Equation	Estimated parameters			R^2
			n	b	$t_{50\%}$	
U	0		62.78	2.513	6.5	0.98
U + S^0ei	0.86	$\hat{y} = \frac{n}{1 + (\frac{1}{10})^{\frac{1}{b(t-t_{50\%})}}}$	57.63	2.072	6.8	0.99
U + S^0e	0.86		49.38	2.007	6.0	0.99
U + S^0i	0.86		54.62	2.022	5.2	0.98
U + S^0	0.86		57.09	2.297	6.3	0.99
CRUi	0.86	$\hat{y} = bt$	0.04235 ^(0.10)			0.72
CRU	0.86		0.10758 ^{**}			0.69
U + S^0ei	2.29	$\hat{y} = \frac{n}{1 + (\frac{1}{10})^{\frac{1}{b(t-t_{50\%})}}}$	55.76	1.365	7.8	0.99
U + S^0e	2.29		53.99	1.947	6.6	0.99
U + S^0i	2.29		52.38	2.149	6.0	0.96
U + v	2.29		54.87	1.971	6.0	0.98

Note. For sigmoidal equations: $\text{NH}_3\text{-N}$ maximum (n); maximum rate of NH_3 volatilization ($1/b$), $\text{dag kg}^{-1} \text{d}^{-1}$; days for 50% of $\text{NH}_3\text{-N}$ maximum ($t_{50\%}$). For linear equations: (**) and (0.10) indicate significance at 1 or 10% by t-test. U = Urea; U + S^0ei = Urea + early S^0 + *A. thiooxidans*; U + S^0e = Urea + early application; U + S^0i = Urea + S^0 + *A. thiooxidans*; U + S^0 = Urea + S^0 ; CRUi = Controlled release urea + *A. thiooxidans*; CRU = Controlled-release urea.

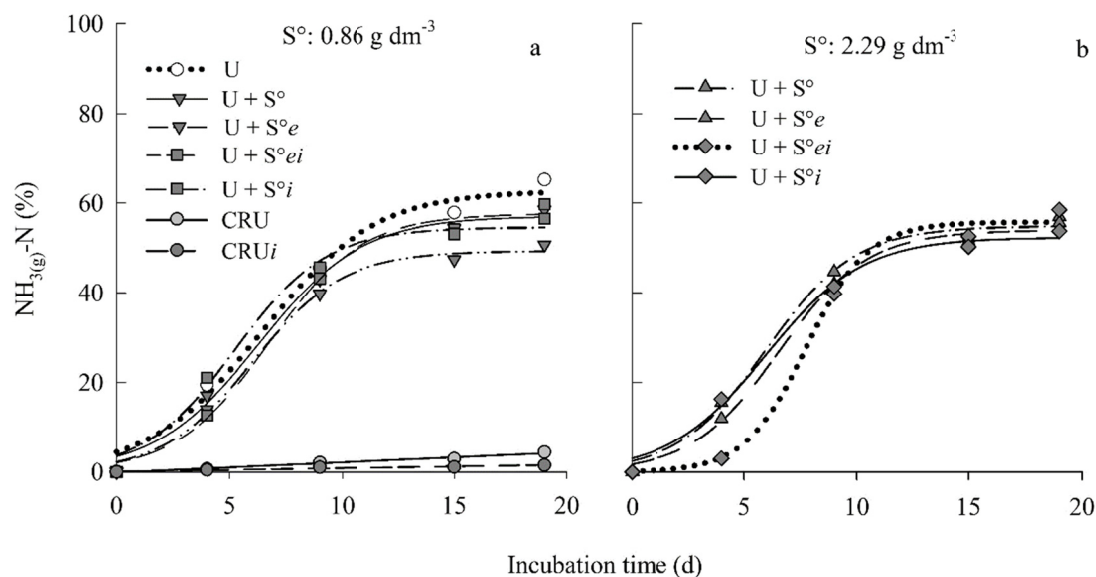


Figure 1. Accumulated $\text{NH}_3\text{-N}$, as a percentage of urea-N applied, estimated by sigmoidal and linear equations. Treatments: urea (U); urea + application of elemental sulfur ($\text{U} + \text{S}^0$); urea + early application of elemental sulfur at 12 d ($\text{U} + \text{S}^{0e}$); urea + early application of elemental sulfur and *A. thiooxidans* at 12 d ($\text{U} + \text{S}^{0ei}$); urea + application of elemental sulfur and *A. thiooxidans* ($\text{U} + \text{S}^{0i}$); controlled-release urea (CRU) or controlled-release urea + application of *A. thiooxidans* (CRUi)

