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# Ammonia volatilization from enhanced-efficiency urea on no-till maize in brazilian cerrado with improved soil fertility

## Volatilização de amônia por ureia de eficiência aumentada no milho cultivado em solo de fertilidade construída

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## ABSTRACT

High nitrogen losses by ammonia volatilization are expected when urea is used as the source of N. The use of controlled-release urea and urease inhibitors are possible strategies to reduce such losses and increase nitrogen use efficiency. This study aimed to evaluate nitrogen losses by ammonia volatilization from stabilized, slow and controlled release urea and its absorption by maize grown under no-till in an improved Cerrado soil. Four N sources were used: conventional urea, urea + N-(n-butyl) thiophosphoric triamide (NBPT), urea + Cu and B and urea coated by sulfur + polymers. These N sources were surface applied along the rows using three N doses of 100, 150 and 200 kg ha$^{-1}$. No N was added to the control. Data were collected regarding N losses by volatilization, the N contents accumulated in the stubble and grains, and the yields of the stubble and grains. Stabilized urea and slow release urea were efficient for postponing the ammonia volatilization peaks. The urease inhibitors postponed the peaks for up to two days, reducing the accumulated volatilization by 18% when compared with common urea. Polymer sulfur coated urea resulted in a 37% reduction in ammonia volatilization. Increasing the N application rate to 200 kg ha$^{-1}$ resulted in 16% greater yields and 37% greater N accumulation in the plants relative to the control. However, the stabilized and slow-release urea did not improve the N accumulation or yield. Consequently, the nitrogen use efficiency of maize was not improved relative to the use of conventional urea.

**Index terms:** Nitrogen fertilizers; $NH_3$-N losses; polymer sulfur coated urea; urease inhibitors; *Zea mays* L.

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## RESUMO

A aplicação de ureia, frequentemente, gera grandes perdas de N por volatilização e o uso de revestimentos e inibidores de urease, podem reduzir essas perdas. Neste estudo, objetivou-se avaliar as perdas de nitrogênio pela ureia estabilizada e de liberação lenta ou controlada e sua absorção pelo milho cultivado em plantio direto, em solo de Cerrado, com fertilidade construída. Quatro fontes de N foram utilizadas: ureia convencional, ureia + N-(n-butyl)thiophosphoric triamide (NBPT), ureia + Cu + B e ureia revestida por enxofre e polímeros. Essas fontes de N foram aplicadas em superfície nas doses de 100, 150 e 200 kg ha$^{-1}$. Não houve aplicação de N no controle. Avaliaram-se as perdas de N por volatilização, o acúmulo de N nos grãos e palhada e produção de grãos e de palhada. A ureia estabilizada e de liberação controlada foi eficiente em atrasar os picos de volatilização de amônia. Os inibidores de urease atrasaram os picos de volatilização em até dois dias, reduzindo a volatilização acumulada em até 18%, quando comparado à ureia comum. A ureia revestida por enxofre e polímeros resultou em uma redução de 37% na volatilização de amônia. O aumento da dose de N até 200 kg ha$^{-1}$ resultou em aumento de 16% na produtividade e 37% no acúmulo de N em relação ao controle. Entretanto, a ureia estabilizada e de liberação controlada não aumentou o acúmulo de N ou a produtividade. Consequentemente, a eficiência no uso de N pelo milho não foi aumentada em relação ao use da ureia convencional.

**Termos para indexação:** Fertilizantes nitrogenados; perdas de N-$NH_3$; ureia revestida por enxofre e polímeros; inibidores de urease; *Zea mays* L.

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## INTRODUCTION

The global fertilizer industry faces growing challenges regarding the development of improved products that result in greater nutrient use efficiencies, especially regarding nitrogen sources. Moreover, the industry should aim to minimize negative environmental impacts, avoid mineral leaching into the water table or volatilization, and minimize the emissions of N oxides (a greenhouse gas) (Novoa; Tejeda, 2006; Stehfest; Bouwman, 2006; Vilain et al., 2014). These objectives have been achieved by aggregating available technologies with conventional fertilizers, such as urea, by reducing N losses and by increasing agronomic efficiency (Watson et al., 2008; Trenkel, 2010).

There are two methods for defining the agronomic efficiencies of fertilizer: i) the plant response to increasing rates and ii) the rate of applied nutrients that actually reach the plant. To increase fertilization efficiency, management practices have been developed worldwide (Du et al., 2006; Trenkel, 2010). Trenkel (2010) compiled various recommendations regarding the application of the right nutrients at the necessary quantities at a suitable time and place to supply the plant demands. In this context, various management practices have been developed, such as enhanced efficiency nitrogen fertilizers.

The consumption of stabilized fertilizers has increased around the world. The leading countries include the USA and Japan, followed by several West European countries. The American market for fertilizers has surpassed those of Europe and Japan by five and thirteen times, respectively. Stabilized urea or nitrogen fertilizers with nitrification inhibitors have been used in European countries, while in the USA and Japan the coated urea forms have dominantly been used (Trenkel, 2010). Currently, the prospect for increasing their use in these countries is approximately 1.5 – 5%.

Although there are no reports regarding the use of these forms and sources of nitrogen in Brazil, their demand has been increasing. With the growing demand and market, multiple queries have been made regarding stabilized or slow release fertilizers. For example, what are they and how can they improve fertilization efficiency, and how technically and economically viable are they?

