

## Volatilization of ammonia in tropical soil with different moisture after application of polymer-coated urea

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### Abstract

Nitrogen fertilizer has a significant participation in the cost of agricultural production. It is less efficient agronomically and requires more studies to find strategies to be absorbed by crop. Polymer-coated urea is an alternative for the production of increased efficiency fertilizers. Validation of this technology should be performed for safe adoption in agriculture. The objectives of this work were to evaluate the nitrogen losses by volatilization of ammonia and the nitrogen contents in the nitric ( $\text{N-NO}_3^-$ ) and ammoniacal ( $\text{N-NH}_4^+$ ) forms in the tropical soil after application of urea sources. Three greenhouse experiments with different soil moisture conditions were carried out after application of urea, urea treated with NBPT and urea coated with Policote polymer as treatments. Then volatilization of ammonia,  $\text{N-NO}_3^-$  and  $\text{N-NH}_4^+$  contents in the soil was evaluated. The volatilization of ammonia was observed after using Policote-coated urea, which was similar to urea treated with NBPT. However, both of which were lower than that observed under urea application. In dry or very humid soil, the ammonia volatilization rate was low. The reduction of the volatilization of ammonia in the soil with Policote-coated urea was related on the humidity, whereas more effective when the conditions were more propitious to the volatilization of ammonia. The Policote-coated urea increased the content of  $\text{N-NH}_4^+$  in the tropical soil compared to urea. The content of  $\text{N-NH}_4^+$  in the soil was higher than  $\text{N-NO}_3^-$  after application of fertilizers due to the low organic matter content.

**Keywords:** Nitrogen reactions; N-ammoniacal; N-nitric; Policote; oxisoil.

### Introduction

Nitrogen (N) is one of the mineral elements required in greater quantity by plants (Souza and Fernandes, 2006) and also what mostly limits agricultural production. Nitrogen is a component of chlorophyll and essential for photosynthesis. It is also the basic element of proteins, including the genetic material such as DNA and RNA.

Nitrogen fertilizers such as urea require strategies that increase its efficiency of use by crops due to its necessity of use in agriculture, its significant participation in the cost of production and its low efficiency. Baligar et al. (2001) concluded that increasing nitrogen use efficiency (NUE) is vital to increase crop productivity and quality, reduce nitrogen use, and improve soil, water and air quality. Among the strategies to increase the NUE, the use of increased efficiency fertilizers (IEF) which contains aggregate technologies stands out. They control the release of nutrients or stabilize their chemical reactions in the soil, increasing their availability to plants (AAPFCO, 1997).

The IEF can be classified into three classes: slow release, controlled release and stabilized. Controlled and slow release fertilizers are those from which nutrient release into the environment occurs in more or less slow and controlled manner (Shaviv, 2000). Stabilized nitrogen fertilizers contain some additives capable of inhibiting the nitrogen reaction in the soil in some undesirable form (AAPFCO, 1997). Thus, slow/controlled release fertilizers act when the nutrient is

available to the plants, while stabilized fertilizers act on the chemical form, in which the nutrient is made available to the plants. Stabilized fertilizers control the dynamics of chemical reactions of nitrogen in the soil, involving the processes of ammonia volatilization, nitrate leaching and nitrous oxide emission. These processes, besides reducing the efficiency of the nitrogen fertilization, bring environmental damages. Of these processes of N loss, the most studied is volatilization of ammonia, especially urea application. Losses by volatilization of ammonia due to nitrogen fertilization have been reported in the order of 31.2% (Cancellier, 2013), 11% (Rochette et al., 2013), 27% (Schwenke et al., 2014) and 25% (Li et al., 2015).