The maximum percentage of NH_3 loss estimated by sigmoidal and linear models ranged from 63 (U) to 49% ($\text{U} + \text{S}^{0e}$; $0.86 \text{ g kg}^{-1} \text{ S}^0$) of N applied (Table 2, Figure 1). The highest rates of NH_3 volatilization were $7.3 \text{ g kg}^{-1} \text{ d}^{-1}$ for the $\text{U} + \text{S}^{0ei}$ treatment and the lowest was $4.4 \text{ g kg}^{-1} \text{ d}^{-1}$ for the $\text{U} + \text{S}^0$ treatment (Table 2).

The application of S^0 (0.86 or 2.29 g kg^{-1}) and urea at the same time, regardless of inoculation, had no significant effect on NH_3 volatilization. Comparisons between treatments, not including controlled-release urea, highlighted $\text{U} + \text{S}^{0ei}$ (at 2.29 g kg^{-1} of S^0) by promoting a dramatic reduction in NH_3 volatilization for up to 9 d after incubation (Figure 1).

3.2 $\text{NH}_4^+\text{-N}$ in Soil

The controlled-release urea (CRU and CRUi) had a more gradual release and hydrolysis; consequently, the concentration of NH_4^+ in soil was lower than (50%) other treatments, up to day 9 after N application (Figure 2). However, the concentration of NH_4^+ in the soil gradually increased until day 19, when there were no differences in NH_4^+ concentrations in the soil.

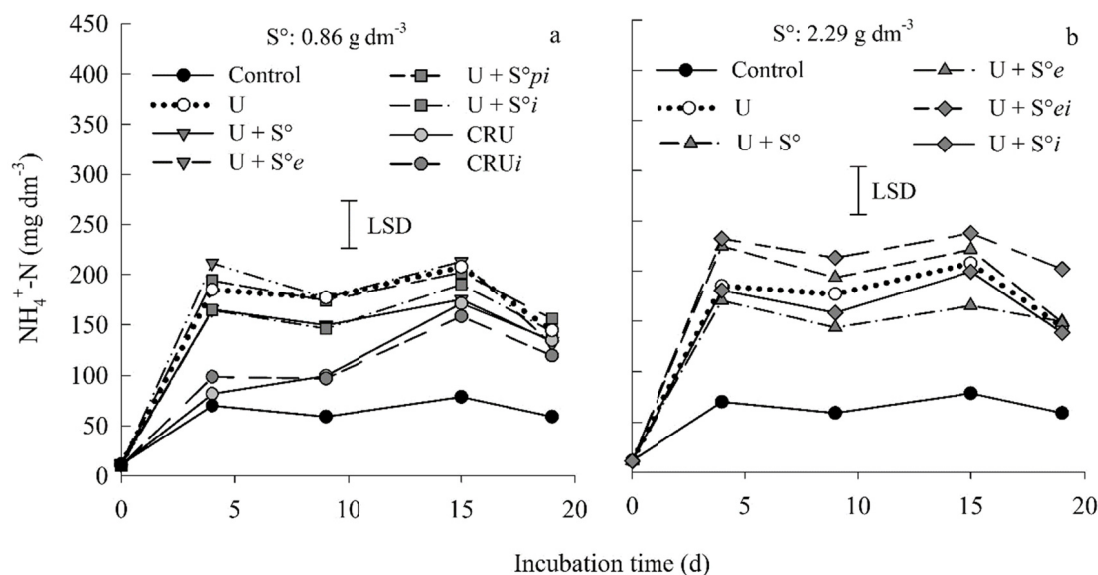


Figure 2. Concentration of $\text{NH}_4^+\text{-N}$ in soil. Treatments: control without fertilizer application; urea (U); urea + application of elemental sulfur ($\text{U} + \text{S}^0$); urea + early application of elemental sulfur at 12 d ($\text{U} + \text{S}^0e$); urea + early application of elemental sulfur and *A. thiooxidans* at 12 d ($\text{U} + \text{S}^0ei$); urea + early application of elemental sulfur and *A. thiooxidans* ($\text{U} + \text{S}^0i$); urea protected with elemental sulfur and polymer coating (CRU) or urea protected with elemental sulfur and polymer coating + application of *A. thiooxidans* (CRUi). Vertical bars indicate the least significant difference (LSD = 47.54) between treatments (Tukey test, $p = 0.05$)

