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Nitrogen release from urea with different coatings Odirley R Campos,^{*}© Edson Marcio Mattiello, Reinaldo Bertola Cantarutti and Leonardus Vergütz

Abstract

BACKGROUND: Coatings or urease inhibitors are designed to reduce losses of ammonia $[NH_{3(g)}]$ from urea fertilizers. However, nitrogen (N) release and its effects on soil solution have not previously been evaluated under standardized conditions in soils. In this study, the urea fertilizers were incubated in chambers filled with sandy loam soil, adapted for the collection of $NH_{3(g)}$ and soil solution by centrifugation.

RESULTS: In the fast-release N fertilizers, around 93% and 100% of urea-N applied was recovered within the first hours of incubation. In contrast, in the slow-release N fertilizers, less than 40% of urea-N applied, was recovered at 19 days of incubation. The maximum N release from the fertilizers followed the order: UP1 (106%) \approx UNBPT (102%) \approx urea (93%) > USP2 (57%) \approx USP3 (57%) > USP4 (31%) \approx USP5 (18%). NH_{3(g)} volatilization accounted for only 3% of the applied N in the slow-release fertilizers, which corresponded to about 88% less than the NH_{3(q)} loss from prilled urea.

CONCLUSION: This study demonstrated distinct N release patterns, which changed the N dynamics in the soil. Some coatings effectively delayed urea release from granules and reduced NH_{3(g)} gas losses, while other were not efficient. © 2017 Society of Chemical Industry

Keywords: hydrolysis; *N*-(*n*-butyl) thiophosphoric triamide; slow-release fertilize; volatilization

INTRODUCTION

Urea production has increased worldwide as a result of the increase in more affordable and low-cost raw materials, such as nitrogen gas (N_2) and natural gas.¹ However, nitrogen (N) losses from urea potentially reduce the agronomic efficiency of urea fertilizers.

Adequate soil moisture is needed to dissolve the applied urea fertilizer granules and allow the conversion of urea into ammonium carbonate (NH₄HCO₃) by urease, resulting in the release of ammonium (NH₄⁺) into the soil.² This process promotes a temporary pH increase around the granules or within the entire application area. However, NH₄⁺ is relatively unstable at high pH, and the N is lost as gas if converted into ammonia [NH_{3(g)}]. N loss in the form of NH_{3(g)} may reach up to 77% of the N applied when using urea.³⁻⁵ Accordingly, a rapid increase in urea concentration in the soil solution, arising from a fast-release source application, could be a key factor in reducing the fertilizer agronomic efficiency,^{6,7} strongly impeding the use of urea.

Consequently, fertilizer companies have been seeking alternatives other than urea to reduce N losses. Some developed products, containing urease/nitrification inhibitors or coatings with substances that are able to reduce dissolution in the soil, such as elemental sulfur (S⁰) and hydrophobic polymers, have shown slower nutrient release.⁸

Among the urease inhibitors, *N*-(*n*-butyl) thiophosphoric triamide (NBPT) is one of the most efficient and widely available substances and is generally used at doses varying from 400 to 1000 mg kg⁻¹ urea.^{8–10} Once in contact with the soil, NBPT is converted to its analog *N*-(*n*-butyl) phosphoric triamide (NBPTO),¹¹ which has an inhibitory action on urease, thereby ensuring urea longevity in its applied chemical form. Polymers and/or elemental sulfur are used in coated fertilizers to act as a physical barrier to water permeability. Such products delay the release and diffusion of urea out of the granule, thereby altering the dynamics of N forms.^{8,12,13} Thus, recognizing the patterns of nutrient release is important for the prediction of soil reactions, as well as plant N availability and absorption.

N release from slow release fertilizers has been estimated by dissolution in water or acidic solutions.⁸ Such tests provide important information on nutrient release rates. However, this test does not permit the effects of the release rate on the N dynamics in soil to be distinguished, particularly regarding urea hydrolysis, volatilization of N and changes in the pH of the application region.

The objectives of the present work were to evaluate N release and dynamics using sandy loam soil samples with slow-release urea fertilizers.

