

# Additives incorporated into urea to reduce nitrogen losses after application to the soil

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**Abstract** – The objective of this work was to develop urea-based fertilizers with internal incorporation of urease inhibitors and other additives in the granule. The effects of the incorporation of NBPT, copper ( $\text{Cu}^{+2}$ ), boric acid ( $\text{H}_3\text{BO}_3$ ), elemental sulphur ( $\text{S}^0$ ), and a clay mineral from the zeolite group in powder urea – with ten different combinations of these additives – were evaluated as to N losses by volatilization and leaching. The losses in laboratory-developed formulations were compared with those of commercial fertilizers coated with the same additives (Super N, FH Nitro Mais, and FH Nitro Gold). The evaluations were made in greenhouse conditions, using a Ultisol accommodated in PVC columns. Nitrate and ammonium leaching was evaluated in the solution percolated through the soil columns. Ammonia volatilization was measured with a semi-open static chamber. The incorporation of urease inhibitors (NBPT,  $\text{H}_3\text{BO}_3$ , and  $\text{Cu}^{+2}$ ) into the urea granules was efficient to reduce N volatilization. Ammonia volatilization in the laboratory-developed ureas was lower than in commercial fertilizers coated with the same additives, while ammonium sulfate losses by leaching were similar. The addition of zeolite does not reduce N volatilization. Mineral N leaching in the soil profile is not affected by urease inhibitors.

**Index terms:** ammonia volatilization, leaching, NBPT, nitrogen fertilizers, urease inhibitors.

## Aditivos incorporados à ureia para reduzir perdas de nitrogênio após aplicação ao solo

**Resumo** – O objetivo deste trabalho foi desenvolver fertilizantes à base de ureia com a incorporação interna no grânulo de inibidores de urease e outros aditivos. Os efeitos da incorporação de NBPT, cobre ( $\text{Cu}^{+2}$ ), ácido bórico ( $\text{H}_3\text{BO}_3$ ), enxofre elementar ( $\text{S}^0$ ) e um mineral de argila do grupo das zeólitas na ureia em pó – com dez diferentes combinações desses aditivos – foram avaliados quanto às perdas por volatilização e lixiviação. As perdas nas formulações desenvolvidas em laboratório foram comparadas com as de fertilizantes comerciais revestidos com os mesmos aditivos (Super N, FH Nitro Mais e FH Nitro Gold). As avaliações foram realizadas em casa de vegetação, tendo-se utilizado um Argissolo Vermelho, o qual foi acondicionado em colunas de PVC. A lixiviação de nitrato e amônio foi avaliada na solução percolada através das colunas do solo. A volatilização da amônia foi estimada por meio de uma câmara estática semiaberta. A incorporação de inibidores de urease (NBPT,  $\text{H}_3\text{BO}_3$  e  $\text{Cu}^{+2}$ ) nos grânulos de ureia foi eficiente para reduzir a volatilização de N. A volatilização de amônia das ureias desenvolvidas em laboratório foi menor do que nos fertilizantes comerciais revestidos com os mesmos aditivos, enquanto as perdas do sulfato de amônio por lixiviação foram semelhantes. A adição da zeólita não reduz a volatilização de N. A lixiviação de N mineral no perfil do solo não é afetada pelos inibidores de urease.

**Termos para indexação:** volatilização de amônia, lixiviação, NBPT, fertilizantes nitrogenados, inibidores de urease.

### Introduction

Urea [ $\text{CO}(\text{NH}_2)_2$ ] is the main nitrogen fertilizer used in agriculture, accounting for 60% of the commercialized N fertilizers worldwide (Heffer & Prud'homme, 2015). However, the main concern for agricultural use of this fertilizer is its high N losses

through ammonia ( $\text{NH}_3$ ) volatilization when applied on soil surface, after the hydrolysis reaction catalyzed by urease enzyme (Chien et al., 2009).

$\text{NH}_3$  losses from urea depend on temperature, humidity, soil pH and presence of crop residues on soil surface, which increase urease activity in the soil (Frankenberger Jr. & Tabatabai, 1982; Watson et al.,

2008). High N losses are observed in humid regions, like Brazil, commonly reaching up to 20–30% of the total N applied via fertilizer; or even higher, around 60% (Cantarella et al., 2008; Rochette et al., 2013).

Urease activity is the greatest regulator of  $\text{NH}_3$  volatilization, and it can be inhibited by complexing the enzyme with small molecules or with specific ions during the fertilizer formulation. Thus, urease inhibitors like N-(n-butyl) thiophosphoric triamide (NBPT), copper ( $\text{Cu}^{+2}$ ) and boric acid ( $\text{H}_3\text{BO}_3$ ), as well as polymers and elemental sulphur that interfere with solubilization, have been studied to reduce N losses by volatilization (Du et al., 2008; Trenkel, 2010; Soares et al., 2012; Nascimento et al., 2013). Moreover, clay minerals of the zeolite group are currently being tested with the same objective. These clay minerals present some cation exchange capacity (CEC), which is responsible for  $\text{NH}_4^+$  retention in the soil and for its gradual release to the soil solution (Calvo et al., 2009). According to Bernardi et al. (2007), urea mixtures with 25% of zeolite improved N use by plants, especially with higher application rates.

