

Volatilization of ammonia in stabilized slow-release nitrogen fertilizer under controlled conditions

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Abstract

The loss of nitrogen through volatilization leads research to the search for new technologies that release nutrients in a manner synchronized with the crop demand, minimizing losses and increasing efficiency of its use in agriculture, as is the case with the stabilized slow-release nitrogen fertilizer. This work sought to evaluate the losses of volatilized N-NH₃ in stabilized slow-release nitrogen fertilizer applied to the soil. The treatments followed a 5 × 3 × 2 factorial as follows: five nitrogen fertilizer sources (conventional urea - CU; urea combined with zeolite - UZ; sulfur coated urea - US; NBPT coated urea - U_{NBPT}, and urea combined with organic material - OU); three application times; and two managements (surface and incorporated applications) with three replications. The experiment was conducted using a collection chamber to capture NH₃ for 25 days, with samples taken at 2, 4, 7, 9, 11, 14, 16, 18, 21, 23 and 25 days after the start of the experiment. The ascending order of N-NH₃ volatilization was: UZ < US < CU < U_{NBPT} < OU, regardless of the time and management adopted. For all the sources used there was a loss reduction from 20.45% to 12.29%, when N sources were parceled, and from 19.63% to 13.95% when they were incorporated.

Keywords: nitrogen fertilization; N losses; NH₃ release; coated urea.

Abbreviations: Ca_calcium; Mg_magnesium; K_potassium; P_phosphorus; N_nitrogen; H + Al_acidity potential; CEC_cation exchange capacity; NH₃_ammonia; CU_convencional ureia; UZ_urea combined with mineral zeolite; US_elemental sulfur coated urea; U_{NBPT}_ureia coated with NBPT (N-(n-butyl) thiophosphate triamide); OU_urea combined with organic material (filter cake); T1_Time1; T2_Time2; T3_Time3; IM_Incorporated management; SM_Surface management.

Introduction

The integration of technology is assuming an important role in helping farmers in the management of factors produced in the field. Each segment, be it agricultural mechanization, biotechnology, or product efficiency, is enabling production improvements, creating a link between the primary sector, science and industry (Kreimeyer, 2015). This approach is ensuring many positive results, particularly by increasing the efficiency in the use of nitrogen fertilizers (Fernandes et al., 2005). The management of nitrogen fertilizer is one of the most studied agricultural practices in order to improve its use efficiency (Cantarella et al., 2008; Frazão et al., 2014). This need exists because of the low efficiency of nitrogen fertilization, due to losses by leaching, denitrification and mainly via volatilization, losses which can reach over 70% (Lara Cabezas et al., 1997), especially under tropical conditions. New technologies have been adopted in order to minimize the losses of ammonia (NH₃) through volatilization. The principal one is the use of urea as a coating (covering) with chemically altered products and, or pellets (Bennett, 1996). Sato and Morgan (2008) observed that the N loss to the environment may be reduced with the use of coated fertilizers, corroborating Medina et al. (2008). According to these authors, the coated fertilizers offer low N volatilization (10 to 30%) when compared to the conventional fertilizers.

However, contradictory results can be found in the literature, indicating advantages in the use of polymer coated urea (Wang et al., 2015; Nash et al., 2015) and others that report low efficiency compared with the common urea (Cahill et al., 2010; Carneiro et al., 2014). This study was conducted in order to quantify the N volatilized as NH₃ after application of higher efficiency nitrogen fertilizer at different times and under different soil application managements.

Results and Discussion

The use of stabilized controlled release nitrogen (N) fertilizers affected the amounts of NH₃ volatilized since its application in the soil samples (Table 1), as demonstrated by contrasts C1, C2 and C3 (Table 2), as well as by the different application times and managements studied. When calculating the total amount of N- NH₃ lost via volatilization for the applied sources (Table 1) the following order of N-NH₃ volatilized was observed: UZ < US < CU < U_{NBPT} < OU. The values lost by volatilization were, respectively, 14.12% (or 5.30 mg ring⁻¹); 15.12% (or 5.67 mg ring⁻¹); 15.58% (or 5.85 mg ring⁻¹); 16.41% (or 6.16 mg ring⁻¹); 22.70% (or 8.52 mg ring⁻¹).