3.3 $\text{SO}_4^{2-}\text{-S}$ in Soil

There were significant effects of treatments on the $\text{SO}_4^{2-}\text{-S}$ concentration in soil. When S^0 was applied earlier, in the presence of *A. thiooxidans* ($\text{U} + \text{S}^0ei$), $\text{SO}_4^{2-}\text{-S}$ concentrations reached higher values (Figure 3), also demonstrating on contrasting S^0 doses. In fact, for $\text{U} + \text{S}^0ei$ treatment, the concentrations of $\text{SO}_4^{2-}\text{-S}$ in soil were 51 and 167 mg dm^{-3} for 0.86 and 2.29 g dm^{-3} S^0 , respectively, which corresponded to the recovery of 6 and 7% of the total S^0 applied, for low and high S^0 doses, respectively. For other treatments containing S^0 , there were no significant increases in the concentrations of $\text{SO}_4^{2-}\text{-S}$ in soil, even under the inoculation with *A. thiooxidans* (Figure 3).

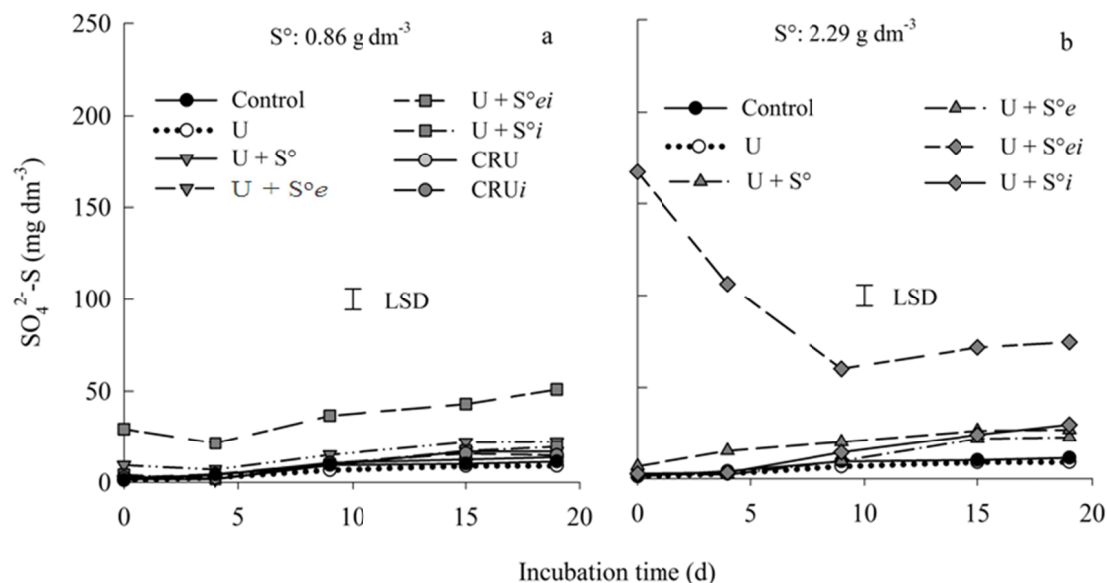


Figure 3. Concentration of $\text{SO}_4^{2-}\text{-S}$ in soil. Treatments: control without fertilizer application; urea (U); urea + application of elemental sulfur ($\text{U} + \text{S}^0$); urea + early application of elemental sulfur at 12 d ($\text{U} + \text{S}^0e$); urea + early application of elemental sulfur and *A. thiooxidans* at 12 d ($\text{U} + \text{S}^0ei$); urea + early application of elemental sulfur and *A. thiooxidans* ($\text{U} + \text{S}^0i$); urea protected with elemental sulfur and polymer coating (CRU) or urea protected with elemental sulfur and polymer coating + application of *A. thiooxidans* (CRUi). Vertical bars indicate the least significant difference (LSD = 11.40) between treatment (Tukey test, $p = 0.05$)

3.4 pH

The previous S^0 application associated with the inoculation with *A. thiooxidans* affected soil pH for both S^0 doses. Indeed, the pH values decreased from 6.0 to 5.3 and 6.0 to 4.0 when S^0 was applied at doses of 0.86 and 2.29 g dm^{-3} , respectively (Figure 4). However, when urea was applied, the soil pH increased for all fertilizer treatments. The soil pH reached maximum values of 6.36 for the control, 7.49 for urea, 6.85, 7.01, 7.60, 7.68, 7.73, and 8.01 when the dose 0.86 g kg^{-1} of S^0 was used for CRU, CRUi, $\text{U} + \text{S}^0ei$, $\text{U} + \text{S}^0i$, $\text{U} + \text{S}^0$, and $\text{U} + \text{S}^0e$, respectively. When we used 2.29 g kg^{-1} of S^0 , the maximum pH values were 7.01, 7.76, 7.90, and 8.15 for $\text{U} + \text{S}^0ei$, $\text{U} + \text{S}^0i$, $\text{U} + \text{S}^0e$, and $\text{U} + \text{S}^0$, respectively.