Commercial fertilizers like Super N, FH Nitro Mais, and FH Nitro Gold have NBPT,  $\text{CuSO}_4 + \text{H}_3\text{BO}_3$ , and  $\text{S}^0$  as surface coating of their granules, respectively. The incorporation of these urease inhibitors into the granules has not yet been evaluated as an alternative to maximize the control of urea  $\text{NH}_3$  losses. Therefore, this study can help improve the production process of these fertilizers by adding these additives internally in the composition of the granules. This process is already being explored in some high efficiency fertilizers (resin or membrane coated fertilizers), which, however, have impeditive prices for large scale agricultural crops.

The objective of this work was to develop urea-based fertilizers with internal incorporation of urease inhibitors and other additives in the granule, in order to minimize N losses through ammonia volatilization or ammonium and nitrate leaching.

## Material and Methods

The experiment was carried out in a greenhouse at the Soil Science Department of the Escola Superior de Agricultura “Luiz de Queiroz” (Esalq, USP), in the municipality of Piracicaba, state of São Paulo, Brazil, in the first semester of 2013. The 0–0.20-m layer

of a Ultisol (Argissolo Vermelho, according to the Brazilian classification) was used, collected from the research cropping area of the institution (22°46'08"S; 47°37'03"W).

Soil chemical analysis was performed according to Raij et al. (2001), with the following results: pH ( $\text{CaCl}_2$ ), 5.2; organic matter (OM), determined by carbon oxidation with potassium dichromate, 22  $\text{g kg}^{-1}$ ; ion exchange resin of P, K, Ca, and Mg, respectively, of 23  $\text{mg dm}^{-3}$ , 1.8  $\text{mmol}_c \text{ dm}^{-3}$ , 23  $\text{mmol}_c \text{ dm}^{-3}$ , and 8  $\text{mmol}_c \text{ dm}^{-3}$ ; S extracted with ammonium acetate 0.5  $\text{mol L}^{-1}$  ( $\text{S-SO}_4$ ) of 4  $\text{mg dm}^{-3}$ ; B determined in hot water of 0.16  $\text{mg dm}^{-3}$ ; DTPA extracted Cu, Fe, Mn, and Zn respectively of 1.5  $\text{mg dm}^{-3}$ , 51  $\text{mg dm}^{-3}$ , 11.8  $\text{mg dm}^{-3}$ , and 2.9  $\text{mg dm}^{-3}$ ;  $\text{Al}^{3+}$  extracted by KCl, 0  $\text{mmol}_c \text{ dm}^{-3}$ ; CEC, 48  $\text{mmol}_c \text{ dm}^{-3}$ ; and V, 69%. Soil textural composition was formed by 178.2, 17.1, and 804.7  $\text{g kg}^{-1}$  of clay, silt and sand, respectively. Predominant minerals in the clay fraction were kaolinite and iron/aluminum oxides.

The experimental units were formed by 50x15 cm PVC columns. The column bottom of each PVC pipe was closed with a cap allowing a 0.5 cm diameter hole to collect the leached solution. An acrylic blanket was allocated at the bottom to avoid soil losses and to filter the percolated solution. Each pipe was filled with 8.2 kg of soil, up to the 45-cm height; then, the soil was saturated with deionized water and kept in 70–90% of the water retention capacity throughout the experimental period, by periodically weighing the columns.

The water retention capacity of the soil in the columns was determined by the difference between saturated and dried soil. Thus, a column with approximately 3 L of water was added to reach saturation of the 8.2 kg of soil conditioned in the PVC. The weighing was performed after a 48-hour drainage period. The water retention capacity in the soil was determined by the formula  $U (\%) = (\text{M}_{\text{su}} - \text{M}_{\text{ss}}) / \text{M}_{\text{ss}}$ , where  $\text{M}_{\text{su}}$  is the mass of damp soil, and  $\text{M}_{\text{ss}}$  is the mass of dried soil ( $U = 28\%$  in the evaluated soil).

The incorporation of urea plus additives in laboratory was performed in the Laboratory of Fertilizer Technologies of Embrapa Solos, a unit of the Brazilian Agricultural Research Corporation (Embrapa), in municipality of Rio de Janeiro, state of Rio de Janeiro, Brazil. Commercial urea with diameter between 1 and 2 mm, micronized in a chamber mill for thermostatzation with cooled chilled water, model

MA.090/CFT (Marconi, Piracicaba, SP, Brazil), was used to produce ten different formulations, with the following additives internally incorporated to the fertilizer powder: boric acid ( $H_3BO_3$ ), copper ( $CuSO_4$ ), and elemental sulphur ( $S^0$ ). The additives were incorporated in the same amount of the products already being used to coat the urea granule in some commercial formulations: B, 0.15%; Cu, 0.4%; and S, 16%. Agrotain commercial fertilizer contains the urease inhibitor N-butyl thiophosphoric triamide (NBPT) in a proportion of 2.5 L of the product per ton of urea; thus, NBPT was also added to the powdered urea in liquid form, with a sprinkler, in the same proportion, correspondent to 2.5 mL of the product per kg of urea. Moreover, the clay mineral clinoptilolite (Celta Brasil, Cotia, SP, Brazil), from the zeolite group, was added in the proportion of 20% of the mixture, in the mass of powdered urea.