The form of the product combinations or coatings with urea may lead to a lower N release rate and therefore reduce its losses by volatilization. The values of volatilized NH_3 observed are consistent with those reported in the literature by several authors (Volk, 1959; Lara Cabezas et al., 1997; Wang et al., 2015; Nash et al., 2015). The average values for loss-via-volatility were greater in the stabilized controlled release fertilizer group when compared to the use of conventional urea (C1, Table 2). The explanation rests in the high N losses with the application of OU and U_{NBPT} fertilizers, which increased the average above the levels when compared to the CU. The OU fertilizer used volatilized $2.67 \text{ mg ring}^{-1}$, equivalent to 7.12% more than CU (Table 2). These results reinforce the need for more studies on these new coating technologies related to the effect of the reduction of volatilized N- NH_3 loss, considering the type of coating, its quality and thickness and control of the experimental environment, such as temperature and soil moisture, among others. Khalil et al. (2006) found lower N losses through volatilization with an increase in the size of the fertilizer granules. However, research has also showed an increase in the N volatilization with increasing granule size (Lara Cabezas et al., 1992). The application of urea promoted a volatilization of 15.58% N- NH_3 ($5.85 \text{ mg ring}^{-1}$, Table 2). A similar result was observed by Peng et al. (2015), who obtained losses of up to 18% for urea. Kiehl and Sengik (1995) found volatilized N- NH_3 loss for urea reaching approximately 16% in sandy soil and 12% in clay soil. According to Connell et al. (1979), the N dose applied also has an effect on the NH_3 losses by volatilization. The authors observed increased volatilization from 19% to 36% when the urea dose varied from 100 to $150 \text{ mg dm}^{-3} \text{ N}$.

For Almeida and Sanchez (2013) the use of controlled slow release N fertilizer is an alternative to reduce N loss. However, Zavaschi et al. (2014) in an assessment of N losses, noted that the application polymer coated urea did not reduce ammonia loss by volatilization and did not interfere in soil ammonium and nitrate levels. The use of the urease inhibitors does not necessarily lead to lower NH_3 losses, only causing delays in the peak volatilization (Tasca et al., 2011).

Stafanato et al. (2013) evaluated the effectiveness of urea with associated technologies, and found a reduction of approximately 54% in N- NH_3 losses by volatilization when compared with the loss caused by commercial urea.

When comparing the OU fertilizer with other technologies, (Contrast C2, Table 2) NH_3 loss showed a significant and positive value, resulting in an increased NH_3 volatilization by the OU fertilizer. The OU fertilizer volatilized $8.52 \text{ mg ring}^{-1}$, equivalent to 22.70%, being the source that volatilized the most NH_3 into the environment.

For Bono et al. (2006) the organomineral fertilizers can be used in a single application at planting as the N is concentrated in the mineral and organic form, this mineral N being absorbed quickly, and the organic N present in the organic fertilizer released throughout the crop cycle. As the organic N needs to be mineralized in the soil to be utilized by plants in nitric or ammoniacal forms, it remains in the soil longer (Bono et al., 2006). However, these results do not corroborate those found in the present study, in which the OU underwent higher losses than the use of CU, indicating that the studied OU fertilizer is not an efficient source for reducing the N- NH_3 loss in the soil.

Comparing the chemical coating (U_{NBPT}) and the physical coating technologies (US and UZ) (Contrast C3, Table 2), it was observed that losses by N- NH_3 volatilization of fertilizer U_{NBPT} were higher than for other sources. For the experimental conditions of this study (temperature, soil

moisture and soil type), the physical coatings were more efficient in reducing N losses in relation to chemical coatings. Carmona et al. (1990) reported that the use of the NBPT may not be able to completely control the N- NH_3 loss, because this type of coating does not withstand temperatures between 25 to 32°C . According to the authors these temperatures favor the hydrolysis of urea and over time there is a decrease in the concentration of the inhibitor. This may result in a U_{NBPT} fertilizer efficiency loss, because of the higher soil temperatures in tropical environments.

