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## Comissão 3.2 - Corretivos e fertilizantes

# AMMONIA VOLATILIZATION AND YIELD COMPONENTS AFTER APPLICATION OF POLYMER-COATED UREA TO MAIZE<sup>(1)</sup>

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### SUMMARY

A form of increasing the efficiency of N fertilizer is by coating urea with polymers to reduce ammonia volatilization. The aim of this study was to evaluate the effect of polymer-coated urea on the control of ammonia volatilization, yield and nutritional characteristics of maize. The experiment was carried out during one maize growing cycle in 2009/10 on a Geric Ferralsol, in Uberlândia, MG, Brazil. Nitrogen fertilizers were applied as topdressing on the soil surface in the following urea treatments: polymer-coated urea at rates of 45, 67.5 and 90 kg ha<sup>-1</sup> N and one control treatment (no N), in randomized blocks with four replications. Nitrogen application had a favorable effect on N concentrations in leaves and grains, Soil Plant Analysis Development (SPAD) chlorophyll meter readings and on grain yield, where as coated urea had no effect on the volatilization rates, SPAD readings and N leaf and grain concentration, nor on grain yield in comparison to conventional fertilization.

**Index terms:** nitrogen, polymer-coated urea, N fertilizer, ammonia volatilization, *Zea mays*, SPAD reading.

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## RESUMO: VOLATILIZAÇÃO DE AMÔNIA E COMPONENTES DA PRODUÇÃO DO MILHO COM A APLICAÇÃO DE UREIA REVESTIDA COM POLÍMEROS

*Uma das maneiras de aumentar a eficiência dos fertilizantes nitrogenados, visando, por exemplo, à redução de perdas de amônia por volatilização, é o revestimento desses com polímeros. Objetivou-se avaliar o efeito da aplicação de ureia revestida com polímeros no controle da volatilização de amônia e a sua influência nos componentes da produção na cultura do milho. O experimento foi instalado na safra 2009/10 no município de Uberlândia, MG, em um Latossolo Vermelho-Amarelo (LVA) distrófico textura argilosa. Os tratamentos consistiram na aplicação, em cobertura no milho, de ureia revestida com polímeros e ureia convencional nas doses de 45; 67,5; e 90 kg ha<sup>-1</sup> de N, mais um tratamento-controle (sem N), dispostos em blocos casualizados. A aplicação de N influenciou positivamente o teor do nutriente nas folhas e nos grãos, a leitura SPAD e a produtividade de grãos, porém a ureia revestida não alterou as taxas de volatilização de amônia, a leitura SPAD e o teor de N nas folhas e grãos, assim como a produtividade de grãos em relação à aplicação do fertilizante convencional.*

*Termos de indexação: nitrogênio, ureia revestida com polímeros, fertilizante nitrogenado, volatilização de amônia, Zea mays, leitura SPAD.*

## INTRODUCTION

The average maize yield in Brazil is far below that observed in experimental fields and areas with greater use of technology or in other countries such as the United States. Among the main factors contributing to this low average crop yield is mainly the insufficient supply of N, the most absorbed nutrient, which influences grain yield most and is the greatest cost driver in maize production (Sangoi & Almeida, 1994; Silva et al., 2005).

One of the most commonly used N fertilizers is urea, typically a solid granular fertilizer with N in amide form. Among the advantages of urea is the very high N concentration (45 %), the low cost of production, transportation, storage, and application, as well as the high solubility, low corrosivity and ease of mixing with other sources. However, urea is highly hygroscopic and is a source with great potential for N loss by volatilization (Melgar et al., 1999). This is due to the rapid hydrolyzation of urea on the soil surface by extracellular enzymes called ureases, produced by microorganisms such as soil bacteria, actinomycetes and fungi. During urea hydrolysis, ammonium carbonate  $[(\text{NH}_4^+)_2\text{CO}]$  is formed, which is not stable but decomposed into ammonia  $\text{NH}_3\text{-N}$ ,  $\text{CO}_2$  and water. Thus,  $\text{NH}_3\text{-N}$  is emitted in the form of gas to the atmosphere, particularly and at higher intensity immediately after fertilizer application (Sangoi et al., 2003). However, the amount of  $\text{NH}_3\text{-N}$  volatilization depends mainly on weather conditions such as wind speed, temperature, relative air humidity, and pluvial precipitation, as well as on soil properties such as the cation exchange capacity, moisture, temperature, amount of organic matter, nitrification potential, pH, and  $\text{NH}_4^+\text{-N}$  concentration in the soil solution (Rochette et al., 2009).