The incorporation of additives was performed in a V-type mixer, and then they were granulated. The granulation was done in a small-sized pelletizer with a 400-mm diameter plate, similar to the industrial large-scale fertilizer granulator. The estimated zeolite CEC ( $140 \text{ cmol}_c \text{ dm}^{-3}$ ) was determined according to Richards (1954), and the density ( $0.224 \text{ g dm}^{-3}$ ) was obtained from Celta Brasil. The specific surface ( $11.4 \text{ m}^2 \text{ g}^{-1}$ ) was determined with the Quantachrome apparatus, with high-speed gas sorption analyzer, using the BET surface area and pore size analyzer (Brunauer et al., 1938), with the aid of the NovaWin program.

The ten laboratory-developed formulations (Table 1), with the theoretical percentages of each additive, are described as follows: urea plus zeolite (20%); urea plus NBPT (0.25%); urea plus  $S^0$  (16%); urea plus B (0.4%) and Cu (0.15%); urea plus NBPT (0.2%) and Cu (0.14%); urea plus Cu (0.15%); urea plus B (0.3%), Cu (0.11%), and zeolite (20%); urea plus NBPT (0.2%) and zeolite (20%); urea plus  $S^0$  (11.2%) and zeolite (17.5%); and urea plus NBPT (0.19%), Cu (0.11%), and zeolite (19.9%). Other six treatments were formed by the five commercial fertilizers that use these inhibitors externally coating the urea granules. The commercial fertilizers were used as a baseline for comparison.

For the formulations urea plus NBPT (0.25%), urea plus B (0.4%) and Cu (0.15%), and urea plus NBPT (0.2%) and zeolite (20%), a patent request was applied at Brazil's institute of industrial property (Instituto

Nacional da Propriedade Industrial, INPI), under the title: "Micronized urea-based fertilizers and their achievement process" (Embrapa & Universidade de São Paulo, 2016).

The chemical analysis of the total contents of N, S, B and Cu in the formulations of urea and additives, as well as in the commercial products (Table 1), was performed according to the official methods of fertilizer analysis of the Brazilian Ministry of Agriculture, Livestock and Food Supply (Brasil, 2007).

The treatments were applied 10 days after soil incubation, a period preserved for biota acclimatization and enzyme activity reactivation in soil, since the soil had been previously air dried and sieved at 2 mm. A completely randomized design with four replicates was used, totaling 64 experimental units (PVC pipes). The fertilizers were evenly applied on the soil surface of each column, at  $120 \text{ kg ha}^{-1}$  N rate.

Volatilized  $NH_3$  was quantified in a semi-open static collector, developed by Nömmik (1973) and adapted by Lara Cabezas et al. (1999), top-fixed to each soil column immediately after fertilizer application. The foam from the collector was collected 1, 2, 3, 4, 5, 7, 9,

**Table 1.** Treatment description and analytical results for nitrogen, copper, boron, and elemental sulphur in the laboratory-developed formulations and in the commercial N fertilizers used in the study.

Treatment	Composition	N	Cu	B	S
U_Z-i	Urea+Zeolite	35.2	-	-	-
U_NBPT-i	Urea+NBPT	43.3	-	-	-
U_S-i	Urea+Elemental S	35.5	-	-	14.6
U_BCu-i	Urea+B+Cu	41.9	0.13	0.38	-
U_NBPTCu-i	Urea+NBPT+Cu	42.7	0.13	-	-
U_Cu-i	Urea+Cu	44.3	0.14	-	-
U_BCuZ-i	Urea+B+Cu+Zeolite	37.2	0.10	0.27	-
U_NBPTZ-i	Urea+NBPT+Zeolite	35.1	-	-	-
U_SZ-i	Urea+Elemental S+Zeolite	30.7	-	-	10.2
U_NBPTCuZ-i	Urea+NBPT+Cu+Zeolite	34.5	0.11	-	-
U	Commercial pearly urea	43.9	-	-	-
Super N	Urea+NBPT	42.4	-	-	-
FH Nitro Mais	Urea+B+Cu	43.1	0.14	0.39	-
FH Nitro Gold	Urea+S	37.5	-	-	15.1
AS	Ammonium sulfate	19.3	-	-	-
Control	No fertilizer	-	-	-	-

11, 13, 15, 18, 22, and 29 days after fertilizer application, totaling 13 samplings. At each sampling, the top foams were discarded and the bottom ones were stored in plastic bags in a freezer (-7°C) until extraction and analysis. For the extraction, the foams were washed with deionized water in a Büchner funnel with porous filter plate, using a Kitasato flask and a vacuum pump. Final volume was quantified and a 50-mL aliquot was stored in Falcon tubes for later N-NH<sub>3</sub> determination. The N-NH<sub>3</sub> concentration was determined using an autosampler linked to a Flow Injection Analysis (FIA) device (Kamogawa & Teixeira, 2009).