In Contrast, in the C4 treatment (Table 3), which compares the nitrogenous fertilizer US and UZ, the UZ was superior, resulting in less N- NH_3 volatilization. Thus, the UZ was the nitrogenated fertilizer that presented the lowest amounts of N volatilized as NH_3 , only 14.12% ($5.30 \text{ mg ring}^{-1}$). For Torma et al. (2014) nitrogenous fertilizer, combined with mineral zeolite, can be used in agriculture as a soil conditioner due to its high element retention capacity (elements like nitrogen, phosphorus and potassium, in addition to water), releasing them slowly, and it may reduce nitrate (NO_3^-) leaching losses and NH_3 volatilization. One should also consider the reduced accessibility that microorganisms have to the NH_4^+ adsorbed on the zeolite structure, preventing the transformation of NH_4^+ into NO_3^- and reducing nitrogen losses (Mumpton, 1999).

The ability of zeolite to significantly reduce losses by volatilization makes its use as a new technology for more efficient urea-based fertilizer relevant, when it is applied in coverage. Werneck (2008) found a 20% decrease in N losses by volatilization when using a urea/zeolite mixture compared to conventional urea.

According to Yang et al. (2011), volatilization of NH_3 from the sulfur-coated nitrogen fertilizer depends on the thickness of the coating (capsule) in relation to the granule size, because the total N content of urea coated with sulfur can decrease from 46% to 30 to 42%. However, nutrients in sulfur coated fertilizers can be released quickly, in less than 3 months (Trenkel, 2010).

Regarding the N application form, all sources used in this study had higher N- NH_3 losses when applied to the soil surface, compared to their incorporated application (2-3 cm deep) (Table 3). Soil surface application of nitrogen fertilizer led to 19.62% volatilization ($7.36 \text{ mg ring}^{-1} \text{ N-NH}_3$) on average, and incorporated, 13.94% of the total applied ($5.23 \text{ mg ring}^{-1}$ of N- NH_3). The incorporation reduces the NH_3 losses by volatilization. The incorporation of the N virtually eliminates NH_3 volatilization (Rodrigues and Kiehl, 1986; Silva et al., 1995; Lara Cabezas et al., 2000) because it enhances the contact between the fertilizer and the soil, favoring the adsorption of NH_4^+ to the soil negative charges. The incorporation of nitrogen fertilizer to the soil may decrease NH_3 volatilization by up to 90% (Ceretta et al., 2002; Ernani et al., 2003).

Gott et al. (2014) found that by incorporating nitrogen fertilizer to the soil, the losses are lower. However, this practice is not widely used by farmers in nitrogen fertilization, either for lack of adequate equipment for incorporation, for damage that this incorporation can promote in the root system, or by increased application cost. Ernani et al. (2003) observed that with the surface application of urea, in sandy soil as well as loamy, NH_3 losses increased from 15.7 to 29.3% by volatilization in relation to its incorporation, regardless of the black oat crop residue management, soil texture, soil organic matter content (SOM) and soil CEC.

However, it is important to note that even the sources with associated technologies were more efficient when

Table 1. Average values of cumulative total N-NH₃ losses via volatilization per nitrogen source application under different managements and application times.

Sources	Surface N			Incorporated N		
	T1	T2	T3	T1	T2	T3
	-----mg ring ⁻¹ N-NH ₃ -----					
CU	8.04	7.22	5.78	5.60	4.59	3.85
UZ	7.53	7.01	4.28	5.16	4.90	2.90
US	7.84	6.71	5.10	5.01	4.86	4.51
U _{NBPT}	9.48	8.30	5.72	7.52	3.50	2.43
OU	10.56	10.03	6.84	9.99	8.90	4.78
Time Averages	8.69	7.85	5.54	6.65	5.35	3.69
Management Averages		7.36			5.23	

CU: Conventional urea; UZ: Urea combined with mineral zeolite; US: Urea coated with elemental sulfur; U_{NBPT}: Urea coated with NBPT; and OU: Urea combined with organic material; Time 1: 100% of the N dose applied at the beginning of the experiment; Time 2: 50% of the N dose initially applied and 50% after seven days; and Time 3: 33.4% of the N dose initially applied and two applications of 33.3% in two intervals of seven days; NBPT: N-(n-butyl) thiophosphate triamide.

Table 2. Average contrast between total N-NH₃ losses per nitrogen source applications and different soil managements and application times.