One of the ways to increase the N fertilizer- use efficiency is the application of controlled or slow-release

fertilizer, or of fertilizer with inhibitors to prevent the rapid transformation of N contained in the fertilizers in less stable N forms in certain environments (Cantarella, 2007). This type of fertilizer is called "Enhanced-Efficiency Fertilizer" (Trenkel, 1997). Slow or controlled-release fertilizers are those that diminish the immediate release of nutrients or increase their availability over time by different mechanisms, in order to supply crops with nutrients for a longer period of time and optimize the plant uptake, reducing losses. This type of fertilizer is characterized by granule coating by sulfur films or various polymers (Trenkel, 1997).

The nutrient release from controlled-release fertilizers is efficient when water is available at and the soil temperature is around 21 °C (Chitolina, 1994). The nutrient release rate by fertilizer granules is directly proportional to soil temperature or substrate, since a temperature increase promotes expansion of the resin layer, increasing the water permeability. The thickness and chemical nature of the resin coating, number of micro-cracks in the surface and fertilizer granule size also contribute to determine the nutrient release curve over time (Trenkel, 1997). Enhanced-efficiency fertilizers are a new tool to stabilize fertilizer consumption and minimize environmental pollution (Tang et al., 2009; Machado et al., 2011).

According to results of Boman & Battikhi (2007), the use of slow-release N fertilizer reduces the need for splitting fertilization. Barati et al. (2006) detected greater N recovery from sulfur-coated urea than from ammonium chloride and urea.

Noellsch et al. (2009) compared the efficiency of fertilization with 168 kg ha<sup>-1</sup> of polymer-coated urea N with conventional urea in maize and observed a higher N uptake and grain yield in the treatment with polymerized urea. These authors stressed that a slower release from fertilizer reduced nutrient losses,

resulting in higher plant uptake. Despite the potential of slow-release fertilizers of increasing the N fertilizer-use efficiency, the high cost of these products, compared to traditional fertilizers, limits their use (Cantarella, 2007).

The use of polymers in urea coating has been described as a new option for N volatilization reduction, but for being a pilot product, little is known yet about their behavior (Reis Junior, 2007). This study aimed to evaluate the effect of the application of polymer-coated urea on ammonia volatilization, and on nutritional and biometric aspects and maize yield.

## MATERIAL AND METHODS

The experiment was carried out in the 2009/10 growing season in Uberlândia, MG, Brazil (19° 25' S and 47° 59' W; 700 m asl). The climate is classified as Cwa (Köppen), with dry winters and wet summers and an average temperature between 18 and 22 °C. The experimental area, on a clayey Geric Ferralsol (FAO, 1998), had been used in a no-tillage system with crop rotation for 18 years. Prior to the experiment, the soil of the experimental area was sampled for chemical analyses as described by Raij et al. (2001), and by Vitti (1989) for sulfur determination, in the 0-10 and 10-20 cm layers (Table 1).

Rainfall during the evaluation of N volatilization is shown in figure 1.

The treatments consisted of the application of polymer-coated (PCU) and conventional urea (CU) as maize topdressing. The coated and conventional fertilizers contained 41 and 45 % N, respectively. The coating of PCU consisted of compounds based on polymers and minerals, forming a double membrane. The polymer fraction was based on the association of different polymers, resulting in different molecular conformations after the final polymerization process that occurs after applying the fertilizer coating.

The experiment was arranged in a randomized block, 2 × 4 factorial design, i.e., two N fertilizers at four rates, with four replications. The two fertilizer forms were evaluated at rates of 0; 45; 67.5 and 90 kg ha<sup>-1</sup> N, of which the highest is the recommended rate for the region. In the volatilization measurements, the treatment without N application was used as correction factor component and was therefore not considered a treatment.