After 29 days of N-NH<sub>3</sub> volatilization, ammonium and nitrate leaching were estimated in the soil columns. For that, soil water content was raised to saturation, by weighing the columns and adding distilled water. This procedure was done in order to standardize the soil columns humidity. Then, more water was added in order to allow the outflow of leached solution for N measurement.

Distilled water was added to simulate a 15 mm day<sup>-1</sup> precipitation, equivalent to 0.264 L per column, during four consecutive days. The leached solution was collected in recipients containing 3 mL of HCl (1%), fixed under the soil columns. This acidification aimed at stabilizing N as ammonium or nitrate in the solution. This leached solution was measured and filtered; then, a 50-mL aliquot was stored in Falcon tubes in a freezer (-7°C). The ammonium concentration in the leached solution was analyzed by FIA (Kamogawa & Teixeira, 2009). Nitrate concentration was determined with the spectrophotometric method, according to Olsen (2008).

Right after the evaluations on leached solutions, soil samples were collected with a probe, in the layers 0–0.10, 0.10–0.20, and 0.20–0.45 m. The samples were homogenized and stored in a freezer (-7°C). Ammonium and nitrate in the soil were extracted with KCl 1 mol L<sup>-1</sup> (Silva, 2009). Soil NH<sub>4</sub><sup>+</sup> concentration was quantified by FIA (Kamogawa & Teixeira, 2009). Soil nitrate was determined with the spectrophotometric method (Olsen, 2008).

N losses and N accumulation data were subjected to the analysis of variance, using SAS 8.1 program (SAS Institute Inc., Cary, NC, USA). The means were compared using the Scott-Knott test, at 5% probability.

## Results and Discussion

Ammonia volatilization data of the urea formulations evaluated were distinct (Figure 1). Regardless of the formulation, the highest volatilization rates were observed between the second and the fourth day after application. The urea hydrolysis in the present study was facilitated by soil humidity and temperature (minimum average of 19°C and maximum average of 33.5°C). The formulations with highest loss peaks in this initial period were, in decreasing order: urea plus zeolite (U\_Z-i), commercial urea (U), urea plus S<sup>0</sup> (U\_S-i), and commercial fertilizer FH Nitro Gold (coated with elemental S). The lowest peaks of volatilization were observed in the laboratory-developed formulations, where the following stood out positively: urea plus NBPT (U\_NBPT-i), urea plus NBPT and zeolite (U\_NBPTZ-i), and urea plus B and Cu (U\_BCu-i). The other commercial and laboratory-developed formulations had intermediate NH<sub>3</sub> volatilization losses.

The fertilizers with the highest accumulated N losses by volatilization were commercial urea (U), commercial urea coated with elemental S (FH Nitro Gold), and urea plus zeolite (U\_Z-i), and they did not differ statistically from each other (Table 2). The laboratory-incorporated formulations with urease inhibitors NBPT, B, and Cu (U\_NBPT-i, U\_NBPTZ-i, and U\_BCu-i) were statistically similar to the ammonium sulfate (AS) and to the control (C) (Figure 1 and Table 2). These three formulations were more efficient in reducing volatilization than the commercial fertilizers Super N and FH Nitro Mais, which use the same inhibitors coating the granule, instead of internally incorporated to it.