MATERIAL AND METHODS

The soil was collected at Três Marias, in Minas Gerais State, Brazil, from the top layer (0–30 cm), then air-dried and sieved to <2 mm before use. The soil was a Red–Yellow Latosol (Oxisol) and had the following physical and chemical properties: clay 190 g kg⁻¹; water retention capacity 170 g kg⁻¹; cation exchange capacity 4.8 cmol_c dm⁻³; pH 4.8 in water and organic carbon 15 g kg⁻¹.

Soil samples (180 g) were placed into incubation chambers adapted to separate the soil solution by centrifugation (Fig. 1). The

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Figure 1. The soil solution collecting system consists of a soil incubator and a soil-solution collector. The soil incubator and soil solution collector internal parts are shown in the diagram on the left side and a sectional view of structure on right side. It was made of PVC pipe, an inner ring and a perforated Tecnil plate. The measures are shown in millimeters.

low NH_4^+ adsorption is a crucial process in the soil N dynamics. Because of this, the N release from the fertilizers could be assessed in an easier way with sandy textured soils.

The incubation chambers were constructed of 70-mm PVC pipes and a perforated plate (3 mm) placed at the bottom. A slow-filtering paper (JP42, Φ pores $\approx 8 \mu$ m) was positioned at the end of the incubation chamber to avoid mixing clay and soil solution. The incubation chambers were kept in static collectors of NH_{3(g)} made of PVC tubes ($\Phi \approx 8 \text{ cm}$). Foam discs saturated with a solution of glycerine and H₂SO₄ (1 mol L⁻¹) were placed inside the collectors to capture NH_{3(g)} as NH₄⁺, according to the models of Cabezas *et al.*¹⁴ The N in the foams was determined by Kjeldahl distillation. A portion of the soil solution was removed by centrifuging the samples at 2500 × g at 25 °C in a centrifuge containing four buckets of 400 mL. A soil solution sampler was assembled as proposed by Miranda *et al.*¹⁵ with some adaptations (Fig. 1).

The experiment consisted of a randomized block design with four replications. Treatments were arranged in a $(7 + 1) \times 9$ factorial scheme, comprising seven fertilizers and a control without N, plus nine incubation times, which ranged from 1 h to 54 days. The maximum evaluation period was set in compliance with the N release of the tested fertilizers, reaching less than 54 days for fast-release ones.

The four commercially available coated urea fertilizers (USP2, USP3, USP4 and USP5), a non-commercial coated urea fertilizer (UP1), a urea fertilizer with urease inhibitor (UNBPT) and a prilled urea (U) were evaluated. A control without N was also included. Both UNBPT and U contained 45% N each.

Regarding the coated fertilizers, UP1 (37% N) was coated with polyolefins and USP2 (34% N, 24% S), USP3 (39% N, 16% S), USP4 (39% N, 13% S), and USP5 (37% N, 11% S) were coated with S⁰, polyolefins and ethylene-vinyl acetate co-polymers. Polymers

were accounted for 1-3% of coated fertilizers weight according to their release rate. Both S⁰ and polymers had a hydrophobic character. Even though NBPT urease inhibitor loses efficiency with storage time,⁹ UNBPT was stored for 60 days before use because storing is a common practice.

Fertilizers were applied at a 2 g kg⁻¹ rate of N in the center of the incubator and 0.5 cm into the soil, allowing it be fully immersed in the soil. After application of fertilizer, the incubators with NH_3 collectors were placed in a greenhouse where the minimum and maximum air temperature measured were 25 and 30 °C, respectively.