The benefits of reduction in ammonia volatilization and nitrate leaching have been widely discussed. However, the benefits of promoting a higher N-ammoniacal supply to the plants, promoted by certain stabilized nitrogen fertilizers are scarce. N-nitric ( $\text{N-NO}_3^-$ ) is the predominant mineral form of N in aerated soils (Sangoi et al., 2003; Carelli et al., 2006), due to the rapid oxidation of N-ammoniacal ( $\text{N-NH}_4^+$ ) to  $\text{N-NO}_3^-$  by the nitrifying bacteria. The  $\text{N-NH}_4^+$  contents found in agricultural soils are generally 10-1000 times lower than  $\text{N-NO}_3^-$  (Marschner, 1995). Thus,  $\text{N-NO}_3^-$  is the predominant form available for plant absorption when using conventional nitrogen fertilizers and slow/controlled release. It is known that cationic nutrients, such as  $\text{N-NH}_4^+$ , are absorbed

passively, without energy cost (Marschner, 1995), while anionic nutrients such as  $\text{N-NO}_3^-$  are absorbed with metabolic cost. About 45% of the ATPs reserve in the root hair cells can be consumed with the active absorption of the anions (Carvalho et al., 2008). The preferential absorption of ammonium compared to nitrate can be advantageous, offering lower metabolic energy cost and the not necessary nitrate reductase action in the roots (Grespan et al, 1998). Studies comparing the performance of urea-coated polymers with respect to common urea have not been conclusive, because while there are reports pointing to advantages of the use of polymer-coated urea (Fan et al., 2004; Noellsch et al., 2009; Pereira et al., 2009; Wilson et al., 2009; Garcia et al., 2018; Ribeiro et al., 2016), others point inefficiency, compared to urea (Nelson et al. 2009; Cahill et al. 2010; Mckenzie et al. 2010; Civardi et al. 2011; Prando et al. 2013; Martins et al., 2014). Therefore, it cannot be concluded that any coating with polymers will result in the same result. Thus, validation studies of technologies using polymer coating for IEF production are necessary so that these fertilizers can be safely adopted in agriculture. The objectives of this work were to evaluate the losses of nitrogen by volatilization of ammonia, the contents of  $\text{N-NO}_3^-$  and  $\text{N-NH}_4^+$  in the soil in response to urea sources.

## Results

### *Volatilization of ammonia in the soil with high humidity*

The accumulated volatilization of ammonia (AVA) was significantly influenced ( $p < 0.05$ ) by the doses and sources of nitrogen during the evaluated days (Figure 1a and 1b). The control treatment (without use of N), presented the lowest AVA ( $0.2 \text{ kg ha}^{-1}$  at 18 days after application of N). The largest AVAs were observed at the highest N dose ( $100 \text{ kg ha}^{-1}$ ). At 18 days after fertilizer application, the AVA that observed for Policote-coated urea (U+P) at doses of 50 and  $100 \text{ kg N ha}^{-1}$  were  $1.51 \text{ kg ha}^{-1}$  and  $2.63 \text{ kg ha}^{-1}$ , respectively; while these values increased to  $2.71 \text{ kg ha}^{-1}$  and  $3.63 \text{ kg ha}^{-1}$  under urea (U), respectively. U+P reduced AVA by 44.3% and 27.5% when compared to U.

### *Volatilization of ammonia at dry and low humidity soils*

The evaluations up to first irrigation (14<sup>th</sup> day) showed no significant volatilization influenced by nitrogen sources (Figures 2a and 2b). In the period when the soil remained dry, the AVA was lower than  $1.8 \text{ kg ha}^{-1}$ , which is explained by the low soil moisture. There was a statistical difference between the treatments for AVA ( $p < 0.05$ ) only in the evaluations from the 16<sup>th</sup> to the 23<sup>rd</sup> day. The control, without N, had the lowest AVA ( $2.24 \text{ kg ha}^{-1}$ ), while urea had the highest AVA ( $54.3 \text{ kg ha}^{-1}$ ). U+P and urea treated with NBPT (U+NBPT) presented AVA statistically equal to each other ( $20.3$  and  $17.3 \text{ kg ha}^{-1}$ , respectively). The peak of volatilization was occurred on the 20<sup>th</sup> day of evaluation (five days after irrigation), when urea was the fertilizer with the highest ammonia volatilization. Only on day 20<sup>th</sup>, ammonia volatilization with urea was  $30.7 \text{ kg N ha}^{-1}$  (56.5% of AVA observed with urea). U+P ( $9.2 \text{ kg ha}^{-1}$ ) and U+NBPT ( $9.1 \text{ kg ha}^{-1}$ ) also showed a peak of volatilization at the same time as urea, but with a reduction of 70% in relation to volatilized ammonia in urea. In total, 36.2% of the N in urea was volatilized, while U+P and U+NBPT volatilized 13.5% and 11.5%, respectively. The increased efficiency of fertilizers