Slow release or controlled release fertilizers have been defined as nutrient sources that retard or extend nutrient availability to plants over a longer time period than a reference source and synchronize nutrient release with plant demand (Trenkel, 2010). Generally, the reference source of nitrogen is urea. Stabilized fertilizers are those in which a compound is added to inhibit its transformation into other chemical forms, such as in urea. These compounds increase the time that N remains in its initial form, either as urea or ammonium. These can be grouped into two classes, i) nitrification inhibitors, which are substances that inhibit biological oxidation (such as ammonium to nitrate), and ii) urease inhibitors, which are substances that inhibit urease enzymes and retard urea hydrolysis.

However, these definitions do not include differences between slow release and controlled release fertilizers. The definition of controlled release fertilizers has been accepted as when the speed of nutrient release is controlled by the addition of a compound during processing. Therefore, slow release fertilizers differ from reference fertilizers, for which the rate at which nutrients become available is not controlled. These concepts can be exemplified by considering urea, which is the most widely used N source worldwide. When urea contacts moist soil, it instantly releases N. When urea is coated with sulfur, the nutrient granule is protected, which slows the N release, but does not control it. In addition, coating the granule with a plastic resin can promote controlled N release from urea to the soil. Interestingly, the controlled release N sources are more expensive than the stabilized and slow release N sources, which restricts its use in low value field crops (Trenkel, 2010). Overall, one benefit of using stabilized, slow or controlled release urea is the reduced volatilization when it is used as the only N source.

This work aimed to evaluate N losses by volatilization from stabilized, slow or controlled release urea (compared with pure urea) and to evaluate nutrient use by maize in no-till Cerrado soils.

## MATERIAL AND METHODS

### Experimental site and treatments

This experiment was conducted at the Federal University of Lavras (UFLA), which is located at 21°13’30”S and 44°58’51”W at the altitude of 915 m.a.s.l. The soils in this area are classified as dystrophic Red Latosols (Empresa Brasileira de Pesquisa Agropecuária-Embrapa, 2013) or Hapludox (Soil Survey Staff, 1999) and were limed, fertilized and subjected to no-till cultivation during the last 15 years. The climate is classified as Cwb according to the Köppen-Geiger climate classification system (Kottek et al., 2006), with mild and rainy summers and dry winters. The annual rainfall and average temperature were 1,493 mm and 19.3 ºC, respectively.

Before the experiment, soil samples were collected at a depth of 0-20 cm depth for chemical and physical characterization which presented the following results: $pH_{(water\ 2.5:1)} = 5.7$, $K^+ = 64$ mg dm$^{-3}$, $P_{(Mehlich\text{-}1)} = 33$ mg dm$^{-3}$, $Ca^{2+} = 3.3$ cmol$_c$ dm$^{-3}$, $Mg^{2+} = 1.2$ cmol$_c$ dm$^{-3}$, $Al^{3+} = 0.1$ cmol$_c$ dm$^{-3}$, H+Al = 3.62 cmol$_c$ dm$^{-3}$, SOM = 3.0 dag kg$^{-1}$, $P_{rem} = 5.3$ mg L$^{-1}$, Zn = 11.2 mg dm$^{-3}$, Fe = 28.9 mg dm$^{-3}$, Mn = 33.5 mg dm$^{-3}$,Cu = 4.5 mg dm$^{-3}$, B = 0.10 mg dm$^{-3}$, $S\text{-}SO_4^{2-} = 14.7$ mg dm$^{-3}$, Clay = 640 g kg$^{-1}$.

A complete randomized block experimental design was used with a 4 × 3 + 1 factorial and three repetitions. The following treatments were used: urea; coated urea with sulfur and organic polymer; urea + boron + copper; and urea + NBPT. These treatments were banded using three doses, 100, 150 and 200 kg ha$^{-1}$ N, and including a control with no added N. Ammonia volatilization was not included for the 200 kg ha$^{-1}$ dose. Thus, for this variable, the experimental design was conducted using a 4 × 2 + 1 experiment with three repetitions.

Each plot consisted of six rows that were 7 m long with a row spacing of 0.6 m. The harvested area was comprised of 5 m within four central rows, where the two external rows and 1 m of the ends of the rows were used as borders. The method resulted in a population density of 80,330 plants ha$^{-1}$.

### Fertilizer characteristics and analyses

Urea: Conventional urea fertilizer prilled with 45% N.

Urea + Cu + B: Urea fertilizer prilled with 44.6% of N and with 1.5 g kg$^{-1}$ Cu in the form of copper sulfate and 4 g kg$^{-1}$ B in the form of boric acid. Both, copper sulfate and boric acid have particle sizes of less than 0.015 mm and evenly spread over the granules in the rotating drum.

Urea + NBPT: Urea fertilizer granules with 45% of N with industrial applied NBPT urease inhibitor at the urea granule surface.

Coated urea: Urea coated with an elemental sulfur layer plus an organic polymer with 30% of its total N in the form of conventional urea and no coating for immediate N release. The total nitrogen content was 40%, with 7.9% elemental sulfur ($S^0$). This treatment represents the controlled nitrogen release due to a physical barrier, which prevents its dissolution in water. According to the supplier, the nitrogen is released for up to three months.

Once the N fertilizer sources were chosen to use as treatments, they were characterized using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). These analyses were made in the Electronic Microscopy and Ultrastructural Analysis Laboratory at the Plant Pathology Department at UFLA. The fertilizer samples were mounted on stubs and cut using a scalpel before metalizing in a carbon evaporator (model Union CED 020) and obtaining the SEM images (model LEO EVO 40 XVP Zeiss). The samples were qualified and mapped to determine their chemical compositions using EDS (model Quantax XFlash 5010 Bruker) (Figure 1).