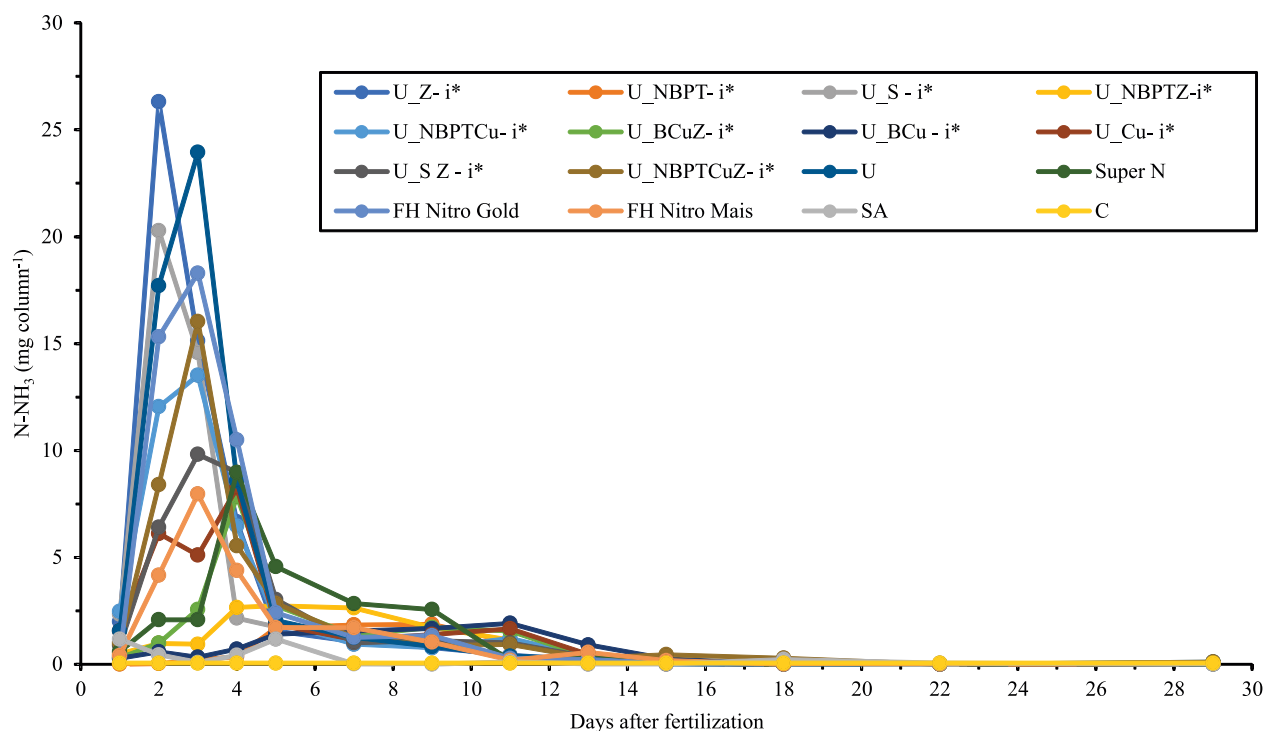
Incorporation of zeolite together with the urease inhibitors B and Cu (U\_BCuZ-i) increased the volatilization, compared to the formulations without zeolite (U\_BCu-i), but it was statistically similar to the commercial urea coated with B and Cu (FH Nitro Mais) and Super N, as well as to the laboratory formulation U\_Cu-i. The formulations U\_Cu-i and U\_BCuZ-i were statistically similar to the commercial fertilizers Super N and FH Nitro Mais. The other laboratory-incorporated formulations with sulphur, U\_Z-i and U\_S-i, showed expressive losses compared to AS. However, these losses were much lower than in commercial urea (Table 2).

Combination of NBPT and Cu in the urea (U\_NBPTCu-i) – which are additives that inhibit different action mechanisms of volatilization – and this same formulation plus zeolite (U\_NBPTCuZ-i) had similar results, and did not differ statistically from the formulations U\_SZ-i and U\_S-i. These laboratory-developed formulations reduced the volatilization compared to commercial urea, but were less efficient to reduce N volatilization than other laboratory-incorporated formulations tested, as already mentioned.

As already known, urea applied on soil surface has a high potential for N losses by volatilization. Urea hydrolysis is directly correlated to the increase in soil moisture (Kelliher et al., 2008; Tasca et al., 2011; Cancellier et al., 2016). In this work, the soil was kept at all times under high moisture conditions, which

may have favored higher volatilization than that in the crop field. Werneck et al. (2012), working in field with adequate moisture level for crop growth, but with high temperature, reported a substantial  $\text{NH}_3$  volatilization from urea, which peaked between the first and the third day after fertilizer application. This behavior was also observed in the present study. In all cases, the loss peak happened between the second and the fourth day after fertilizer application.

The laboratory-incorporated fertilizers with urease inhibitors (NBPT, B and Cu), U\_NBPT-i and U\_BCu-i were more efficient to control the volatilization compared to the commercial fertilizers coated with these additives (Super N and FH Nitro Mais) (Table 2). Cantarella et al. (2008) reported N losses by volatilization around 25% in commercial urea and 15% in urea coated with NBPT. Reports



**Figure 1.** Daily  $\text{N-NH}_4^+$  volatilization rate from the evaluated nitrogen fertilizers: U\_Z-i, urea+zeolite incorporated; U\_NBPT-i, urea+NBPT incorporated; U\_S-I, urea+elemental sulphur incorporated; U\_BCu-i, urea+B+Cu incorporated; U\_NBPTCu-I, urea+NBPT+Cu incorporated; U\_Cu-i, urea+Cu incorporated; U\_BCuZ-i, urea+B+Cu+zeolite incorporated; U\_NBPTZ-i, urea+NBPT+zeolite incorporated; U\_SZ-i, urea+elemental sulphur+zeolite incorporated; U\_NBPTCuZ-i, urea+NBPT+Cu+zeolite incorporated; U, urea; Super N, NBPT-coated urea; FH Nitro Mais, urea coated with B and Cu; FH Nitro Gold, urea coated with polymer and elemental sulphur; AS, ammonium sulfate; and C, control treatment without fertilizer.

of average reduction of 50–78% in N volatilization under NBPT-coated urea, compared to commercial urea, were observed under field conditions (Scivittaro et al., 2010; Soares et al., 2012; Nascimento et al., 2013; Stafanato et al., 2013). These results indicate that NBTP is an efficient additive for reducing N volatilization, but also that the incorporation of the additives into urea granules, performed in this study, was even more efficient in the control of N losses by volatilization, possibly due to the homogeneous contact between the inhibitor and urea in the granules promoted by the incorporation. Thus, whereas in humid soil conditions, surface coating disintegrates fast, making urea molecules more susceptible to urease action, the incorporation of the additives prevent this from happening.