The pH of the soil solution extracts (SS) was determined and solutions were treated with 0.05 mL phenylmercuric acetate (PMA) solution (500 mg L⁻¹), which is sufficient to inhibit ure-ase. The total-N and NH₄⁺-N concentrations,¹⁶ as well as urea-N concentration¹⁷ in the soil and the soil solution, were measured. The percentage of N recovered, which was regarded as released N, was calculated using the following equation:

$$N_{Released} = \left(\frac{\sum N_{Fertilized treatments} - \sum N_{Control}}{N_{Applied}}\right) \times 100$$

where $\sum N$ is the sum of the total N forms in soil, soil solution and NH₃-N and N_{applied} is the amount of urea-N with reference rate of 2 g kg⁻¹. The percentage of volatilized N (N_{vol}) was calculated by:

$$N_{vol} = \left(\frac{N_{NH_{3(g)}Fertilized treatments} - N_{NH_{3(g)}Control}}{N_{Applied}}\right) \times 100$$

The rate of N in different forms (urea-N or NH_4^+ -N) in the soil solution was calculated by:

$$N_{x} = \left(\frac{N_{x_{Cumulative}} \times Volume_{SS}}{N_{Applied}}\right) \times 100$$

where N_x is the concentration (g L⁻¹) of N as urea-N or NH_4^+ -N forms in soil solution after removal of the treatment control effect and Volume_{SS} is the volume of water in soil (liters), based on water retention capacity of the soil (170 g kg⁻¹).

The rate of N in different forms (urea-N or NH_4^+ -N) in the soil system was calculated using the following equation:

$$N_{x} = \left| \begin{array}{c} \left(N_{x \text{ in } SS} \times \text{Volume}_{SS} \text{ extracted} \right) \\ + \left(N_{x \text{ in } soil} \times \text{Volume}_{Soil \text{ sample}} \right) \\ \hline N_{\text{Applied}} \end{array} \right| \times 100$$

where $N_{x \text{ in }SS}$ is the concentration (g L⁻¹) of N as urea-N or NH₄⁺-N forms in soil solution after removal of the treatment control effect, $N_{x \text{ in soil}}$ is the concentration (g dm⁻³) of N as urea-N or NH₄⁺-N forms in soil sample after removal of the treatment control effect, Volume_{SS} is the volume of water in soil (liters), based on water retention capacity of the soil and Volume_{soil sample} is the volume of the soil sample (0.18 dm³).

Data underwent variance and regression analyses for response variables according to incubation time by using SAS 9.1 statistical software (SAS Institute, Inc., Cary, NC, USA). Non-linear models were fitted to release (N_{released}) and volatilization (N_{vol}) patterns, through which maximum released N was estimated. Results of N forms (N_x) were displayed in graphs with mean values and standard deviations, showing N form dynamics in the soil solution.

Table 1. Equations used to estimate nitrogen release from urea fertilizers, percentage of released nitrogen (\hat{y}) and respective estimated time (x) used in sandy loam soil samples (Oxisol)

Fertilizer	Equation	R ²	N _{released} (%)	Time (days)
UNBPT	$\widehat{y} = \frac{61.48 - 34.24^{**}x + 5.11^{***}x^2}{1 - 0.5863^{***}x + 0.081101^{***}x^2 + 0.002838^{**}x^3}$	0.99	102.2	3
UP1	$\widehat{y} = \frac{55.36 - 27.32^{**}x + 3.962^{**}x^2}{1 - 0.595669^{***}x + 0.094866^{**}x^2 + 0.0008^*x^3}$	0.96	106.2	3
U	$\widehat{y} = \frac{55.92 - 58.30^{***} x^{0.5} + 15.60^{***} x}{1 - 1.00299^{***} x^{0.5} + 0.19084^{**} x + 0.03542^{\circ} x^{1.5}}$	0.99	93.0	3
USP2	$\widehat{y} = \frac{26.17 - 2.68^{**} x^{0.5}}{1 - 0.30088^{***} x^{0.5} + 0.02983^{***} x}$	0.93	56.8	18
USP3	$\widehat{y} = \frac{20.27 - 11.59^{**} x^{0.5} + 2.061^{**} x}{1 - 0.56978^{***} x^{0.5} + 0.088173^{**} x}$	0.96	57.4	12
USP4	$\hat{y} = \frac{9.789 + 0.3458^* x}{1 - 0.03923^{***} x + 0.000919^{**} x^2}$	0.87	31.3	27
USP5	$\widehat{y} = \frac{19.37 - 8.88^{**} x^{0.5} + 1.236^{**} x}{1 - 0.4626^{***} x^{0.5} + 0.05931^{***} x}$	0.93	37.4	18
The two right columns show the maximum percentage of released N and the related time to maximum released N. $^{\circ}$, *, **, ***, coefficients, statistically significant at 10, 5, 1 and 0.1% of probability by the <i>t</i> test.				