For the maize crop, the Geneze 9626 VT PRO Yield Gard® hybrid was used. Seeds were treated with Furazin® insecticide at the rate of 22.5 mL kg$^{-1}$. During sowing, 360 kg ha$^{-1}$ of formulated fertilizer (08-28-16 + 0.05% B, 0.06% Mn and 0.27% Zn) was applied in the rows. Sowing and fertilization were conducted mechanically on 05/12/2012. Thirteen days after sowing, the area received a dressing of 80 kg $K_2O$ ha$^{-1}$ in the form of potassium chloride (KCl). A mixture of 0.2 L ha$^{-1}$ Soberan® and 2.5 L ha$^{-1}$ Atrazine® + 0.5% adjuvant in 200 L ha$^{-1}$ of water was used for weed control and repeated after 15 days.

The N fertilizers (treatments) were applied manually 10 cm apart from maize plants 31 days after sowing. At this time, the plants had five fully expanded leaves ($V_5$ phase).

### Ammonia quantification

The ammonia was quantified by using a semi-open static collector and PVC tubes with a diameter of 20 cm and a height of 50 cm. These tubes were inserted in the soil to a depth of 5 cm and were covered by two discs of polyethylene foam (0.02 g cm$^{-3}$ density and 2.5 cm thick) that were cut to the same diameter as the tubes. Before covering the tubes, the foam discs were soaked by 85 mL phosphoric acid ($H_3PO_4$) and glycerin at 40 and 58.8 mL L$^{-1}$ (0.87 mol L$^{-1}$ $H_3PO_4$) and fixed at 25 and 45 cm from the soil surface. The top sponge was used to avoid contamination of the lower sponge, which was changed on the 1st, 2nd, 3rd, 4th, 5th, 7th, 10th, 13th, 17th, 23rd and 33rd day after treatment.

The solution retained in the foam collected in the field was extracted by filtering through a Büchner funnel using a vacuum pump after 5 sequential washings with 80 mL de-ionized water. From the extract, aliquots were taken to determine the N contents of the samples using the Kjeldahl method.

### Stubble and grain yield and nitrogen accumulation

The estimated stubble yield at harvest was based on 20 plants per plot that were cut at the soil surface. After removing the ear and sheath, the remaining plant parts were weighed and cut in a forage grinder. A sample was collected from the dried material and immediately placed in a muffle furnace at 65 °C until a constant weight was obtained. Finally, the dried sample was milled (Willey TM) and homogenized for N analysis by sulfuric acid digestion, followed by Kjeldahl distillation and titration. Maize ears were harvested and threshed, and the grains were weighted correcting for a moisture content of 14% to obtain the yield.