Contrasts	C2	C3	C4
C1			
-0.57**	2.81**	0.67**	0.37*

C₁ = CU vs (UZ + US + U_{NBPT} + OU); C₂ = OU vs (UZ + US + U_{NBPT}); C₃ = U_{NBPT} vs (US + UZ); C₄ = US vs UZ; CU: Conventional Urea; UZ: Urea combined with mineral zeolite; US: Urea coated with elemental sulfur; U_{NBPT}: Urea coated with NBPT; and OU: Urea combined with organic material (organomineral); NBPT: N-(n-butyl) thiophosphate triamide; °, * and **, Significant at 10, 5 and 1%, respectively.

Table 3. Contrast between average total N-NH₃ losses per different managements adopted and nitrogen sources.

Contrast	CU	UZ	US	U _{NBPT}	OU
C5	2.33**	1.95**	1.76**	3.34**	1.25**

C₅ = Surface management vs. Incorporated management; CU: Conventional urea; UZ: Urea combined with mineral zeolite; US: Urea coated with elemental sulfur; U_{NBPT}: Urea coated with NBPT; and OU: Urea combined with organic material; NBPT: N-(n-butyl) thiophosphate triamide. °, * and **, Significant at 10, 5 and 1%, respectively.

Table 4. Contrast between average total N-NH₃ losses per different application times adopted and the nitrogen sources.

Contrasts	Managements	CU	UZ	US	U _{NBPT}	OU
		C6	Sur. 1.54**	1.89**	1.94**	2.47**
	Inc.	1.38**	1.26**	0.32	4.56**	3.15**
C7	Sur.	1.44**	2.73**	1.61**	2.58**	3.19**
	Inc.	0.74**	2.00**	0.35	1.07**	4.12**

C₆ = Time 1 vs. Time 2 + Time 3. C₇ = Time 2 vs Time 3 Inc. - Incorporated management, Sur - Surface management.; CU: Conventional urea; UZ: Urea combined with mineral zeolite; US: Urea coated with elemental sulfur; U_{NBPT}: Urea coated with NBPT; and OU: Urea combined with organic material; NBPT: N-(n-butyl) thiophosphate triamide. °, * and **, Significant at 10, 5 and 1%, respectively.

Table 5. Coefficients of the logistic equation (time required to reach half the maximum N-NH₃ (t^{1/2} = -b/c) production per time T1, T2 and T3, using soil (IM) and surface (SM) management in 28 days.

Sources	a ⁽¹⁾			b ⁽¹⁾			c ⁽¹⁾			R ²	t 1/2		
	T1	T2	T3	T1	T2	T3	T1	T2	T3		T1	T2	T3
SM													
CU	7.83	7.10	6.12	-8.84	-5.72	-5.42	0.86	0.51	0.36	0.99	10.27	11.28	14.93
UZ	7.57	7.18	4.05	-8.14	-4.51	-10.8	0.61	0.35	1.03	0.99	13.39	13.04	10.49
US	7.96	6.79	5.10	-8.00	-4.22	-4.05	0.54	0.35	0.38	0.99	14.92	12.15	10.86
U _{NBPT}	10.3	8.54	5.73	-3.59	-3.30	-4.69	0.27	0.31	0.38	0.98	13.49	10.80	12.21
OU	10.5	10.3	7.40	-4.60	-6.06	-4.19	0.45	0.43	0.28	0.99	10.17	13.99	14.80
IM													
CU	5.70	4.62	3.78	-8.99	-8.78	-7.18	0.59	0.56	0.66	0.99	15.25	15.73	10.97
UZ	5.13	4.59	2.99	-9.52	-6.66	-6.47	0.65	0.79	0.44	0.99	14.69	8.42	14.80
US	4.91	4.96	5.04	-8.91	-13.1	-3.04	0.66	0.82	0.23	0.99	13.57	15.93	13.40
U _{NBPT}	7.41	3.39	2.39	-11.2	-9.00	-6.18	0.82	0.66	0.44	0.99	13.61	13.67	14.13
OU	10.0	9.22	4.84	-8.81	-6.41	-8.98	0.65	0.46	0.60	0.99	13.46	14.00	14.94