Each experimental plot consisted of seven 10-m crop rows spaced 0.7 m apart, of which the three central rows were used for evaluations, disregarding 2.5 m on either end. The fertilizers were applied by hand in bands, without incorporation, at a distance of approximately 0.10 m from the maize plants when these had four fully expanded leaves (leaf stage V4). The crop was sown in the last 10 days of October, using maize variety P 30F53H. Fertilization at sowing consisted of the application of 40, 152 and 48 kg ha<sup>-1</sup> of N, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O, respectively, and 30 kg ha<sup>-1</sup> K<sub>2</sub>O as topdressing, along with the N treatments.

Samplings for the determination of N volatilization losses were performed 1, 3, 5, 7, 11, 13, 15, 16, 17, and 18 days after fertilizer application and estimated by the direct method, using static semi-open NH<sub>3</sub> collectors developed by Nömmik (1973) used in a dynamic form, i.e., exchanging the collectors to adjacent bases, using one collector per plot with five support bases of collectors, within which the fertilizer was applied. The collectors consisted of a clear flexible tubular PVC structure (0.35 m height × 0.15 m internal diameter × 1 mm wall thickness) set on PVC supports (height 0.10 m). Correction factors were applied to correct the low efficiency of the collectors in quantifying volatilized N, as proposed by Lara Cabezas et al. (1999).

Within the semi-open collectors, two foams (density 0.02 kg dm<sup>-3</sup>) were fixed on supports (screws). Before installation, they were soaked in 50 mL of phosphoric acid solution (0.2 mol L<sup>-1</sup>) and glycerin (30 mol L<sup>-1</sup>) to retain ammonia. The top foam was fixed 31 cm above the ground for ammonia collection from the atmosphere, isolated from the lower foam, fixed 15.5 cm above the ground, to capture volatilized NH<sub>3</sub>-N (Lara Cabezas et al., 1999). At each sampling, the foams were removed and replaced by others; the upper were discarded and the lower ones refrigerated (5 °C) until analysis.

For analysis, each foam was placed on a porcelain funnel and with a vacuum pump, the foam was washed with approximately 400 mL of deionized water. From the solution extracted from each foam, an aliquot of 50 mL was taken for NH<sub>3</sub>-N distillation and Kjeldahl determination. The volatilized ammonia-N was calculated based on the values of sulfuric acid used for titration, by equation 1:

$$N = (V_s - V_b) \times f \quad (1)$$

where N = nitrogen captured in the collector; V<sub>s</sub> = acid volume for sample titration; V<sub>b</sub> = acid volume used for titration of the blank control and f = 0.7 (value of acid molarity, aliquot volume and volumetric flask extract).

**Table 1. Soil chemical properties prior to the experiment**

Depth	pH(CaCl <sub>2</sub> )	OM	P	S	K	Mg	Ca	H+Al	CEC	V	m
cm		g dm <sup>-3</sup>	— mg dm <sup>-3</sup> —		— mmol <sub>c</sub> dm <sup>-3</sup> —					— % —	
0-10	5.7	29	35	35	2.0	8	34	20	64	69	0
10-20	5.2	27	33	36	1.8	4	19	20	45	55	2

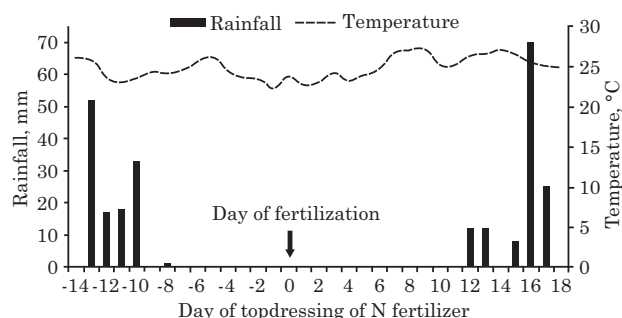


Figure 1. Rainfall during the evaluation of  $\text{NH}_3$  volatilization.

Data of  $\text{NH}_3$  quantified after distillation were corrected by the correction factors described by Lara Cabezas et al. (1999).