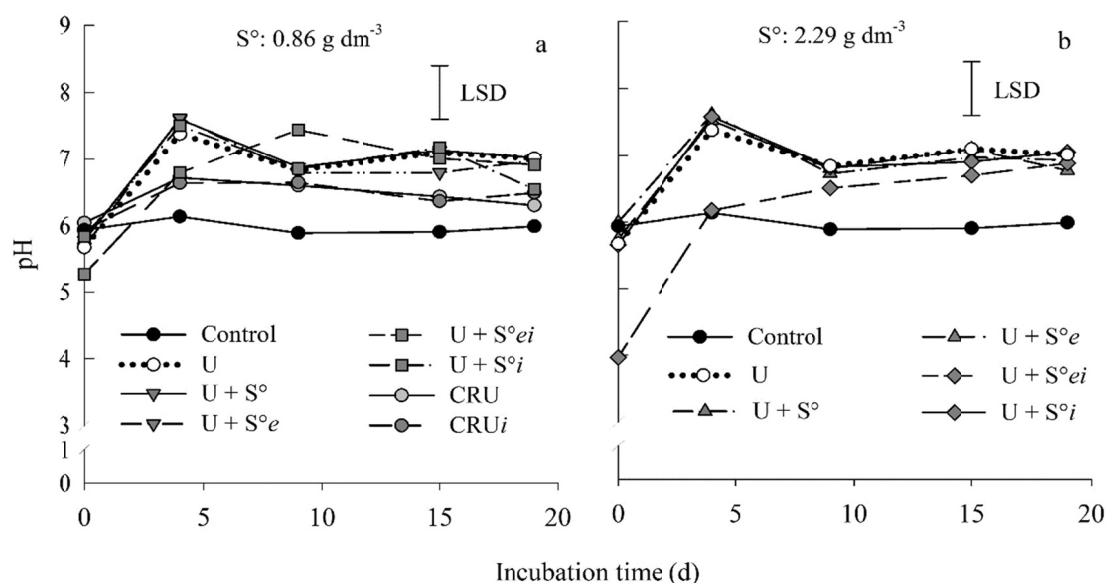


Figure 4. pH of soil: water (1:2.5) suspension. Treatments: control without fertilizer application; urea (U); urea + application of elemental sulfur ($U + S^0$); urea + early application of elemental sulfur at 12 d ($U + S^0e$); urea + early application of elemental sulfur and *A. thiooxidans* at 12 d ($U + S^0ei$); urea + early application of elemental sulfur and *A. thiooxidans* ($U + S^0i$); urea protected with elemental sulfur and polymer coating (CRU) or urea protected with elemental sulfur and polymer coating + application of *A. thiooxidans* (CRUi). Vertical bars indicate the least significant difference (LSD = 0.83) between treatment (Tukey test, $p = 0.05$)

3.5 NO_3^- -N in Soil

The concentration of nitrate in soil tended to increase over incubation time; however, there was no significant difference between control and urea-based treatments. Moreover, controlled-release urea treatments had higher values of nitrate in soil from nine days after its application, especially when the S^0 dose was lower (Figure 5).