⁽¹⁾ logistic equation $Y = a/(1+e^{-(b+cx)})$; IM = Incorporated management; SM = Surface management; Time 1: 100% of the N dose applied at the beginning of the experiment; Time 2: 50% of the N dose initially applied and 50% after seven days; and Time 3: 33.4% of the N dose initially applied and two applications of 33.3% in two intervals of seven days; NBPT: N-(n-butyl) thiophosphate triamide.; CU: Conventional urea; UZ: Urea combined with mineral zeolite; US: Urea coated with elemental sulfur; U_{NBPT}: Urea coated with NBPT; and OU: Urea combined with organic material; NBPT: N-(n-butyl) thiophosphate triamide.

incorporated into the soil, volatilizing less N-NH₃, as noted in C5 (Table 3). This demonstrates improvement possibilities (refinement) of the technologies used in this work, such as improvements in the combinations and thicknesses of the coatings or mixtures (organic and inorganic) for the fertilizers. For fertilizer application times with their different managements, all sources behaved similarly (Table 4). When fertilization is parceled out, the N-NH₃ volatilization decreases. These results corroborate Amado et al. (2002) and Silva et al. (2005) in which the nitrogen fertilizer parceling and application time constitute alternatives to increase N fertilizer efficiency by the crops and mitigate losses. This is supported by better use of N, a result of synchronization between applications and the period of high nutrient demand. The C6 contrast (Table 4) shows that when parceling the nitrogen fertilizer application with different managements (surface and incorporated into the soil), NH₃ losses via volatilization are minimized. Thus, the results obtained in this work with stabilized controlled release nitrogen fertilizer does not corroborate with what is indicated by Boman and Battikhi (2007), for whom the use of slow release nitrogen fertilizer reduces the need for parceling fertilizers. By parceling the application of the nitrogen sources in three times, independently of the management type adopted (surface and incorporated), the NH₃ volatilization decreases (C7, Table 5). Wilson et al. (2009) demonstrated a reduction in the need to split N application when using coated urea, which was not observed in our study. The cumulative NH₃ volatilization values as a function of collection time were adjusted to the logistic equation $[Y = a/(1+e^{-(b+cx)})]$ (Passos et al., 2007; Andrade et al., 2013). For all treatments (Table 6), in general, higher values for the NH₃ saturation evolution (coefficient a) were observed for Time 1 (100% of the N dose applied at the start of the experiment), indicating that this type of nitrogen fertilizer application favored greater volatilization, regardless of the management type. The cumulative production of volatilized NH₃ adequately adjusted to the logistic growth function for all treatments (Table 5). The highest values for NH₃ saturation evolution (coefficient a) were observed for the OU fertilizer, indicating that it has qualitative characteristics that favored its volatilization and / or a higher proportion of more easily volatile NH₃, in both the surface, as well as in the incorporated managements. Parceling the N dose resulted in lower N-NH₃ capture values, regardless of the source applied. In this sense, Time 1 was superior to Time 3.

For the surface management (SM) we observed higher coefficient b values (longer to reach NH₃ saturation) for fertilizer applications at different times (T1, T2, T3), reflecting its higher NH₃ volatilization. This was not observed in the incorporated management (IM) of the fertilizer applied. There was little variation between the growth rate function (coefficient c) for both the SM and IM, suggesting that it was not very sensitive to qualitative variations between nitrogen fertilizer application times (Table 5). This fact apparently induced the same growth curve pattern. Higher $t^{1/2}$ values were found for the UZ, indicating that this fertilizer has a lower rate. It is inferred that the lower N loss rate volatilized in the form of NH₃ can be related to the addition of zeolite (mineral) to the urea granules, via coating or granulation of a mixture of the powdered materials, reducing ammonia losses by volatilization when the fertilizer was applied to the soil.

Materials and Methods

Soil characterization

For this experiment, samples were collected from a Latossolo Vermelho-Amarelo is dystrophic (oxisol) (Embrapa, 2013) at a depth of 20-40 cm. Once collected, the samples were air dried, declodded, and passed through a 2.0 mm sieve to obtain fine air-dried soil (FADS).

The chemical and physical analyzes of the soil samples, performed according to Embrapa (1997) and Almeida et al. (2012), respectively, presented the following soil attributes: pH (in H₂O) = 4.80; P = 6.34 mg dm⁻³; K = 14.00 mg dm⁻³; Ca = 0.70 cmol_c dm⁻³; Mg = 0.70 cmol_c dm⁻³; Al³⁺ = 0.25 cmol_c dm⁻³; H+Al = 4.29 cmol_c dm⁻³; Sum of Bases = 1.44 cmol_c dm⁻³; CEC capacity = 5.73 cmol_c dm⁻³; CECt = 1.69 cmol_c dm⁻³; V = 25.13 %; Sand = 296 g kg⁻¹; Silt = 32 g kg⁻¹; Clay = 672 g kg⁻¹.