(U+P and U+NBPT) caused AVA reductions of 62.6% and 68.1%, respectively.

### *N-ammoniacal and N-nitric in the soil*

The  $\text{N-NO}_3^-$  content of the soil was not influenced by the treatments ( $p < 0.05$ ). However, the incubation time was significant. The  $\text{N-NO}_3^-$  content was increased linearly with the incubation time, ranging from  $9.0$  to  $23.7 \text{ mg kg}^{-1}$  in the soil. The  $\text{N-NO}_3^-$  soil content was increased  $1.05 \text{ mg kg}^{-1}$  per day (Fig 3b). The soil  $\text{N-NH}_4^+$  content was significantly influenced by the sources ( $p < 0.01$ ) and by the incubation time ( $p < 0.01$ ). Nitrogen fertilization increased the  $\text{N-NH}_4^+$  content of the soil. In the control treatment, the  $\text{N-NH}_4^+$  content was increased linearly from  $11.8$  to  $35.7 \text{ mg kg}^{-1}$ , resulting in an increase of  $1.5 \text{ mg kg}^{-1}$  each incubated day (Fig 3a). Under nitrogen fertilizers, the  $\text{N-NH}_4^+$  content presented a quadratic response. Under urea and U+P, the maximum contents of  $\text{N-NH}_4^+$  were  $222.1 \text{ mg kg}^{-1}$  (at 9.9 days of incubation) and  $234.1 \text{ mg kg}^{-1}$  (at 10.6 days of incubation), respectively (Figure 3a).

## Discussion

The process of volatilization of ammonia begins after the enzymatic hydrolysis of urea in the soil. However, soil moisture was the main factor that controlled volatilization. The soils with high humidity showed intensified dissolution and diffusion of urea, decreasing volatilization (Cabezas et al., 1997). In the first experiment, in spite of having a reduction of ammonia volatilization in the U+P treatment, the urea volatilization rate was low (around 5%), due to the soil moisture dissolving and completely diffusing the urea through the soil.

In the second experiment, the dry soil had practically no volatilization, but when the soil was moist enough to start hydrolysis of the urea without diffusion, the volatilization rate was high and the urea volatilized more ammonia than the other treatments. There was ammonia volatilization of 36% in total applied to urea, similar values were observed by Cancellier (2013) and lower values were observed by Rochette et al. (2013), Schwenke et al. (2014) and Li et al. (2015).

The Policote-coated urea (U+P) and urea treated with NBPT (U+NBPT) treatments reduced ammonia volatilization and proved to be effective in reducing N losses. A similar ammonia volatilization rate, equivalent to U+P, occurred with U+NBPT, a recognized additive capable of reducing volatilization (Dunn and Wiatrak, 2014, Gordon, 2014), allowing these additives to be used as tool to increase the efficiency of nitrogen fertilization. However, efficiency is linked to factors intrinsic to the environment and to the plant (Dupas et al., 2016).

