

Stability of urease inhibitor added to urea

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Abstract

The urease inhibitor N-(n-butyl thiophosphoric acid triamide) (NBPT) is being used to reduce ammonia (NH₃) volatilization losses of surface-applied urea but its shelf life is an issue. Urea treated with NBPT was stored for up to one year at two locations in Brazil: Paranaguá, PR (25°30'S and 48°30'W) and Rondonópolis, MT (16°26' S and 54°49' W). Treated urea samples were collected for the determination of NBPT concentration and for NH₃ volatilization from a Latosol under laboratory conditions. Ammonia losses from untreated urea varied from 32 to 48% of applied nitrogen (N); the corresponding values for freshly NBPT-treated urea varied from 8 to 26% of applied N. For fertilizer stored up to 6 months, NH₃ losses from untreated urea were significantly higher than those of urea containing NBPT, with no difference found among NBPT treated urea samples regardless of storage site and bag size. After 6 months, volatilization losses of NBPT treated samples stored in Rondonópolis were higher than those from Paranaguá. When samples were stored for 9 months, NH₃ losses for Paranaguá samples and freshly NBPT-treated urea were about 15% of applied N, while for Rondonópolis samples, losses were about 30% of applied N. Losses for untreated urea were about 45% of applied N. After 1 year, Paranaguá samples were still performing the same as freshly NBPT-treated urea. The degree of degradation of NBPT on urea stored under conditions similar to those of Paranaguá grants a shelf-life longer than those stored under hotter conditions similar to Rondonópolis.

Key Words

NBPT, ammonia volatilization, storage time

Introduction

Ammonia volatilization losses cause economic as well as environmental problems (Sutton et al., 2013). In Brazil, where urea is the dominant N fertilizer source, such N loss can be as high as 50% of surface-applied N under field conditions, depending on the soil and environmental conditions (Costa et al, 2003, Lara Cabezas et al., 2008; Cantarella et al., 2008). Incorporation of urea into the soil is a method of lowering NH₃ losses but surface-application is the preferred method of application in situations such as large-scale farming under no-till, perennial crops, and sugarcane harvested without previous burning due to cost and time savings. In the 1990s the urease inhibitor NBPT became commercially available under the brand AGROTAIN[®] to treat urea and, thus, reduce NH₃ volatilization losses. NBPT has been tested in several countries with studies reporting reduction of losses in the order of 50-80% as compared to untreated urea (Watson et al., 2008, Chien et al., 2009, Li et al, 2015). However, it is known that NBPT applied to urea loses its effectiveness with storage and method of application to urea (Watson et al., 2008). The shelf-life of NBPT-treated urea is thus an issue of concern for the industry as well as for farmers. Therefore, the objective of this study was to investigate the shelf-life of NBPT-treated urea stored in different bag sizes and locations with different climates.

Methods

The study was carried out to evaluate the effectiveness of urea treated with urease inhibitor NBPT stored for up to 1 year in two locations in Brazil: Rondonópolis, MT (16°26' S and 54°49' W) and Paranaguá, PR (25°30'S and 48°30'W). The NBPT formulation used was the commercial product AGROTAIN[®], which was applied at a rate of 4.2 L/tonne of urea, giving a target NBPT concentration of 890 mg NBPT/kg urea. The treated fertilizer, with three replications, was stored in fertilizer warehouses for up to 1 year in sealed plastic bags commonly used for fertilizers: 500 g-bags, 50 kg-bags, and 750 kg-bags. The small bag size (500 g) is used in lab experiments, 50 kg bags are ordinary fertilizer bags, and 750 kg bags are large containers used for bulk sales. After pre-established sampling intervals (1, 2, 3, 4, 5, 6, 9 and 12 months of storage), samples were collected from the bags and taken to the laboratory to determine NBPT concentration and to evaluate NH₃ volatilization from a Red Latosol soil. For the 50 kg and 750 kg bags, NBPT-treated urea samples were collected from the portion close to the bag surface (S), from the center of the bag (I), and from a