Different N sources were added to soil samples at different application and managements times (incorporated and not incorporated). The N sources used were: conventional urea - CU; urea combined with mineral zeolite - UZ; elemental sulfur coated urea - US; NBPT coated urea (N-(n-Butyl) triamide) - U_{NBPT}; and urea combined with organic material (filter cake) - OU. The N dose used was 75 mg dm⁻³, considering the volume of soil used.

Experimental design

The treatments followed a factorial 5 × 3 × 2 where the factors studied were: five N sources (CU, UZ, US, U_{NBPT}, OU) × three application times, Time 1 being: 100% of the N dose applied at the beginning of the experiment; Time 2: 50% of the N dose applied at the beginning of the experiment and 50% after seven days; and Time 3: 33.4% of the N dose applied at the beginning of the experiment and two applications of 33.3% in two intervals of seven days; and two types of managements (surface application and application incorporated to two centimeters). The experiment was arranged in a randomized block design (RBD) with three replications.

Soil samples (2 dm³) were placed in plastic bags for liming by Al³⁺ neutralization and elevated Ca²⁺ + Mg²⁺ concentration method (Alvarez V. and Ribeiro, 1999). Soil moisture was then adjusted to 60% of field capacity (Reichardt, 1988). After 21 days of incubation, the soil was air dried declodded and sieved in a 2 mm sieve (FADS) for mounting the experiment.

Experimental units were PVC rings, 10 cm in diameter and 10 cm high. These rings were filled with 0.5 dm³ of FADS samples. The rings then received phosphorus (300 mg dm⁻³) and potassium (150 mg dm⁻³) application (Novais et al., 1991) and water to reach 60% of the field capacity. After application, the rings were maintained at a temperature of 25°C for three days to acclimate soil biota and for urease production. After this period, the nitrogen fertilizers were applied to the soil at 75 mg dm⁻³ of N, respecting the times and managements adopted. Immediately after the nitrogen fertilizer applications, a static-free, semi-open collection chamber (SALE) (Araújo et al., 2009) was coupled at the top of each ring to capture the ammonia released by the fertilizer. The assembly and conduction of the experiment were carried out under a controlled temperature (25°C).

The experiment was conducted for 25 days, with the collection and exchange of the foams conducted on the 2nd, 4th, 7th, 9th, 11th, 14th, 16th, 18th, 21st, 23rd and 25th days after the start of the experiment. After each collection, the ammonia was quantified according to Silva et al. (2010).

Data analysis

The results were submitted to analysis of variance using the SAEG program (SAEG, 2007) described by Euclides (1983) and the qualitative effects (sources, times and management) were broken down in contrasts and the NH₃ volatilization curve (cumulative N- NH₃ production) with the incubation time, was adjusted in the logistic equation [$Y = a/1+e^{-(b+cx)}$] (Passos et al., 2007; Andrade et al., 2013).

Parameter "a" represents the saturation curve, which is associated with the maximum NH₃ accumulation volatilized; "b" represents the position parameter which shifts the curve horizontally, and the greater its value the longer the time to reach the peak NH₃ volatilized; and "c" represents the parameter related to the function growth rate and which is directly associated with the NH₃ volatilization. Through these coefficients it was possible to estimate the time required to reach half-maximal NH₃ emission ($t^{1/2}$). The $t^{1/2}$ indicates the time (days) that the inflexion curve occurred.

Conclusions

Urea combined with mineral zeolite (UZ) showed lowest NH₃ volatilization values in relation to the other sources used. The ascending order of N-NH₃ volatilization was: UZ < US < CU < U_{NBPT} < OU, regardless of the time and management adopted. The incorporation of nitrogen fertilizers to the soil reduced losses by volatilization, even for fertilizers with associated technology. The parceling of nitrogen fertilization reduces nitrogen losses through volatilization as NH₃, despite the use of fertilizers with associated technology.

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