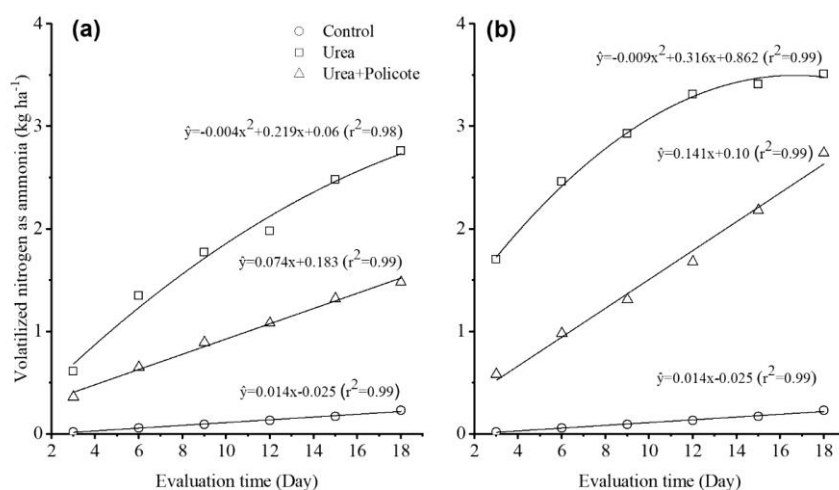
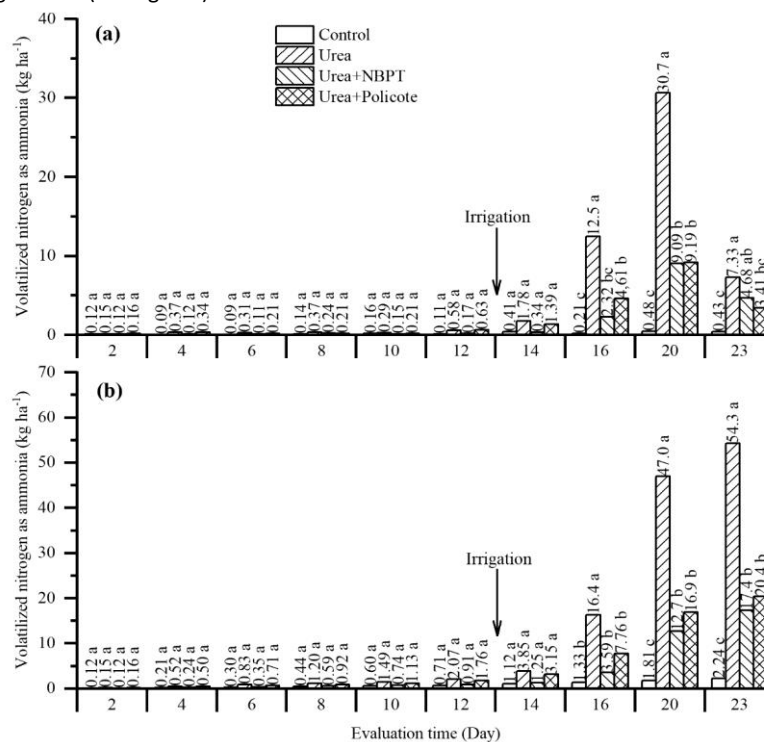
The use of IEF may reduce ammonia volatilization, since some studies reported the low nitrogen use efficiency (NUE), finding values of 36% (Melgar et al., 1991), 30 to 40% (Freny et al., 1993), 44 % (Mattos Junior et al., 2002), 41% (Chen et al., 2008), 33% (Arnall et al., 2009), 40 to 60% (Martínez-Alcántara et al., 2013) and 25.2% (Cannavo et al., 2013). Increasing the NUE leads to greater use of fertilizer by plants, and there is a possibility of reducing the fertilizer dose and the impact on the environment.