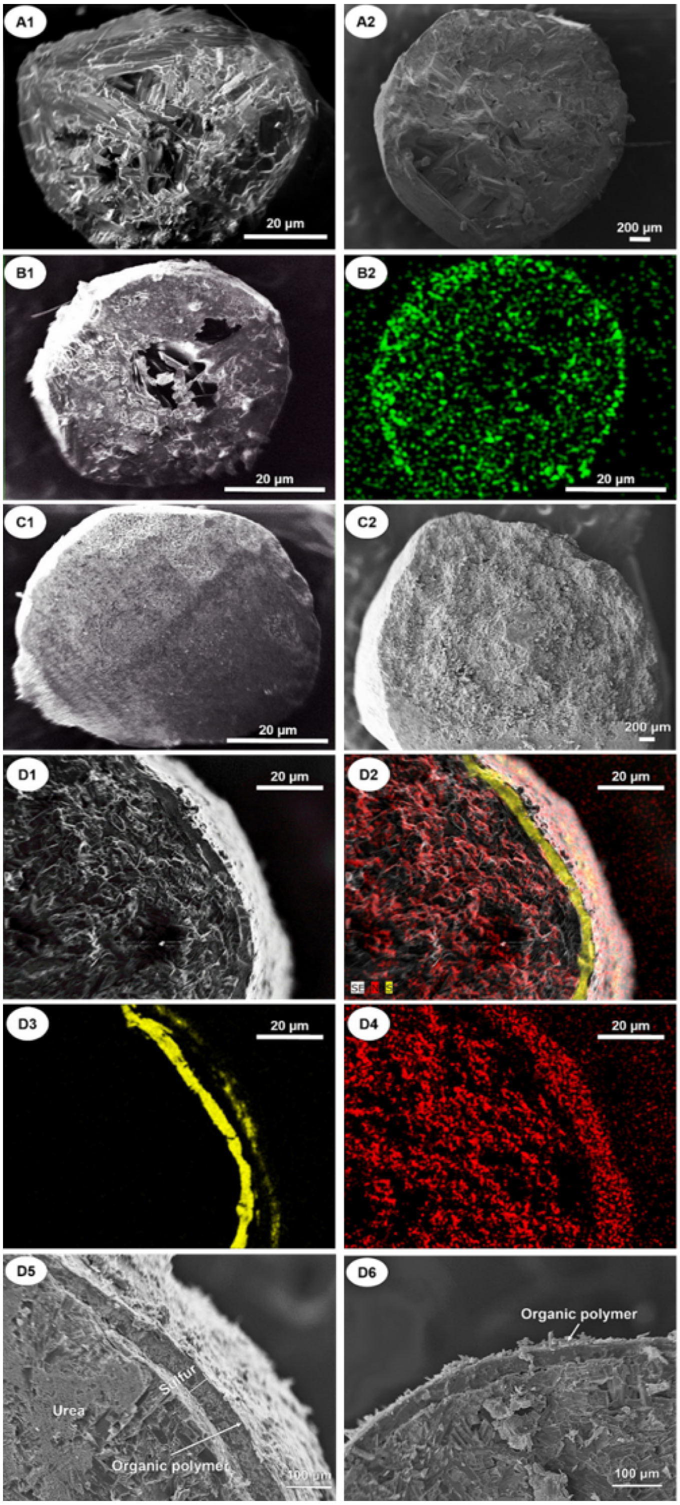

**Figure 1:** Electron micrographs of the fertilizers used as N sources for maize. Urea (A1 and A2); Urea + Cu + B (B1); EDS for Cu (B2); Urea + NBPT (C1 and C2); Urea coated by sulfur and polymers (D1); EDS for N and S (D2); EDS for S (D3); N (D4); and polymer layer image (D5 and D6).

After muffle drying to a constant weight, the N contents in the grains were analyzed as described above for plant material. The accumulated amount of N was obtained by multiplying the N contents by the stubble and grain biomass.

### Data analysis

The data were submitted to an analysis of variance (ANOVA), and the means were compared using a Tukey's test. Differences were considered significant when $p \leq 0.05$. Homogeneity of variance and normality were tested using the Bartlett and Shapiro-Wilk tests, respectively. Linear regression models were used to describe the effects of the different N levels. In addition, a contrast test was used to compare the control (no N) with the treatments with different N levels and sources. All of the statistics were conducted using the SISVAR software (Ferreira, 2011).

## RESULTS AND DISCUSSION

### Weather conditions

The accumulated rainfall and the maximum and minimum temperatures were monitored during the experiment (Figure 2A and 1B). Two dry spells occurred during the experiment, one before N fertilization (22/12/2012 to 09/01/2013) and one after flowering (08/02/2013 to 02/03/2013). These dry spells did not affect plant growth, especially with normal rainfall after N treatment (Figure 2B). The accumulated rainfall during crop development was 920 mm. On the third day after N fertilization 3.2 mm precipitation occurred, and the precipitation increased in the following days.

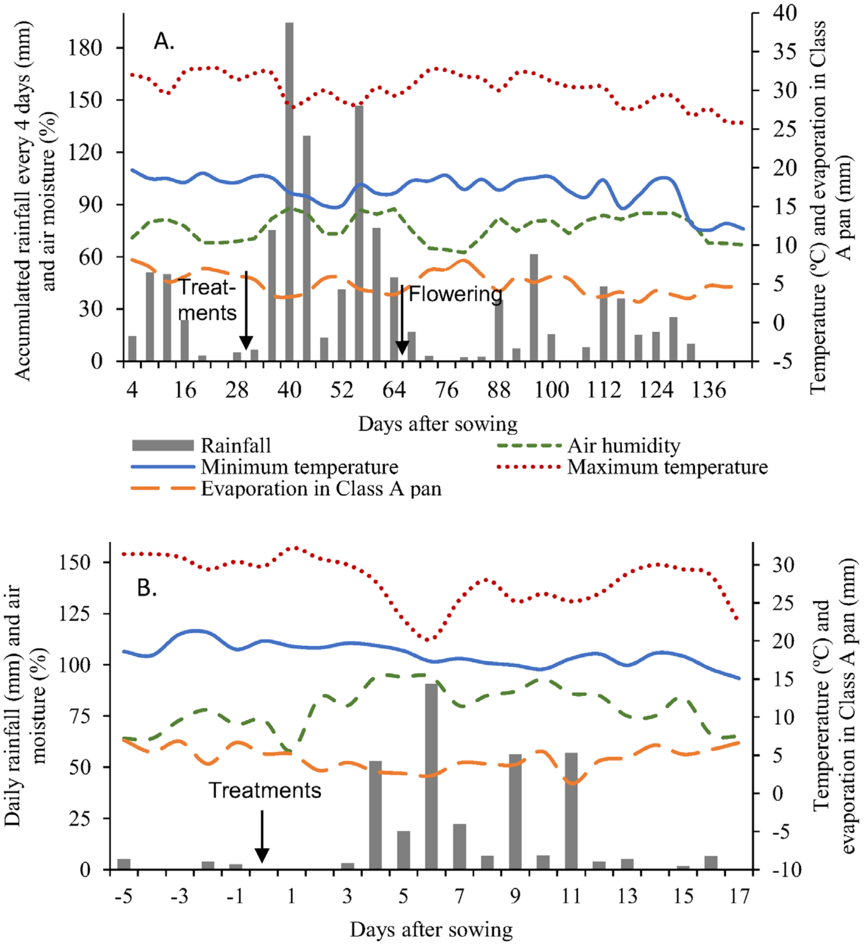

**Figure 2:** Climatic conditions during the experiment. (A) Dates of N fertilizer treatments and maize flowering (indicated by arrows); (B) precipitation, relative humidity, temperature and evapotranspiration before and during the first days after the N fertilizer treatments.

## Nitrogen loss by ammonia volatilization

The values for daily volatilization varied with the different sources of N that were applied to the maize crop by side-dressing (Figure 3). Common urea reached its maximum volatilization peak (12% applied N) on the 2nd day after its application. The other N sources induced delays in the peaks that occurred between the 3rd and 4th days, with lower values than urea.