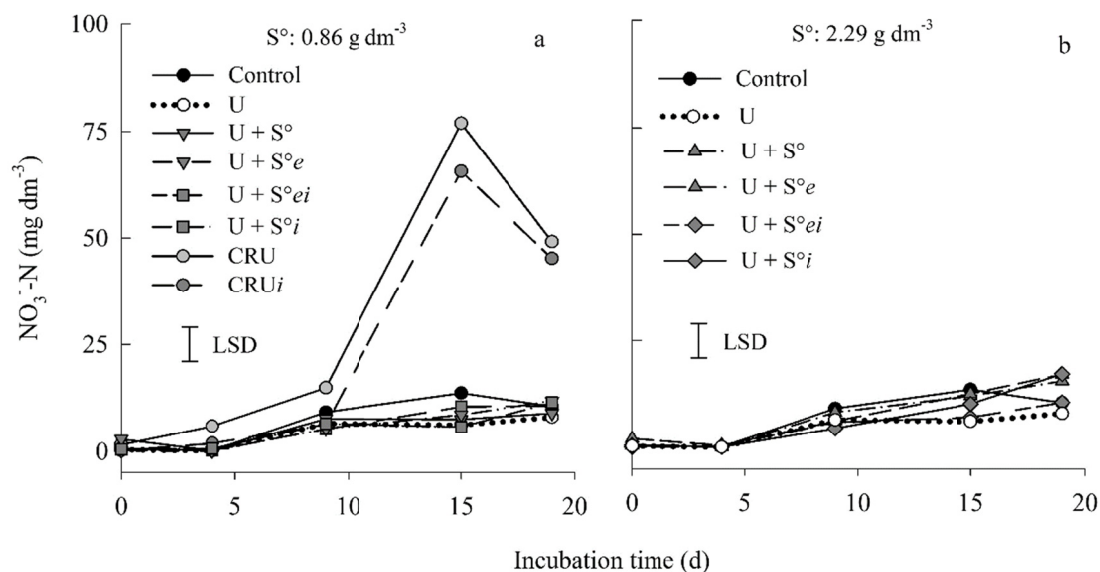


Figure 5. Concentration of NO_3^- -N in soil. Treatments: control without fertilizer application; urea (U); urea + application of elemental sulfur ($U + S^0$); urea + early application of elemental sulfur at 12 d ($U + S^0e$); urea + early application of elemental sulfur and *A. thiooxidans* at 12 d ($U + S^0ei$); urea + early application of elemental sulfur and *A. thiooxidans* ($U + S^0i$); urea protected with elemental sulfur and polymer coating (CRU) or urea protected with elemental sulfur and polymer coating + application of *A. thiooxidans* (CRUi). Vertical bars indicate the least significant difference (LSD = 8.03) between treatment (Tukey test, $p = 0.05$)

3.6 Correlation

There was a significant positive correlation between NH_4^+ and accumulated NH_3 (0.64**), volatilization rate of NH_3 (0.59**) or pH (0.74**), but not with SO_4^{2-} -S (0.15^{ns}) (Table 3). Between pH and accumulated NH_3 , the correlation was 0.55***. Furthermore, there was no correlation between SO_4^{2-} and accumulated NH_3 (0.10^{ns}).

Table 3. Coefficients for Pearson's correlation test

	NH_3 (mg/dm ³ /day)	NH_3 (mg/dm ³ -accumulated)	NH_4^+	NO_3^-	SO_4^{2-}	CE ($\mu\text{S}/\text{cm}^2$)	pH
NH_3 (mg/dm ³ /day)	1						
NH_3 (mg/dm ³ -accumulated)	0.33***	1					
NH_4^+	0.59***	0.64***	1				
NO_3^-	-0.08 ^{ns}	0.67***	0.25**	1			
SO_4^{2-}	-0.09 ^{ns}	0.1 ^{ns}	0.15°	0.08 ^{ns}	1		
CE ($\mu\text{S}/\text{cm}^2$)	0.37**	0.41***	0.65***	0.11 ^{ns}	0.73***	1	
pH	0.57**	0.55***	0.74***	0.19*	-0.33***	0.22**	1

4. Discussion

The oxidation of S^0 in fact induces soil acidification, but it was overall demonstrated not to be enough to reduce ammonia volatilization from urea fertilizer. Our results showed that even with the previous application of powdered S^0 (2.29 g dm⁻³) in soil and inoculation with *A. thiooxidans*, the time was delayed by only one day to reach 50% of the maximum NH_3 volatilization. Moreover, there were no differences between powered S^0 -urea treatments on NH_3 accumulated up to day 19. It was clear that S^0 oxidation is a slow process in the soil, while the dissolution and hydrolysis of the urea granules are very fast reactions in the soil. Therefore, both processes occur without close synchrony in the soil.