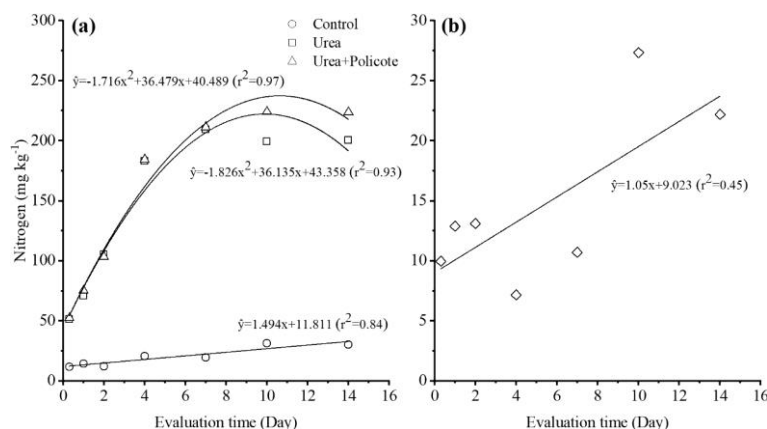
The  $\text{N-NH}_4^+$  content was higher than that of  $\text{N-NO}_3^-$  throughout the evaluation of the third experiment.

**Table 1.** Chemical and physical characterization of the soils used in the experiments.

|                                |                                    | 1 <sup>o</sup> experiment | 2 <sup>o</sup> experiment | 3 <sup>o</sup> experiment |
|--------------------------------|------------------------------------|---------------------------|---------------------------|---------------------------|
| C*                             | g dm <sup>-3</sup>                 | 9.88                      | 10.27                     | 7.44                      |
| N-NO <sub>3</sub> <sup>-</sup> | mg kg <sup>-1</sup>                | 13.45                     | 1.88                      | 14.70                     |
| N-NH <sub>4</sub> <sup>+</sup> | mg kg <sup>-1</sup>                | 8.65                      | 11.85                     | 7.47                      |
| pH CaCl <sub>2</sub>           |                                    | -                         | 5.90                      | -                         |
| pH H <sub>2</sub> O            |                                    | 5.40                      | -                         | 6.10                      |
| P                              | mg dm <sup>-3</sup>                | 15.70                     | 6.40                      | 2.60                      |
| K                              | mmol <sub>c</sub> dm <sup>-3</sup> | 10.5                      | 1.0                       | 1.0                       |
| Ca                             | mmol <sub>c</sub> dm <sup>-3</sup> | 36.0                      | 48.5                      | 40.2                      |
| Mg                             | mmol <sub>c</sub> dm <sup>-3</sup> | 25.0                      | 30.8                      | 33.3                      |
| Al                             | mmol <sub>c</sub> dm <sup>-3</sup> | 0.00                      | 0.00                      | 0.00                      |
| H+Al                           | mmol <sub>c</sub> dm <sup>-3</sup> | 49.6                      | 36.8                      | 29.4                      |
| CTC                            | mmol <sub>c</sub> dm <sup>-3</sup> | 121.1                     | 117.1                     | 103.9                     |
| V                              | %                                  | 59.0                      | 68.6                      | 71.7                      |
| Argila                         | g kg <sup>-1</sup>                 | 750                       | 770                       | 780                       |
| Silte                          | g kg <sup>-1</sup>                 | 130                       | 120                       | 140                       |
| Areia                          | g kg <sup>-1</sup>                 | 120                       | 110                       | 80                        |

\*C determined by the Walkley-Black method; P and K extracted by Mehlich-1; Ca, Mg and Al extracted by KCl 1.0 M; H + Al determined by the SMP, and the granulometry determined by the pipette method.

**Fig 1.** Accumulated volatilization of ammonia (N - kg ha<sup>-1</sup>) as a function of days after application of fertilizer doses, (a) nitrogen dose (50 kg ha<sup>-1</sup>); and (b) nitrogen dose (100 kg ha<sup>-1</sup>).**Fig 2.** Volatilization of ammonia (N - kg ha<sup>-1</sup>) as a function of days after fertilizer application, (a) non-accumulated values, and (b) accumulated values. Equivalent letters, within each evaluation day, are equal to each other by the Tukey test ( $p < 0.05$ ).



**Fig 3.** N content in soil as a function of days after fertilizer application, (a) nitrogen in the ammoniacal form (N-NH<sub>4</sub><sup>+</sup>), and (b) nitrogen in the nitric form (N-NO<sub>3</sub><sup>-</sup>).