Urea + Cu + B (6.8% applied N) and urea coated with polymers (5.6% applied N) resulted in maximum volatilization on the 3rd day after fertilization, while urea + NBPT (7% applied N) had the longest delay in the ammonia volatilization peak on the 4th day (Figure 3).

Field research considering different soils and climatic conditions and controlled environments indicated a longer delay and a reduction in the peak volatilization of urea stabilized with NBPT or with Cu and B when applied in various crops (Cantarella et al., 2008; Dawar et al., 2011; Faria et al., 2013; Fontoura; Bayer, 2010; Grohs et al., 2011; Nascimento et al., 2013; Stafanato et al., 2013; Zaman et al., 2009).

Soares et al. (2012) evaluated $NH_3$-N losses in a controlled environment and reported a volatilization peak at between 7 to 9 days for urea + NBPT. The use of NBPT or Cu and B stabilize urea by maintaining N in the amidic form (N-$NH_2$) for a longer period in the soil by reducing the urease activity. Consequently, the ammonium ($NH_4^+$-N) and nitric ($NO_3^-$-N) forms are also diminished. These forms of urea are the most labile for ammonia volatilization, de-nitrification and leaching in the soil-plant-atmosphere (Grohs et al., 2011; Pereira et al., 2009; Sanz-Cobena et al., 2008; Scivittaro et al., 2010; Stafanato et al., 2013; Watson et al., 2008).

Therefore, in order to reduce $NH_3$-N loss in N fertilization practices that use urea in maize crop, a delay in the ammonia volatilization peak promoted by urease inhibitors, such as NBPT and Cu + B is strategic. The delay maintained the N fertilizer in its amidic form for a longer period before the nutrient was incorporated into the soil in rain-fed cropping systems. This delay allowed the urea to diffuse throughout a greater soil volume, which reduced $NH_3$-N losses important for N use efficiency.

The effects of NBPT additions on reducing ammonia volatilization have been extensively studied for a long time. Recently, these studies included the effects of Cu and B as urease inhibitors (Faria et al., 2013; Grohs et al., 2011; Nascimento et al., 2013; Stafanato et al., 2013) to avoid $NH_3$-N daily losses in areas that were fertilized with copper sulfate + boric acid. An American patent from the 1970's, which is described by Hendries (1976) and is cited by Heringer (2008), presents the theoretical fundamentals for adding Cu and B to urea to reduce urease activity and decrease $NH_3$-N losses.

According to the Brazilian patent PI 0700921-6 A (Heringer, 2008) in the National Institute of Intellectual Property (INPI), in the production process of urea coating, boric acid and copper sulfate must be added in proportions of 1.5-2.4% and 0.6-1.5%, respectively. These compounds

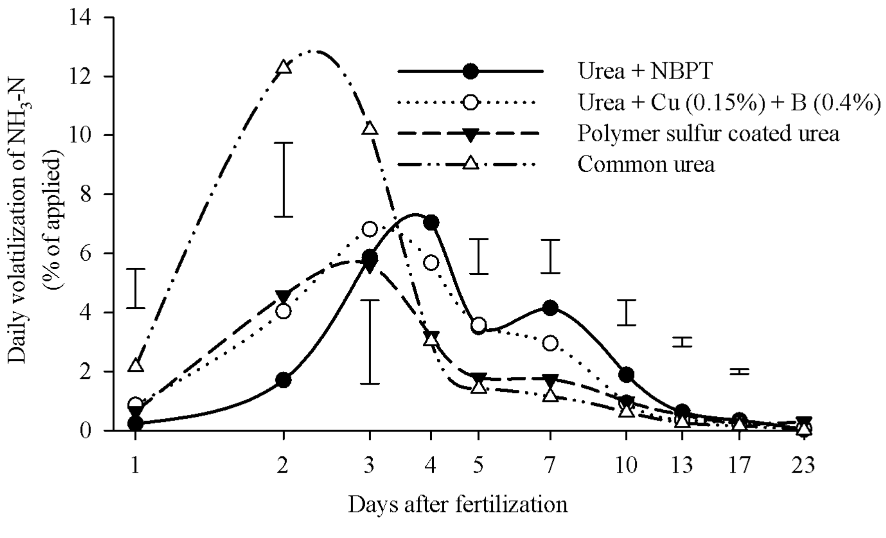

**Figure 3:** Daily losses of volatilized ammonia ($NH_3$-N) from stabilized urea and slow release urea. The X-axis in logarithmic scale is shown using real values. The vertical bars in the graph indicate the LSD (Tukey's test, p = 0.05).

can be added using two methods, dissolution in melted urea before granulation and pearling or after urea processing by adding powdered sources of Cu and B (≤ 0.015 mm) into solid urea, covering the granule.

Reduced urease activity can be explained by the non-competitive and competitive inhibition of B and Cu, respectively. Based on stoichiometric calculations, for 61 parts of boric acid in urea, 42 parts of N will be captured ($H_3BO_3 + 3NH_4OH \rightarrow (NH_4)_3BO_3 + 3\ H_2O$). Thus, this reaction alone does not explain the reduced volatilization by adding 24 g kg$^{-1}$ boric acid into the urea since only 3.4 kg $NH_3$-N is captured per 100 kg $(NH_2)_2CO$-N applied. This event could be justified by the competitive inhibition of urease activity by boron.