The N concentration in maize leaves was determined by collecting 20 leaves per plot, opposite to and below the main ear, at the time of the appearance of the female inflorescence (Malavolta et al., 1997). In the same period, indirect chlorophyll measurements were carried out with a Minolta SPAD 502<sup>®</sup> leaf chlorophyll meter, analyzing the middle third, between the edge and midrib of 10 leaves, also opposite to and below the ear, per experimental unit. Grain yield was estimated by weighing the grain harvested from 5 m of each row of the evaluated area of the plot, i.e., from a total of 15 m. Concomitantly, grain moisture was corrected to a content of  $13 \text{ g kg}^{-1}$  for weight correction. The N grain concentration was determined by the method described by Malavolta et al. (1997).

After analysis of variance, the data were analyzed by the Tukey test, using PROC GLM of the software package Statistical Analysis of SAS Version 9.01 (SAS, 2004).

## RESULTS AND DISCUSSION

The pattern of N volatilization losses was similar in all treatments, with a simultaneous peak intensity of losses, i.e., 15 days after fertilizer application (Figure 2), with no significant difference in the daily amount of N lost by volatilization between treatments or samplings. The findings confirmed results of Pereira et al. (2009), who compared volatilization rates from urea and coated urea, and observed that the moments of greatest ammonia losses from both fertilizers were comparable.

The daily rates of N volatilization showed that until the 13<sup>th</sup> day after fertilizer application, losses were small, due to low soil moisture, caused by the absence of rain for 10 days prior to fertilizer application and 11 days after N fertilization (Figure 1). The low soil water content was insufficient to initiate urea hydrolysis, preventing solubilization of the fertilizer and consequently the onset of N volatilization.

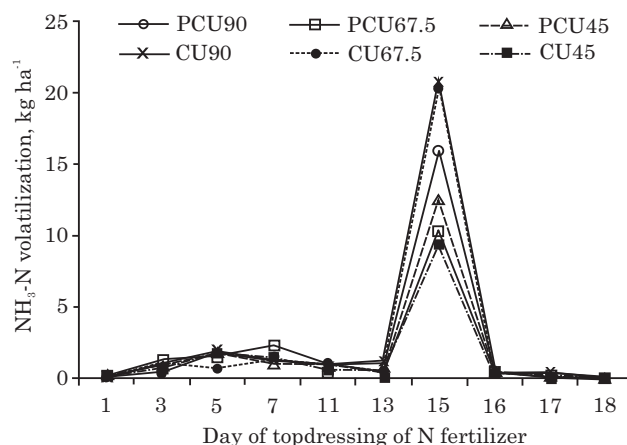


Figure 2.  $\text{NH}_3\text{-N}$  volatilization losses, after application of conventional and polymer-coated urea. PCU 90-Polymer-coated urea ( $90 \text{ kg ha}^{-1} \text{ N}$ ); PCU 67.5-Coated urea ( $67.5 \text{ kg ha}^{-1} \text{ N}$ ); PCU 45-Coated urea ( $45 \text{ kg ha}^{-1} \text{ N}$ ); CU 90-Conventional urea ( $90 \text{ kg ha}^{-1} \text{ N}$ ); CU 67.5-Conventional urea ( $67.5 \text{ kg ha}^{-1} \text{ N}$ ); and CU 45-Conventional urea ( $45 \text{ kg ha}^{-1} \text{ N}$ ).

On the 15<sup>th</sup> day after topdressing, a sharp increase in ammonia volatilization was observed, which can be explained by the occurrence of two rainfall events of 12 mm in the three days before this evaluation (Figure 1). The cumulative rainfall of 24 mm would have been enough to raise the soil moisture, allowing urea hydrolysis, but was insufficient to leach the fertilizer into the soil. In the following samplings, volatilization losses returned to lower levels, that is, to nearly zero N losses (Figure 2). The rainfall events of 8, 70 and 25 mm, respectively, on the 15<sup>th</sup>, 16<sup>th</sup> and 17<sup>th</sup> day after N topdressing (Figure 1), were responsible for these small losses, since this amount of rain would have been enough to incorporate the fertilizer into the soil. The presence of sufficient water to dilute the concentration of hydroxyls ( $\text{OH}^-$ ), which is responsible for the transformation of  $\text{NH}_4^+$  in volatile  $\text{NH}_3^+$  resulting from hydrolysis around the urea granules and incorporate them into the soil, decreases ammonia volatilization (Lara Cabezas et al., 1997). According to Silva et al. (1995), this development promotes increased contact between fertilizer and soil particles, with consequent increase of  $\text{NH}_4^+$  adsorption to the soil negative charges, hampering its transformation in  $\text{NH}_3$ , the form in which N is lost by evaporation.