The higher N volatilization in the formulation U<sub>BCuZ-I</sub>, compared to U<sub>BCu-i</sub>, in this study, indicates

**Table 2.** Total N-NH<sub>3</sub> volatilized, and leaching of N-NH<sub>4</sub><sup>+</sup> and N-NO<sub>3</sub><sup>-</sup> in the soil columns evaluated with different commercial N fertilizers and urea-based laboratory formulations<sup>(1)</sup>.

Fertilizer <sup>(2)</sup>	Total N-NH <sub>3</sub> volatilized (mg per column)	Volatilized proportion (%)	Mineral N leached (mg per column)		
			N-NH <sub>4</sub> <sup>+</sup>	N-NO <sub>3</sub> <sup>-</sup>	Total
C	0.7a	0.3	1.4a	2.9 <sup>ns</sup>	4.3a
AS	3.7a	3.7	2.2a	4.0	6.2a
U <sub>NBPT-i</sub>	7.4a	3.5	2.2a	2.5	4.7a
U <sub>BCu-i</sub>	9.7a	9.7	2.1a	3.2	5.3a
U <sub>NBPTZ-i</sub>	13.9a	6.6	7.1c	2.2	9.3b
U <sub>BCuZ-i</sub>	19.5b	9.2	4.1b	2.7	6.8a
FH Nitro Mais	22.3b	10.6	3.7b	3.1	6.8a
Super N	24.4b	11.6	2.8a	3.7	6.5a
U <sub>Cu-i</sub>	27.6b	13.1	2.1a	3.5	5.6a
U <sub>SZ-i</sub>	32.6c	15.6	3.4a	2.7	6.1a
U <sub>NBPTCuZ-i</sub>	38.0c	18.2	4.0b	2.3	6.3a
U <sub>NBPTCu-i</sub>	39.9c	18.9	2.1a	2.6	4.7a
U <sub>S-i</sub>	44.1c	20.9	3.1a	2.6	5.7a
FH Nitro Gold	50.0d	23.2	2.9a	2.6	5.5a
U <sub>Z-i</sub>	54.2d	25.7	2.9a	3.4	6.3a
U	56.6d	26.8	4.8b	3.8	8.6b
Mean	27.9	-	3.1	3.0	6.2
CV (%)	21.3	-	43.3	29.4	26.4

<sup>(1)</sup>Means followed by the same letter do not differ by the Scott-Knott test at 5% probability. <sup>(2)</sup>Refer to Table 1 for the description of the fertilizers. <sup>ns</sup>Nonsignificant.

a negative effect of zeolite. The ion Cu<sup>2+</sup> has affinity for zeolite negative charges, as described by Kocaoba et al. (2007) and Calvo et al. (2009). Stoichiometric calculations showed that the amount of zeolite in this formulation is capable to retain around 4.4 g kg<sup>-1</sup> Cu<sup>2+</sup> of the final product. Since the formulation U<sub>BCuZ-i</sub> has 1.17 g kg<sup>-1</sup> Cu<sup>2+</sup>, part of the Cu might have been retained in the negative charges of zeolite and, therefore, it was not available for inhibiting urease activity in the soil.

The inclusion of clay minerals in fertilizers mixture has spread up in the last few years in Brazil. It aims to bind the nutrients in order to delay their release into the soil solution. However, no satisfactory results were observed here, with the mixture of urea and zeolite (U<sub>Z-i</sub>). Stoichiometric analysis shows that the contribution of zeolite CEC (140 cmol<sub>c</sub> dm<sup>-3</sup>) for retaining ammonium is relatively small, around 25 g dm<sup>-3</sup> NH<sub>4</sub><sup>+</sup>. Considering that the laboratory-developed formulations have 20% of zeolite, the amount of NH<sub>4</sub><sup>+</sup> bound to be retained is very low, around 5.0 g dm<sup>-3</sup> of the final product. Thus, there is no significant effect of zeolite inclusion on N volatilization. This inefficiency has been reported previously by Tarkalson & Ippolito (2011), who concluded that zeolite (clinoptilolite) did not influence the retention of ammonium in swine manure, probably due to the adsorption competition by other cations. Moreover, Faria et al. (2013) did not observe any effect of coating urea with zeolites on N volatilization, compared to commercial urea.

The clinoptilolite zeolite has a specific surface of only 11.4 m<sup>2</sup> g<sup>-1</sup>, according to the BET method. This and the small amount of zeolite used in the mixture (20%) can justify the lack of efficiency of the clay mineral in controlling N losses. However, Werneck et al. (2012) reported a 69% reduction in N volatilization due to clinoptilolite coating or incorporation into urea granules, compared to commercial pearly urea. This supports the notion that zeolite has some influence on volatilization inhibition, due to the zeolite capacity to decrease NH<sub>4</sub><sup>+</sup> concentration in the soil solution; but the real mechanism of inhibition is not clearly known yet.