Moreover, boric acid is a Lewis acid and has a $pK_a$ of 9.2 (Soares et al., 2005). When added to fertilizers at low concentrations, boric acid promotes $H^+$ buffering around the smaller granules at a lower level than required to neutralize the $NH_3$-N produced in the soil. Therefore, the hypothesis regarding reduced volatilization losses by Cu and B fertilizers by reducing the pH around the granules does not justify the $NH_3$-N losses that were detected in this study.

In contrast with the procedure described in patent PI 0700921-6 A (Heringer, 2008), Benini et al. (2004) reported that the inhibitory activities of urease are competitive due to its similar chemical structure as urea.

The inhibition of urease by $Cu^{2+}$ could be explained by the reaction of the ion with the sulfhydryl group from urease, which would block the enzyme site and reduce is activity in the soil, thus promoting N maintenance in amidic form (Benini et al., 2004; Chaperon; Sauvé, 2007; Fu et al., 2009) and reducing $NH_3$-N loss. Faria et al. (2013) evaluated the addition of Cu + B and sulfur into urea and reported that the addition of these nutrients was efficient for diminishing the N ($NH_3$-N) losses in two maize crops. Similar results were obtained by Nascimento et al. (2013) in sugar cane.

The $NH_3$-N losses from fertilizers can be affected by climate factors, such as temperature, relative air humidity, soil humidity and wind speed, and by soil attributes, such as pH, organic matter, cation exchange capacity and nitrification rate (Tasca et al., 2011; Zaman et al., 2009).

According to Rojas et al. (2012) greater daily N losses result from volatilization in no-till fields with various cover crop species within the first five days after urea application and are highly influenced by rainfall during that period.

On the 4th and 5th days after N fertilizer application in maize, 53 and 19 mm of precipitation occurred, which reduced the amounts of volatilized $NH_3$-N from the 4th day onwards (Figure 2B).

In addition, a reduction in the maximum temperature (Figure 2B) occurred that reduced the urease activity, urea hydrolysis (Clay et al., 1990; Suter et al., 2011) and the potential losses of N through volatilization. At higher temperatures, the solubility of $NH_3$-N in the soil solution was lower, which corresponded with Henry's law and favored gaseous emissions of $NH_3$ (Clay et al., 1990).

The water content of the shallow layers of soil were directly affected by soil management and climatic conditions, such as temperature, wind and relative air moisture, which generate complex interactions that affect N loss intensity by volatilization (Fontoura and Bayer, 2010; Suter et al., 2011; Zaman et al., 2009).

During N application, the initial soil moisture content is very important because it affects the loss of $NH_3$-N into the atmosphere. However, Lara-Cabezas et al. (1992) stated that evaporation rate is more important than the initial soil water content for N fertilizer applications. Furthermore, as the soil dries, the potential $NH_3$-N losses increase (Lara-Cabezas et al., 1997; Malhi et al., 2001; McInnes et al., 1986). Volatilization is directly related to reduced soil water contents because the concentrations of $NH_4$ and $NH_3$ increase in the solution (according to equation $NH_4{}^+{}_{(solution)} \leftrightarrow NH_{3(solution)} \leftrightarrow NH_{3(gas)}$).

Class A tank evaporation between fertilizer applications and four days after (when volatilization peaks occurred) of 4 mm day$^{-1}$ was observed that was associated with the maximum temperatures occurring during this period. The evaporation rate five days before and 17 days after N fertilization was between 1.3 and 7.0 mm (Figure 2B).

The relative efficiency of NBPT for stabilizing the soil urea could be directly related to soil moisture content (Dawar et al., 2011), temperature and the amount of rainfall after fertilization. These are some of the main factors that regulate volatilization potential in cultivated soils. Rainfall at intervals of 3 and 7 days after N application in this study (Figure 2B) favored the efficiency of NBPT in reducing $NH_3$ volatilization (Cantarella, 2007; Pereira et al., 2009).

Losses by ammonia volatilization occurred on the first days after N fertilizer side dressing. From the total amount of $NH_3$-N volatilized, 96.7% of the urea losses occurred within the first seven days. However, for the urea + NBPT, the urea coated with the S + organic polymer and the urea + Cu + B, these values were 88.6, 89.6 and 93.7%, respectively.

The analysis of variance for the accumulated N losses through volatilization over 23 days showed a significant difference ($p \leq 0.05$) between the different N fertilizers (Figure 4). The following decreasing sequence of accumulated N losses through volatilization for stabilized and slow-release urea that was side dressed on maize crops occurred: urea (31.2% total applied N) > urea + Cu + B (25.6%) = urea + NBPT (25.4%) > coated urea (19.6%).

For the N losses by volatilization in sugarcane, Nascimento et al. (2013) obtained the following decreasing sequence for $NH_3$-N: urea (7.6% total applied N) > sulfur coated urea (3.8%) > Urea + Cu + B (1.8%) >ammonium nitrate (0.16%) = ammonium sulfate (0.09%).

Stafanato et al. (2013) reported the following decreasing values of $NH_3$-N: pelleted urea and calcium sulfate (56% total applied N) > pelleted urea (45.7%) = granulated urea (46.6%) > pelleted urea + 2% Cu + 0,5% B (36.5%) = coated urea with 0.06% Cu + 0.3% B = pelleted urea + 0.5% Cu + 0.5% B (31.9%) > pelleted urea + 0.5% Cu + 2.0% B (21.8%) > urea + NBPT (74%) = ammonium sulfate (3.6%) in a controlled environment.