homogeneous sample (H) collected after the whole bag content had been thoroughly mixed. The NH₃ volatilization trials followed a complete randomized design with three replications. The treatments consisted of: a) untreated urea; b) freshly NBPT-treated urea prepared 1 or 2 days before the trial, at IAC's laboratory; c) urea+NBPT stored in 500 g bags; d) surface sample of urea+NBPT stored in 50 kg bags; e) inner sample of urea+NBPT stored in 50 kg bags; f) homogenized sample of urea+NBPT stored in 50 kg bags. Treatments g, h, i, and j were the same as c, d, e, and f, respectively, but at a different storage location, giving a total of 30 experimental units (Table 1). An empty jar and an unfertilized soil were used as experimental controls. For the 12-month storage volatilization trial, additional treatments with NBPT-treated urea stored in 750 kg bags, sampled in the same positions as those for 50 kg bags, were included. Four replications were used. An initial test was conducted with the urea (UR) freshly treated with NBPT at the laboratory and NBPT-treated urea prepared at Paranaguá and Rondonópolis. A total of nine NH₃ volatilization trials were conducted. NH₃ volatilization chambers followed the design described by Soares et al. (2012). N was surface-applied at a rate equivalent to 300 kg N/ha on a surface-area basis to a Red Latosol (pH CaCl₂ 5.5, 371 g/kg clay). Evolved NH₃ was trapped in a boric-acid solution and determined by titration with standardized sulfuric acid solution. Subsamples of urea and NBPT-treated urea used in each volatilization trials were analyzed with three replications for residual NBPT by HPLC.

Results

NH₃ losses from untreated urea treatment varied between 32 and 48% of applied N whereas losses from freshly prepared NBPT-treated urea varied between 8 and 26% of applied N (Table 1). Up to the sixth month of storage, NH₃ losses from the untreated urea were significantly higher than those of all NBPT-treated urea treatments, and there was no difference among NBPT-treated urea treatments regardless of storage location, bag size, and sampling position. After 6 months of storage, the volatilization for NBPT-treated urea samples from Rondonópolis started to become higher than those from Paranaguá. However, losses from untreated urea continued to be significantly higher than all NBPT-treated urea samples. When the samples were stored for 9 months, NH₃ volatilization losses for samples from Paranaguá were similar to those of the freshly prepared NBPT-treated urea (around 15% of applied N), but lower than those of samples from Rondonópolis (around 30% of applied N). Losses from the untreated urea were about 45% of applied N. After 1 year of storage, NH₃ losses from freshly prepared NBPT-treated urea and samples from Paranaguá were around 8% of applied N and significantly different from all others samples. There was no statistical difference for NH₃ losses between untreated urea and Rondonópolis samples stored for 1 year (Table 1).

The differences observed between storage locations were explained by temperature differences: inside the 750 kg bags the temperature from April to October was 5 to 10°C lower in Paranaguá (Figure 2). The experiment was installed in March, which is the end of summer in Brazil, allowing samples in the Paranaguá location to experience milder temperatures during spring and winter. NBPT concentrations on urea gradually declined with time. In Paranaguá at the 9th month of storage about 50% of the NBPT had degraded but the residual concentration of inhibitor was still around 400 mg/kg urea (Figure 2), close to the rate used commercially in Brazil. This may explain the lack of difference of NH₃ volatilization between samples stored in Paranaguá for 1 year and the freshly prepared NBPT-treated urea samples. The decline of NBPT concentration on urea was greater for samples stored at Rondonópolis with almost 100% degraded after 9 months. In addition to the temperature difference, it is possible that the NBPT rate on urea was unintentionally lower in the Rondonópolis location compared to the Paranaguá location. Figure 1 shows that the initial NBPT concentration on urea was different between Paranaguá and Rondonópolis. The concentration in Paranaguá was around 800 mg NBPT/kg urea while in Rondonópolis it was around 560 mg NBPT/kg urea. The target concentration was of 890 mg NBPT/kg urea but it is likely that a lower rate was used in Rondonópolis. The volatilization trials did not show differences between bag size and sampling position in the bags.

The residual concentration of NBPT on urea decreased with time and related well with the NH₃ volatilization data (Figure 1 and Table 1). Opposite to what was expected, the residual NBPT concentrations in the samples stored for 12 months in Paranaguá were higher than those of samples stored for 5, 6, and 9 months. The variation in NBPT concentration for fresh control samples happened because the first two samples were treated at 530 mg NBPT/kg urea instead of 840 mg/kg urea. Nonetheless, the trends observed for the decline in NBPT concentration on urea at both locations are clear, which makes this information useful. The NH₃ losses observed in the nine experiments for the urea control treatment varied from 32 to 48% of the N applied (Table 1, Figure 1). The experimental conditions varied slightly in each test, despite the effort to

standardize laboratory temperature, air flow inside the chambers, soil moisture, among other factors. However, the urea and the fresh NBPT treatments allow adequate conditions to compare the site and storage treatment effects. Up to five months of storage time urea treated with NBPT maintained in Paranaguá and Rondonópolis had similar effectiveness to reduce NH₃ losses but in the last three experiments, carried out after 6, 9 and 12 months, NBPT treatment from Rondonópolis was less effective than at Paranaguá (Figure 1). The residual concentration of NBPT in urea declined with time in both sites, but it was much more intense in Rondonópolis (Figure 1). The difference in temperatures in the two storage sites is the probable reason for the higher decline in the NBPT residual concentration and the reduction of the inhibitor effectiveness in Rondonópolis (Figure 2). The average temperatures within the bags in the first 4 months were 22.9 °C (range 19.1-26.6°C) and 26.9°C (range 23.4-29.1°C) in Paranaguá and Rondonópolis, respectively. Usually NBPT maintained in proper solvents is stable for long time but, once applied to urea it tends to degrade and high temperatures seem to play an important role.