The N losses by volatilization at the different rates and types of urea in the evaluation period were similar (Table 2). These results differed from those of Pereira et al. (2009), who reported significant differences in volatilized N loss from polymerized and conventional urea, with up to 45 % lower losses from the coated form.

Based on the results and climatic conditions of this experiment, it was inferred that the coated fertilizer did not significantly alter the pattern and amount of N volatilized, while rainfall was the main factor of influence in the period.



**Table 2. Loss of volatilized NH<sub>3</sub>-N, nitrogen concentration in maize leaves and grains, SPAD readings and grain yield followed by the significance of the factors**

N source	Rate	Volatilized NH <sub>3</sub>	Leaf N content	Grain N content	SPAD	Yield
		kg ha <sup>-1</sup>	g ha <sup>-1</sup>			kg ha <sup>-1</sup>
Control	0	-	26.9	10.6	38.8	6196
Coated urea	PCU 45	18.1	28.3	10.9	42.6	7258
	PCU 67.5	17.4	30.7	11.2	43.2	7484
	PCU 90	22.8	27.8	11.1	42.5	7389
Conventional urea	CU 45	14.3	26.2	11.2	38.6	6547
	CU 67.5	25.6	30.7	11.2	42.4	6721
	CU 90	26.6	29.6	11.8	43.7	7292
N source		ns	ns	ns	ns	ns
Rate		ns	**	**	*	**
N source × rate		ns	ns	ns	ns	ns
LSD		5.8	1.1	0.3	1.6	444
CV (%)		32.0	5.0	3.0	5.0	9.0

PCU 45: Polymer-coated urea (45 kg ha<sup>-1</sup> N); PCU 67.5: Coated urea (67.5 kg ha<sup>-1</sup> N); PCU 90: Coated urea (90 kg ha<sup>-1</sup> N); CU 45: Conventional urea (45 kg ha<sup>-1</sup> N); CU 67.5: Conventional urea (67.5 kg ha<sup>-1</sup> N); CU 90: Conventional urea (90 kg ha<sup>-1</sup> N). ns non-significant; \* and \*\* significant at 5 and 1% by the F Test.

The relative NH<sub>3</sub>-N losses by volatilization ranged from 26 to 44 % of total applied N; the proportional losses were higher in the treatments with lower rates, and vice-versa (Figure 3). This justifies the absence of significant differences in NH<sub>3</sub>-N losses between the different application rates, which can be explained by urease saturation in the area of fertilizer application (Savant et al., 1987), applied in bands in this experiment; this result might have been different in the case of broadcast fertilizer.

The application of coated fertilizer had no positive effect on yield. The lack of differentiated responses to the application of different sources on N volatilization loss can explain this result, because the soil-climatic conditions induced similar rates of nutrient release from fertilizers. These results confirmed the findings of Pereira et al. (2009), who detected no difference in yield between the application of polymerized and conventional urea, but disagree with Noellsch et al. (2009), who reported a greater effect of polymer-coated urea on maize yield. This higher yield can be explained by the influence of the soil moisture content, resulting in different rates of nutrient release and volatilization losses from the fertilizers. These authors reinforced the need for economic analysis to use this technology, since the higher cost of coated fertilizer limits its use.