Soares et al. (2012) measured the accumulated $NH_3$-N loss in controlled conditions, which reached values of 28% of applied N for urea and 6% for urea + NBPT, which was equivalent to a 78% reduction due to the addition of NBPT. In a second experiment with increasing air flow inside the collecting chamber, the $NH_3$-N losses were 37 and 17% of total applied for urea and the urea + NBPT, which corresponded to a volatilized reduction of 54% following the addition of a urease inhibitor.

In this study, the reduction in the $NH_3$-N loss rates for N fertilizers side dressed on maize, were 18.6, 17.9 and 37.2% for urea + NBPT, urea + Cu + B and coated urea with S + organic polymers, respectively, when compared with conventional urea.

Fontoura and Bayer (2010) reported the average accumulated $NH_3$-N losses for four maize crops under no-till following surface applied urea (12.5% total applied N), incorporated urea (1.1%), urea + polymers (13.5%), urea + urease inhibitor (6.6%), ammonium sulfate (1.9%) and ammonium nitrate (1.0%) fertilizer treatments.

Jantalia et al. (2012) evaluated $NH_3$-N losses in semi-arid regions when using slow release N sources, such as Super U®, urea, polymer-coated urea and a urea-ammonium nitrate solution in irrigated maize (16 and 19 mm). The accumulated $NH_3$-N loss varied between 0.1 - 3.6% and 0.3 - 4.0% of the total N applied in 2010 and 2011. These values were considered low when compared with those observed in irrigated tropical regions, which varied from 38 to 78% (Lara-Cabezas et al., 2000).

## Agronomic performance and N accumulation of maize

The N fertilizers did not promote significant differences in the accumulation of N in grains and stubble.

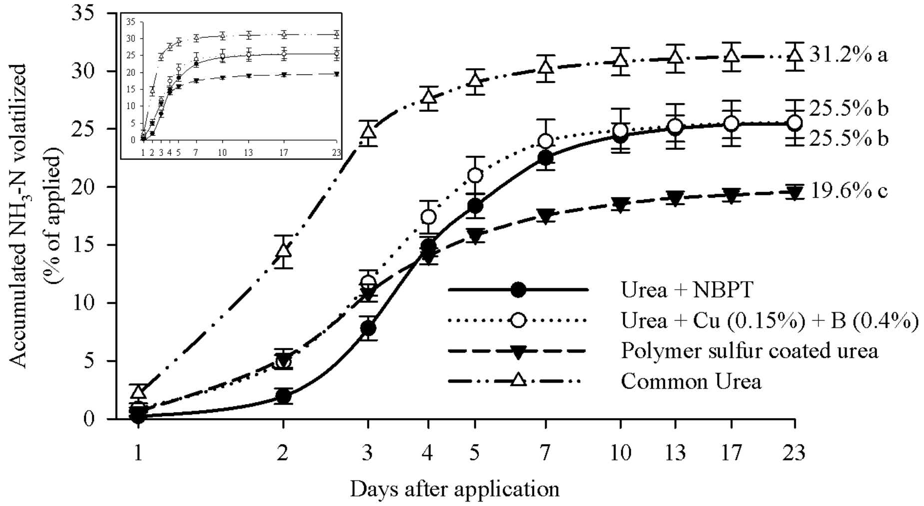

**Figure 4:** Accumulated N losses of $NH_3$-N over 23 days after application of stabilized urea and controlled-release urea in maize crop. The bars indicate the mean standard errors and the different letters explain the significant difference (Tukey's test, p = 0.05). The X-axis in the logarithmic scale indicates the real values and the smaller graph illustrates the performance of the X-axis on a linear scale.

A linear increase in the accumulated N concentration occurred as the side-dressed dose increased (Figure 5).

The amount of N accumulated in the stubble at harvest varied between 61 kg ha$^{-1}$ for the control and an average of 82 kg ha$^{-1}$ for the different doses. These values illustrated the importance of returning the stubble to the soil after harvest. In addition to the soil biological and physical benefits, stubble promotes N cycling and other cycling processes for the next crop.

Accumulated values of 35 and 59 kg N ha$^{-1}$ (mean of two crops) were obtained by Fernandes and Libardi (2012) regarding the accumulation of N by maize in response to doses of 60 and 180 kg N ha$^{-1}$. Rimski-Korsakov et al. (2012) obtaining grain and stubble yields that were similar to those reported in this study, with stubble N contents of 42 - 85 kg ha$^{-1}$ and grain N contents of 74 - 150 kg ha$^{-1}$. In the control, in which 29 kg N ha$^{-1}$ was applied at sowing, 179 kg N ha$^{-1}$ (excluding roots) was measured.

No significant differences ($p > 0.05$) were observed for the doses, sources and their interactions regarding stubble yield. Generally, the dry matter content should increase as the fertilizer N dose increases, as reported by several authors (Fernandes; Libardi, 2012; França et al., 2011; Rimski-Korsakov et al., 2012). However, in some cases, when the crop shows rapid growth and the response to N is low, no increase in stubble production may be observed. This response could become more evident for N accumulation and grain yield (Costa et al., 2012; Rimski-Korsakov et al., 2012). The dry matter production in this experiment was high and above that reported in their cited work.

The grain yield significantly responded to the N doses ($p \leq 0.05$) (Figure 6). In addition, there was a linear increase in the grain yield as a function of the N increment. For a side dressing concentration of 50 kg ha$^{-1}$, a response of 336 kg ha$^{-1}$ grain yield occurred. Furthermore, grain yield increases related to N dose have been reported for maize (Farinelli; Lemos, 2012; Rimski-Korsakov et al., 2012; Silva et al., 2011).