However, there are reports that nitrification occurs rapidly in the soil, most of the N-NH<sub>4</sub><sup>+</sup> applied is nitrified in up to 4 weeks (Paulo, 2012), which did not occur in the present work. It is known that amount of soil organic matter directly affects nitrification (Paulo, 2012). The soil used in this experiment had low organic matter content (Table 1), compromising the nitrification rate. A similar result was observed by Rogeri et al. (2015), in the soil fertilized with urea. The N-NH<sub>4</sub><sup>+</sup> content was equal to N-NO<sub>3</sub><sup>-</sup> only after 22 days of fertilizer application.

### Materials and methods

Three experiments were carried out to evaluate nitrogen losses by ammonia volatilization, N-NO<sub>3</sub><sup>-</sup> and N-NH<sub>4</sub><sup>+</sup> levels in the soil in response to urea sources. All the experiments were conducted in a controlled environment (greenhouse) located at the IAPAR experimental station.

### Characterization of soil and fertilizers

The three soils used in the experiments were collected in the same agricultural area, cultivated with soybean and corn, at the experimental station of the Instituto Agronômico do Paraná (IAPAR), located in the city of Londrina, Brazil, geographical coordinates S23°21'27.34", W51°09'32.64", altitude 572 m. The soils sampled were of basaltic formation, with a high degree of weathering, and classified as Red Latosol Distroferric (Santos et al., 2013). The mineralogy of the clay fraction was composed of kaolinite, hematite, gibbsite and maghemite. Surface samples of the soils, with 0-20 cm depth, were collected, air-dried, sieved with a 2.0 mm opening and physically and chemically characterized (Table 1).

The fertilizers used in this work were urea (45% N), urea treated with NBPT (45% N) and Policote-coated urea (42% N). The NBPT (N-(n-butyl) thiophosphoric triamide), a urease inhibitor, has been reported as one of the most promising compounds to maximize urea nitrogen use in agricultural systems (Espindula et al., 2014). Policote is an additive based on water-soluble polymers.

### Volatilization of ammonia in the soil with high humidity

The first experiment was conducted to evaluate the volatilization of ammonia in the soil with high humidity after

application of sources and doses of urea. The experimental design was formed by a factorial with additional treatment [(2x2) +1] and arranged entirely random with 4 replicates. The factor A was composed of two fertilizers, urea (U) and Policote-coated urea (U+P). The factor B was composed of two doses of nitrogen, 50 and 100 kg ha<sup>-1</sup>. Ammonia volatilization was evaluated at 3, 6, 9, 12, 15 and 18 days after fertilizer application. The additional treatment (control) did not receive the addition of the fertilizers. Each experimental unit was formed by a plastic pot (54.0 x 33.0 cm) containing a soil layer with 5.0 cm height.

To maintain soil with high humidity, each experimental unit received an irrigation sheet (15 mm) of deionized water. The fertilizer was distributed over the entire soil surface in each experimental unit immediately after soil irrigation. A cylindrical chamber (10, 30 cm, diameter and height, respectively) was used to capture volatilized ammonia, containing in its interior, a Falcon tube with 20 mL of solution (0.05 M H<sub>2</sub>SO<sub>4</sub> and 1% glycerin) and filter paper (15.0 x 2.0 cm) with a part immersed in the solution (Marsola et al., 2007). At each evaluation time, the acid solution with the ammonia captured as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was stored in an amber flask for further determination. After each evaluation, soil irrigation (sheet 15.0 mm) was performed with subsequent installation of the chamber in another position on the experimental unit until the 18th day. The determination of the amount of volatilized ammonia was performed by salicylate blue spectrophotometry (Miyazawa et al., 1992). The volatilized ammonia values were calculated by kg ha<sup>-1</sup> unit, and for each evaluation time the previous evaluations were summed up to obtain the accumulated volatilization of ammonia.