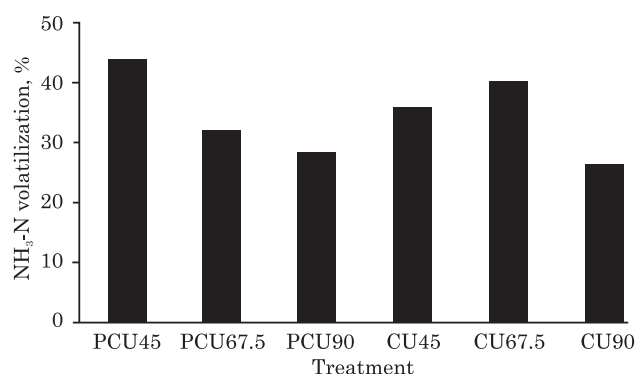
Nitrogen fertilization influenced yield, regardless of the use of coating fertilizer (Table 2). The N fertilization treatments had higher yields than those without fertilization although they did not differ from each other. It was therefore concluded that the application of lower rates than recommended, under these experimental conditions, was sufficient to meet the N requirements of maize. This can be explained by the fact that most N taken up by crops comes from the mineralization of soil organic matter and N

fertilization responsible for stimulating this process, a phenomenon known as “priming effect”, widely discussed in the literature (Jenkinson et al., 1985; Silva et al., 2006). As the experiment was conducted in an area under no-tillage for 18 years, with maize-soybean (N-rich legume) crop rotation and N fertilization of maize, it was concluded that there were considerable N stocks in the soil, and only a stimulus for mineralization would be enough to meet the maize requirement in the experimental period.

In the treatment without N fertilization, N leaf and grain concentrations and SPAD readings were significantly lower than in the fertilized treatments, but no effect of urea coating was detected (Table 2).

In the treatments control and lowest rate of conventional urea, the leaf N concentrations were below the minimum considered appropriate, which according to Büll (1993) is 27.5 g kg<sup>-1</sup> N. This was probably due to the absence of and lower supply with N in these treatments than in the others, because according to Rambo et al. (2004), the leaf N concentration indicates the plant nutritional status. This is based on the assumption that the leaves are the plant organs that respond fastest to changes in nutrient supply from soil and fertilizers.

According to Argenta et al. (2001), the leaf N concentration measurements provided by SPAD-502 are positively correlated. This was verified in this experiment, where the SPAD readings and leaf N concentrations were significantly lower in the treatment without N. This relationship was mainly attributed to the fact that 50-70 % of the total leaf N is integrated in enzymes (Chapman & Barreto, 1997), associated to chloroplasts (Stoking & Ongun, 1962), responsible for the green leaf color. Orioli (2008) tested N rates (0-150 kg ha<sup>-1</sup>) applied prior to maize sowing



**Figure 3. Percentage of ammonia (NH<sub>3</sub>-N) in relation to the total N applied as maize topdressing. PCU 45: Polymer-coated urea (45 kg ha<sup>-1</sup>N); PCU 67.5: Coated urea (67.5 kg ha<sup>-1</sup> N); PCU 90: Coated urea (90 kg ha<sup>-1</sup> N); CU 45: Conventional urea (45 kg ha<sup>-1</sup>N); CU 67.5: Conventional urea (67.5 kg ha<sup>-1</sup> N); and CU 90: Conventional urea (90 kg ha<sup>-1</sup> N).**

and found that SPAD values increased linearly with increasing rates, ranging from 27 to 54.2. The results of Orioli (2008) and those in our experiment were below the threshold considered satisfactory by Argenta et al. (2002), who determined a SPAD threshold of 58 for leaves at flowering as critical. On the other hand, Rambo et al. (2004) argued that the use of the method for determining a critical level of relative chlorophyll concentrations is questionable, since other factors than N availability in the soil can affect the intensity of the green leaf color and the reading of the chlorophyll meter. According to Argenta et al. (2002), the results of the measurement method by SPAD are consistent with the nutritional status of maize plants. One possible explanation for the increased concentrations of leaf N and SPAD values in fertilized treatments and no difference between these is that most of the N plant supply is derived from the mineralization of soil organic matter, which is intensified by the priming effect.

The N application rates increased the N grain concentration as well as SPAD readings and N leaf concentration (Table 2). Data from a study of Coelho et al. (1992) indicated that N concentration in maize grain for maximum production is approximately 11.8 g kg<sup>-1</sup>, similar to the value found in this experiment.

## CONCLUSIONS

1. Polymer-coated urea induced no reduction in ammonia losses by volatilization.

2. The application of coated urea did not increase grain yield, N concentrations in leaves and in grain and SPAD readings compared to conventional urea application.

3. The application of N, independent of the rate, had a positive effect on N leaf and grain concentrations, SPAD readings and grain yield.

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