RESULTS

Nitrogen release

Based on the results, the fertilizers could be divided into three groups according to their N-release patterns (Table 1). Group 1 (G1) comprised U, UNBPT and UP1 sources with a fast-release rate, which had full dissolution (100% on average) at 3 days incubation. Group 2 (G2) was represented by USP2 and USP3 with an intermediary-release rate (57% on average), requiring 18 and 12 days, respectively, to reach maximum released N. Group 3 (G3), represented by USP4 and USP5, had the slowest release rate (34% on average) and the longest time to reach maximum released N, of 27 and 18 days, respectively, in a sandy loam soil texture.

Soil solution characteristics

The soil solution showed distinct characteristics that depended solely on the fertilizer used (Fig. 2). The solution acidity was reduced according to the ability of the fertilizer to release urea. Therefore, maximum pH values for U and UP1 (G1) were 8.6 and 8.8, respectively, while NBPT had a maximum pH of 9.0. Yet, in G2, the USP2 and USP3 fertilizers reached a maximum pH of 7.8 and 7.7, respectively. Moreover, for G3, maximum pH values of 5.9 and 5.6 were found for USP4 and USP5, respectively.

On the fourth day, around 22% and 11% of the added N was in urea form when using U and UP1, respectively. For such fertilizers, urea form availability peaks occurred before the N-NH₄⁺ ones, which corresponded to 16% and 14%, respectively, of the applied N (Fig. 2).

Nitrogen forms and dynamics in the soil system

In the fast-release N fertilizers (U, UP1 and UNBPT), around 93% and 100% of the urea-N applied were recovered within the first incubation hours (Fig. 3). However, significant reductions in urea-N concentration were noted after 1 h for U and after 1 and 2 days for UP1 and UNBPT, respectively (Fig. 3). Urea in the soil system was reduced to zero rate within the first week, which demonstrates a fast-release and conversion of the amidic form of these fertilizers by urease activity (Fig. 3). Concurrent with the decline in urea concentrations, NH₄⁺-N concentrations increased in the soil, accounting for 62% and 67% of the applied N on the fourth day after U and UP1 application, respectively. Afterward, NH₄⁺-N concentrations in the soil decreased, representing, on average, 23% of the applied N at 32 d incubation for G1 fertilizers (Fig. 3).

The G2 fertilizers (USP2 and USP3) presented low concentrations of urea-N; however, concentrations were even lower for G3 fertilizers (USP4 and USP5). Thus, it was assumed that dissolution rates decreased based on granule coating type (Fig. 3). Additionally, the rates of recovered NH₄⁺-N were low compared to G1, i.e. 48% at 12 days for USP2, 45% at 16 days for USP3, 36% at 19 days for USP4, and 32% at 19 days for USP5 (Fig. 3).

NH_{3(g)} volatilization

Volatilization of NH₃ represented, on average, 24% of the applied N for G1 fertilizers (Fig. 4). NBPT urease inhibitor reduced volatilization by less than 3% compared to U.

Volatilization rates were 20% and 11% for USP2 and USP3, respectively (Fig. 4). These rates were equivalent to 15% and 54% reductions in N volatilization when compared with U, respectively. Furthermore, the time to reach a maximum volatilization value was increased up to 13 days compared to the time needed for prilled urea.

For G3 fertilizers, $\mathrm{NH}_{\mathrm{3(q)}}$ volatilization accounted for only 3% of the applied N, being about 88% lower than NH_{3(g)} loss from prilled urea (Fig. 4).

DISCUSSION

Evaluating the N released from fertilizers into the soil is crucial in determining the most effective release patterns and chemical reactions that affect N use efficiency of urea fertilizers under field conditions. Soil solution sampling and analysis, besides being rapid procedures, may provide the most reliable results with the advantage of requiring less dilution compared to the use of extractant solutions and direct pH evaluations using soil suspensions in water.