### Volatilization of ammonia with dry and low humidity soil

The second experiment was conducted to evaluate the volatilization of ammonia in initially dry soil and later with low humidity after application of urea sources. The experimental design was formed by a factorial (4x10) and arranged entirely random with 4 replicates. The factor B was composed by the application of nitrogen (150 kg ha<sup>-1</sup>) in the form of: urea (U), urea treated with NBPT (U+NBPT), Policote-coated urea (U+P), and a treatment (control) without nitrogen application. The factor B was composed of 10 periods of evaluation of ammonia volatilization at 2, 4, 6, 8, 10, 12, 14, 16, 20 and 23 days after fertilizer application.

Each experimental unit composed of a plastic pot (54.0 x 33.0 cm) containing a soil layer 5.0 cm height.

The fertilizer was distributed over the entire surface of the dry soil in each experimental unit. A cylindrical chamber (10 and 30 cm, diameter and height, respectively) were used to capture volatilized ammonia, containing its interior, a falcon tube with 20 mL of solution (0.05 M H<sub>2</sub>SO<sub>4</sub> and 1% glycerin) and filter paper (15.0 x 2.0 cm) with a part immersed in the solution (Marsola et al., 2007). At each evaluation time, the acid solution with the ammonia captured (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and stored in an amber flask for further determination. After the exchange of the Falcon tube, the chamber was installed in another position on the experimental unit. This procedure was repeated until the 23<sup>rd</sup> day. The samples were collected until the 12<sup>th</sup> day in the dry soil, and immediately after the 12<sup>th</sup> collection, an irrigation sheet (5.4 mm) of deionized water was applied, keeping low humidity until the end of the experiment. The volatilized ammonia was determined according to the methodology proposed by Miyazawa et al. (1992).

#### **N-ammoniacal and N-nitric in soil**

The third experiment was conducted to evaluate the ammoniacal and nitric nitrogen content after application of urea sources. The experimental design was formed by a factorial (3x8) and arranged entirely random with 5 replicates. The factor A was composed by the application of nitrogen (200 mg kg<sup>-1</sup>) in the form of: urea (U), Policote-coated urea (U+P), and a treatment (control) without application of nitrogen. The factor B was composed of 7 incubation times, 0.3, 1, 2, 4, 7, 10 and 14 days after fertilizer application. A plastic container containing 1.0 kg of soil formed each experimental unit.

The soil was moistened to 60% of the field capacity ten days before fertilizer application. The fertilizer was homogenized throughout the soil for each experimental unit. Soil samples were collected from each experimental unit after each incubation time. The samples were dried in an 60°C oven until constant mass, for later homogenization and extraction with 1.0 M KCl + 0.05 M HCl (1:10 soil:extractor ratio). The N-NH<sub>4</sub><sup>+</sup> content was determined by salicylate blue spectrophotometry (Miyazawa et al., 1992), with N-NO<sub>3</sub><sup>-</sup> reduced with metallic Zn. The content of N-NO<sub>3</sub><sup>-</sup> was calculated by the difference between the contents of N-NH<sub>4</sub><sup>+</sup> determined with and without reduction by metallic Zn.

#### **Statistical analyzes**

The data were submitted to analysis of variances (ANOVA) according to each experiment; and when there was significance by the F test (p≤0.05) in ANOVA; the mean values of the qualitative variables were analyzed by the Tukey test (p≤0.05). For the quantitative variables, the means were adjusted to regression models (p≤0.05).

#### **Conclusion**

The volatilization of ammonia was observed by application of Policote-coated urea. This was similar to that observed for urea treated with NBPT and lower than that observed with urea. In dry or very humid soil, the ammonia volatilization rate was low. The reduction of the volatilization of ammonia in the soil with Policote-coated urea was dependent on the humidity, being more effective when the conditions were more propitious to the volatilization of ammonia. The

Policote-coated urea increased the content of N-NH<sub>4</sub><sup>+</sup> in the soil, compared to urea. The content of N-NH<sub>4</sub><sup>+</sup> in the soil remained higher than that of N-NO<sub>3</sub><sup>-</sup> after application of the fertilizers due to the low organic matter content of the soil.

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