Coating urea with other compounds, like elemental S, can theoretically reduce volatilization, since it would reduce pH around the fertilizer granule in the soil (Saik, 1995). However, this study's results did not prove that, and small reduction was observed in Nitro Gold

(urea coated with elemental S). Other studies have also showed that urea covered with sulfur does not reduce ammonia losses by volatilization (Faria et al., 2014; Oliveira et al., 2014). The laboratory-incorporated formulations with elemental S and zeolite (U\_S-i and U\_SZ-i) showed a better result than Nitro Gold. Nascimento et al. (2013) observed that S-coated urea reduced N losses by 50%, but the authors reported lack of rain for around 15 days after fertilizer application, which may have favored microbial S oxidation and the acidification of the environment around urea granules in the soil.

In general, the laboratory-developed formulations were able to inhibit ammonium losses by leaching, when compared to urea (Table 2). However, small N contents as ammonium were found in the leaching solution, in all urea formulations evaluated. The laboratory-incorporated formulation U\_NBPTZ-i had the highest ammonium loss by leaching; and commercial urea, U\_NBPTCuZ-i, FH Nitro Mais, and U\_BCuZ-i were statistically similar, with greater ammonium losses by leaching than U\_Z-i, FH Nitro Gold, U\_S-i, U\_NBPTCu-i, U\_SZ-i, U\_Cu-i, Super N, U\_BCu-i, U\_NBPT-i, and AS (Table 2).

Nitrate losses by leaching were very low, and there was no significant difference between urea formulations (Table 2). The total mineral N leached (ammonium + nitrate) was lower in the laboratory-developed formulations (except U\_NBPTZ-i) and in the commercial formulations with urease inhibitors than in commercial urea. Up to 9.3 mg N per column was percolated to layers deeper than 0.45 after four simulated precipitations, in the worst treatment (U\_NBPTZ-i). This amount is substantial, considering the whole crop cycle, specially in rainy seasons.

Many studies have reported significant nitrate leaching losses in agricultural soils (Ghiberto et al., 2009; Dourado-Neto et al., 2010; Yang et al., 2015). However, according to Oliveira et al. (2007), N losses by leaching in Brazilian soils are very low in most of the situations.

In general, the formulations with the lowest N volatilization had also the lowest mineral N leaching (Table 2). However, U\_NBPTZ-i formulation showed the highest N-NH<sub>4</sub><sup>+</sup> leaching.

The presence of zeolite with the additives B and Cu<sup>+2</sup> (U\_BCuZ\_i) reduced NH<sub>4</sub><sup>+</sup> leaching and, therefore, this

clay mineral contributes to soil ammonium retention, due to its negative charges (Andrade et al., 2010).

The reduction in nitrate leaching by urease inhibitors can also be significant, although it is not their main purpose. This study observed small amounts of nitrate leaching through the soil (mean of 3.0 kg ha<sup>-1</sup>), which did not differ between the evaluated sources (Table 2). Sanz-Cobena et al. (2012) evaluated the topdressing application of NBPT-coated urea in maize and observed that the inhibitor was able to reduce N leaching by 47% compared to commercial urea. More specific researches reported that most of the leached N comes from mineralized organic matter (Roberts et al., 2011). But in this study, this probably was not the case, since the study considered only four simulated light rain events, in four consecutive days.

The upper layers (0–0.10 and 0.10–0.20 m) accumulated less N-NH<sub>4</sub><sup>+</sup> than the deepest one (0.20–0.45 m). Most of the laboratory-developed formulations had a uniform ammonium distribution through soil profile (Table 3). The accumulated ammonium differed between sources only in the layer of 0.10–0.20 m, where the values under U\_Z-i and U\_NBPTZ-i, although not significantly different from commercial urea (U), were higher than the other sources tested.

The amount of N-NO<sub>3</sub><sup>-</sup> accumulated in the soil profile was much higher than N-NH<sub>4</sub><sup>+</sup>, for all formulations (Table 3). The highest N-NO<sub>3</sub><sup>-</sup> accumulation occurred in the upper layers (0–0.10 and 0.10–0.20 m), and U\_BCuZ-i stood out. The formulations U\_NBPT-i, U\_S-i, U\_NBPTCu-i, U\_Cu-i, U\_SZ-i, U\_NBPTCuZ-i and the commercial Super N also had significant nitrate accumulations in the upper layers, much higher than other formulations tested and than control.

Total mineral N in the soil profile, down to 0.45-m depth, was higher for sources that left more N-NO<sub>3</sub><sup>-</sup> in the upper layers, notably U\_BCuZ-i (Table 3), and decreased following the order: U\_NBPT-i, U\_NBPTCu-i, U\_S-i, U\_SZ-i, U\_Cu-i, U\_NBPTCuZ-i, and commercial Super N. The other laboratory-developed formulations and commercial sources left lower mineral N in the profile.