We hypothesize that the kinetic of H^+ production by S^0 oxidation (Equation 1) was below the requirement to stabilize N- NH_4^+ (Equation 4), due to the fast hydrolysis of urea and the resulting N- NH_3 volatilization (de Oliveira et al., 2014) (Equations 3 and 4) associated with the low rate of S^0 oxidation in soil. Consequently, the NH_3 volatilization was reduced only up to day 9 after the application of urea, even under suitable conditions for S^0 oxidation, such as a higher S/N ratio (1.1:1), early S^0 application, and inoculation with *A. thiooxidans*. Although S^0 is a hydrophobic substance, the simple mixture with urea does not change urea granule dissolution and the dynamics of N in the soil. On the other hand, controlled-release urea, coated by S^0 and polymers, had a slowed dissolution and reduced N volatilization over time.



Nitrogen fertilizers such as $(\text{NH}_4)_2\text{SO}_4$ or NH_4NO_3 have less NH_3 volatilization (de Oliveira et al., 2014; Cabezas et al., 2008) because of their acid reaction in soil. On the other hand, urea hydrolysis causes the formation of CO_2 , water, and NH_3 (Zavaschi et al., 2014). Such reaction tends to increase soil pH (less H^+ to convert NH_3 to NH_4^+) around the point of its application and the losses by volatilization are intensified (Longo & José De Melo, 2005; Behera et al., 2013). Subsequently, H^+ is produced again in the soil by nitrification under oxidic conditions (Equations 5 and 6).



The previous S^0 application and inoculation with *A. thiooxidans*, especially in the higher proportion of S^0 :N (1.1:1), increased the SO_4^{2-} concentration in the soil. Even though the increased concentration of SO_4^{2-} -S is an indicator of S^0 oxidation, the extractable S in the soil may underestimate the total oxidation, as our results suggest, because of both the immobilization of SO_4^{2-} -S and adsorption by soil colloids (Zhao et al., 2016). The S^0 oxidation rate in the soil is influenced by the particle size and S^0 dose (Lucheta & Lambais, 2012; López-Mosquera et al., 2015); consequently, the use of the higher dose (2.29 g dm⁻³) powdered S^0 produced more H^+ compared to the dose of 0.86 g dm⁻³, as was demonstrated here.

Like already demonstrated, even though inoculating S^0 with *A. thiooxidans* suspension may accelerate the S^0 oxidation in soil, the amount of produced H^+ was insufficient to counteract the urea hydrolysis reactions in terms of H^+ consumption. Moreover, we obtained low correlation coefficients between SO_4^{2-} concentrations and NH_3 volatilization rates. Interestingly, NH_4^+ and pH were positively correlated, suggesting that the effect of hydrolysis on the increase of soil pH is more predominant than the acidity due to S^0 oxidation.

From an analysis of nitrate concentration in the soil during the evaluation time, data showed that nitrification did not have important contributions to soil acidification. However, controlled-release urea treatments had more nitrate in soil compared to other fertilizer treatments, possibly because nitrification was inhibited under high NH_3 concentration and low acidity in soil (pH > 7.7) (Maharjan & Venterea, 2013; Katipoglu-Yazan et al., 2015). Hydrolysis reactions tend to be less intense with CRU because of the controlled release of urea from granules, leading to lower pH around the fertilizer application point compared to fast release urea fertilizers. The controlled-release urea has a double physical barrier that temporarily prevents the dissolution of the granule (Trenkel, 2010). Less dissolved urea in the soil solution reduces the urease activity and consequently, both the NH_4^+ concentration in soil and NH_3 volatilization are reduced.

Elemental sulfur composing controlled-release urea is less accessible for S-oxidizing microorganisms (Yasmin et al., 2007; Zhao et al., 2016) and therefore, these fertilizers have little value as a source of SO_4^{2-} in the first year of application (Boswell & Friesen, 1993; Solberg et al., 2007). In addition, our data support that inoculating *A. thiooxidans* in controlled-release urea has no influence on S^0 oxidation during the experimental time.

This study demonstrates that the chemical effects from the oxidation of S^0 in the soil are negligible in terms of stabilization of NH_4^+ when S^0 is applied in a mixture with urea or as a coating of controlled-release urea. However, applying S^0 in N fertilizers can be an inexpensive strategy to supply sulfur to plants in the medium and long term, because of its slow oxidation in soil.

5. Conclusions

Our results support that application of S^0 with urea has little effect on the chemical stability of the NH_4^+ -N in the soil due to the asynchrony between the reactions of S^0 oxidation and hydrolysis of urea. Although the application of *Acidithiobacillus thiooxidans* accelerates the acidity production through S^0 oxidation, the extra H^+ was consumed by urea hydrolysis when applied in a localized manner. On the other hand, the physical barrier in controlled-release urea had less dissolved urea in soil and reduced NH_3 volatilization losses.

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