At 200 kg N, the maize yield was 12,017 kg ha$^{-1}$. However, in the absence of N fertilizer (control), the yield of 10,673 kg ha$^{-1}$ was considerably high. The low response, which corresponded to an 11% yield increase for 200 kg ha$^{-1}$, emphasized the need to obtain the cropping record before defining a N fertilization plan for maize. In areas under no-till for long periods (such as 15 years in this study), the soil has a high capacity for supplying N and for cycling N from mineral and organic forms. This explains the high yield in the absence of the evaluated mineral N because the organic forms of N in the soil could supply the N.

Carneiro et al. (2013) evaluated N mineralization in a dystrophic Red Latosol, which had physical and chemical characteristics similar to those in this study. The authors reported a mineralization rate of 124 mg N kg$^{-1}$ soil over 270 days. Considering a soil depth of 0-30 cm and 110 days of N absorption by the maize crop, a supply of 152 kg ha$^{-1}$ N was estimated. In connection with the preceding crop, the decomposition of stubble justifies the yield response to N (Figure 6) and the high N level in the control (Figure 5).

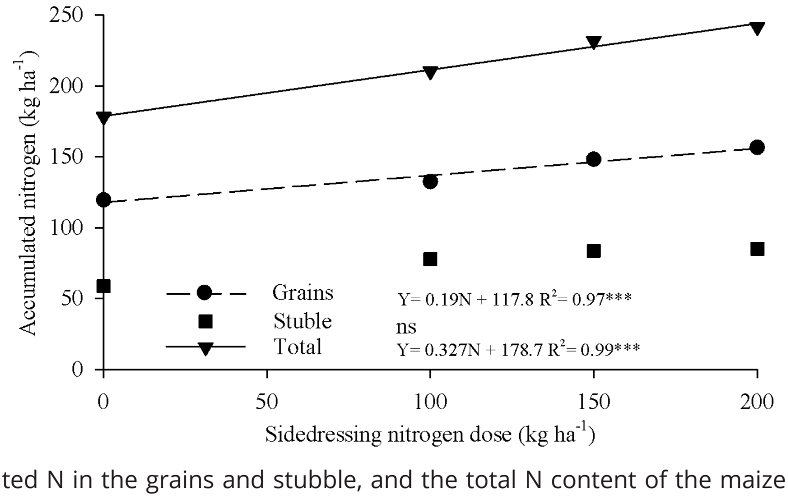

**Figure 5:** Accumulated N in the grains and stubble, and the total N content of the maize at harvest relative to the applied N doses. ***Significant (n = 3 for 0 kg ha$^{-1}$ N and 12 for other doses, $p \leq 0.001$ for F test of regression parameters).

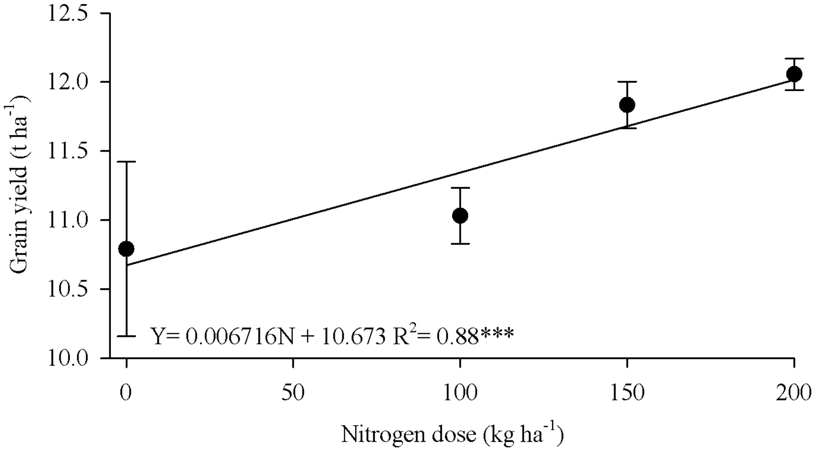

**Figure 6:** Maize grain yield in response to the different N doses applied by side dressing. The vertical bars indicate the mean standard errors. ***Significant (n = 3 for 0 kg ha$^{-1}$ N and 12 for other doses, $p \leq 0.001$ for F test of regression parameters).

When the N supplied by the soil is medium or high concentrations (even though losses from N fertilizers are high), their detection could be masked. Thus, the differences would not be visible. Fontoura and Bayer (2010) did not observe any differences in maize yields when fields were fertilized with common urea and with stabilized and slow release forms. However, the yield response was considerably high (between 15 - 22 kg kernel per kg applied N), an increased by 29% in relative to the control.

## CONCLUSIONS

Stabilized and slow release urea did not increase the N contents in the maize stubble or grains relative to using urea in long-term no-till soil. The amount of N accumulated in the plant is directly related to an increase in the N rate. Stabilized and slow release urea reduced the accumulated N losses by volatilization but did not promote a yield increase in maize and did not improve the agronomic efficiency of N fertilization in soils under long-term no-till cultivation. The urea + polymer, urea + NBPT and urea + Cu + B treatments reduced the volatilization peak of $NH_3$-N relative to urea. The urea coated by sulfur + organic polymers promoted lesser N volatilization among the evaluated N fertilizer sources.

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