The low N-NH<sub>4</sub><sup>+</sup> accumulation in the soil profile can be related to the intense nitrification of this amide source with increased pH around the granule due to the hydrolysis of the urea-based fertilizers (Chien et al., 2009). The accumulated N-NH<sub>4</sub><sup>+</sup> in the soil profile (from 1.0 to 4.3 kg ha<sup>-1</sup>) were similar to those reported

**Table 3.** N-NH<sub>4</sub><sup>+</sup> and N-NO<sub>3</sub><sup>-</sup> accumulation (mg dm<sup>-3</sup>) in different soil layers with the application of different nitrogen commercial fertilizers and urea-based laboratory formulations<sup>(1)</sup>.

Fertilizer	0–0.10 m		0.10–0.20 m		0.20–0.45 m		Total
	N-NH <sub>4</sub> <sup>+</sup>	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	N-NO <sub>3</sub> <sup>-</sup>	N-NH <sub>4</sub> <sup>+</sup>	N-NO <sub>3</sub> <sup>-</sup>	
C	1.1 <sup>ns</sup>	1.9a	1.1a	2.0a	3.0 <sup>ns</sup>	4.6 <sup>ns</sup>	13.8a
AS	2.2	4.9a	1.0a	2.5a	3.6	8.9	21.1a
U_NBPT-i	1.5	17.1b	1.7a	20.2b	2.8	7.2	50.4b
U_BCu-i	1.6	6.5a	1.2a	8.3a	1.7	4.5	23.8a
U_NBPTZ-i	1.7	3.6a	2.9b	3.3a	3.8	5.4	10.8a
U_BCuZ-i	3.7	31.9c	2.2a	24.6b	2.6	13.5	78.6c
FH Nitro Mais	1.5	4.3a	1.3a	2.8a	4.0	7.4	21.3a
Super N	1.7	13.8b	2.0a	20.5b	3.5	8.0	49.9b
U_Cu-i	1.4	15.2b	1.5a	12.5a	4.4	6.6	41.7b
U_SZ-i	1.6	17.6b	1.9a	10.2a	2.3	10.9	44.5b
U_NBPTCuZ-i	1.5	14.5b	1.5a	7.9a	4.2	7.9	37.5b
U_NBPTCu-i	2.1	14.8b	1.6a	14.7b	4.4	10.3	47.8b
U_S-i	2.3	18.4b	1.3a	10.2a	3.9	8.9	45.0b
FH Nitro Gold	2.2	4.5a	1.5a	3.7a	3.6	6.4	21.8a
U_Z-i	2.3	8.6a	3.5b	7.6a	4.3	6.3	32.5a
U	2.7	7.8a	2.8b	6.4a	3.4	6.0	28.9a
Mean	2.0	11.6	1.7	8.0	3.5	7.7	34.5
CV(%)	56	46.9	55.6	83	63.4	57.8	40.8

<sup>(1)</sup>Means followed by the same letter do not differ by the Scott-Knott test at 5% probability. <sup>(2)</sup>Refer to Table 1 for the description of the fertilizers. <sup>ns</sup>Non-significant.

by Primavesi et al. (2006) in equivalent soil layers. The authors, however, applied 200 kg ha<sup>-1</sup> N in a pasture, during a rainy period, which meant significantly different experimental conditions compared to this study (120 kg ha<sup>-1</sup> N, under controlled conditions).

N-NO<sub>3</sub><sup>-</sup> levels (Table 3) accumulated in surface layers (0–0.10 and 0.10–0.20 m), especially for the sources with lower volatilization (Table 2), which preserved more N in the soil. When evaluating ammonium and nitrate contents in soil, at the 51<sup>st</sup> day after the application of commercial urea and ammonium sulfate in corn cultivation, Lara Cabezas & Souza (2008) found similar patterns of nitrate and ammonium distribution using urea+ammonium sulfate and urea+agricultural gypsum, which decreased in the soil profile. Mariano et al. (2013), evaluating the mineralized N by aerobic incubation down to 0.60-m depth, observed that the highest mineralization rate was found at the 0–0.20 m layer. The authors attributed this result to the higher organic matter content and to the greater activity of microorganisms in this layer.

It should be highlighted that the total and the organic N accumulated in soil profile were not evaluated here. This information could help explain the fate of N over time and evaluate the hypothesis that, actually, a substantial amount of N from fertilizers may be immobilized in the soil layers, even in a sandy soil with low organic matter content, as the one used in this study.

## Conclusions

1. The new laboratory-developed formulations, with the incorporation of urease inhibitors (NBPT, H<sub>3</sub>BO<sub>3</sub>, and Cu) into the urea granules, are more efficient in reducing N volatilization losses than commercial fertilizers coated with these same additives, showing similar results to ammonium sulfate.

2. The addition of zeolite in the laboratory-developed formulations containing urease inhibitors and elemental sulphur does not reduce N volatilization; and no promising results were observed for N leaching.



3. Ammonium and nitrate leaching and total N mineral accumulation in the soil profile are not affected by the urease inhibitors.

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