The coated fertilizers presented varied patterns of release, loss and forms of N in the soil. The results showed that some coatings were effective (G3) at delaying granule dissolution, hence, proved the importance of low permeability coating materials. The rate of urea release affects N dynamics in the soil and the reactions that lead to volatilization and leaching losses. Moreover, the residual N effect should be higher than that of non-coated fertilizers.^{18,19} Nevertheless, fertilizers with low N release ability should be used cautiously to avoid the supply of nutrients below that required by plants,²⁰ mainly for short cycle crops.

Most $NH_{3(q)}$ volatilization observed in G1 was associated with high soil solution pH values. Rapid dissolution of granules and urea release into the soil solution is followed by urea hydrolysis and



Incubation time (d)

Figure 2. Soil solution pH and percentage of recovered nitrogen as urea-N and NH_4^+ -N forms in soil solution after application of fertilizer. U, pearly urea; UP1, urea coated with polymer 1; USP2, urea coated with S⁰ and polymer 2; USP3, urea coated with S⁰ and polymer 3; USP4, urea coated with S⁰ and polymer 4; USP5, urea coated with S⁰ and polymer 5.

subsequent NH₄⁺ formation, a process that consumes hydrogen protons.^{6,7} Given the instability of NH₄⁺ in alkaline conditions, it is converted to NH₃, which is lost in gas form.^{21,22} Therefore, NH_{3(g)}-N losses are more pronounced in fast-release fertilizers, such as G1, compared to G2 and G3 (Fig. 3).

The NBPT inhibitor maintains urea in its chemical form for a long time, thus reducing volatilization.^{4,7,23} However, the current results

showed that when stored for 60 days, UNBPT had similar reactions in soil compared to prilled urea. Urease inhibitor loses efficiency with storage time. Therefore, long-term storage is not advisable, as recommended by Watson *et al.*,⁹ especially when temperatures are high, as in Brazil.

Soil solution characteristics may indicate the release capacity and behavior of fertilizers in the soil. Concentrations of urea-N



Figure 3. Percentage of nitrogen recovered as urea and NH₄⁺ form in soil after application of fertilizer. U, pearly urea; UP1, urea coated with polymer 1; USP2, urea coated with S⁰ and polymer 2; USP3, urea coated with S⁰ and polymer 3; USP4, urea coated with S⁰ and polymer 4; USP5, urea coated with S⁰ and polymer 5.

and NH_4^+-N , as well as soil solution pH at field conditions, can be very similar to those found in the current experiment, particularly considering the formation of microenvironments with high concentrations of N around the fertilizers granules. Although N dissolution tests in water or acidic solutions provide

a method to rapidly gain information about coating effectiveness, soil incubation methods are essential for assessing N dynamics from slow- or controlled-release fertilizers. In contrast, some fertilizers, with characteristics similar to prilled urea, were no longer feasible as slow-release fertilizers. Moreover, the



Figure 4. Volatilization of NH₃ after application of fertilizer. U, pearly urea; UP1, urea coated with polymer 1; USP2, urea coated with S⁰ and polymer 2; USP3, urea coated with S⁰ and polymer 3; USP4, urea coated with S⁰ and polymer 4; USP5, urea coated with S⁰ and polymer 5.

current results are in agreement with the results from similar studies. $^{\rm 13,24-26}$

CONCLUSIONS

The current work verified distinct release patterns of N, which changed the N dynamics in the soil. The maximum N released from the fertilizers followed the order: UP1 (106%) \approx UNBPT (102%) \approx urea (93%) > USP2 (57%) \approx USP3 (57%) > USP4 (31%) \approx USP5 (37%). Fast-release urea fertilizers had complete dissolution in soil at 3 days incubation, while the slowest release fertilizer only released 31% N at 27 days incubation. The increase in soil pH with urea hydrolysis, combined with high NH₄⁺ concentrations as a result of fast-release urea, results in higher NH_{3(q)} losses.

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