Table 1. NH₃ volatilization losses for NBPT-treated urea samples stored for up to 12 months in two locations.

Treatments ⁽¹⁾	NH ₃ volatilization losses (% of applied N) after months of storage							
	1	2	3	4	5	6	9	12
	(% of the N applied)							
UR	48 a	32 a	44 a	46 a	40 a	41 a	46 a	37 c
NBPT fresh	26 b	13 b	20 b	15 b	15 b	16 bcd	20 c	8 a
P 500 g	22 b	10 b	16 b	13 b	15 b	10 d	16 c	8 a
P 50 kg S	20 b	7 b	15 b	14 b	9 b	19 bcd	14 c	9 a
P 50 kg H	18 b	8 b	14 b	21 b	14 b	13 cd	16 c	9 a
P 50 kg I	24 b	12 b	21 b	19 b	15 b	16 bcd	18 c	7 a
R 500 g	26 b	9 b	19 b	19 b	17 b	24 cd	30 b	34 c
R 50 kg S	24 b	11 b	17 b	18 b	17 b	24 cd	30 b	25 c
R 50 kg H	21 b	7 b	20 b	14 b	12 b	19 bcd	33 b	25 bc
R 50 kg I	24 b	12 b	23 b	23 b	21 b	28 b	34 b	27 c
P750 kg S	-	-	-	-	-	-	-	12 ab
P 750 kg H	-	-	-	-	-	-	-	7 a
P 750 kg I	-	-	-	-	-	-	-	7 a
R 750 kg S	-	-	-	-	-	-	-	30 c
R 750 kg H	-	-	-	-	-	-	-	28 c
R 750 kg I	-	-	-	-	-	-	-	28 c

⁽¹⁾Sites (P: Paranaguá; R: Rondonópolis); bag weights, and sampling position in the bags (S: surface; H: homogenized; I: inner samples).

Different letters following means indicate statistically significant differences within each volatilization test (columns) (Tukey p≤0.05)

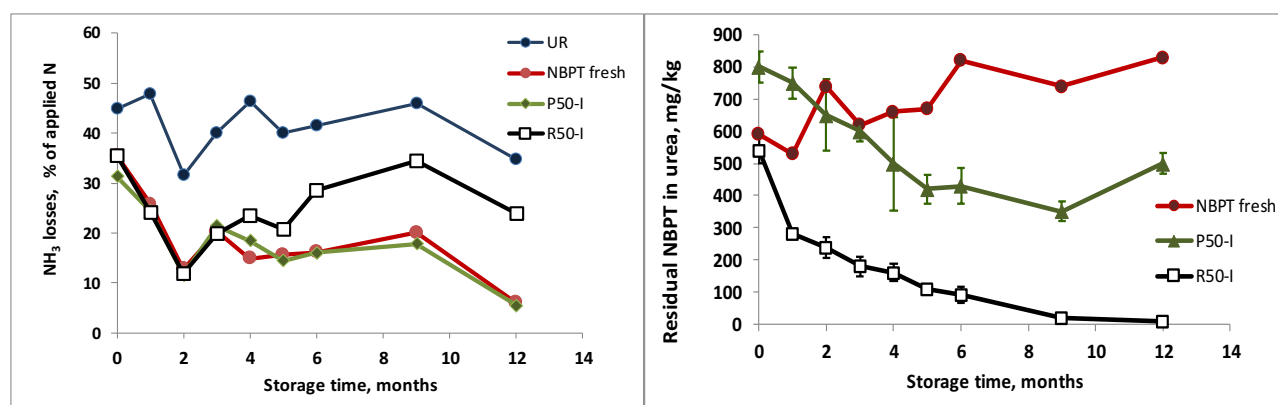


Figure 1. Ammonia volatilization losses and residual NBPT in urea samples from selected treatments as a function of site and storage of urea treated with NBPT. P: Paranaguá; R: Rondonópolis. Vertical bars in the residual NBPT data indicate ± standard deviation. For comparison of NH₃ volatilization treatments see Table 1.

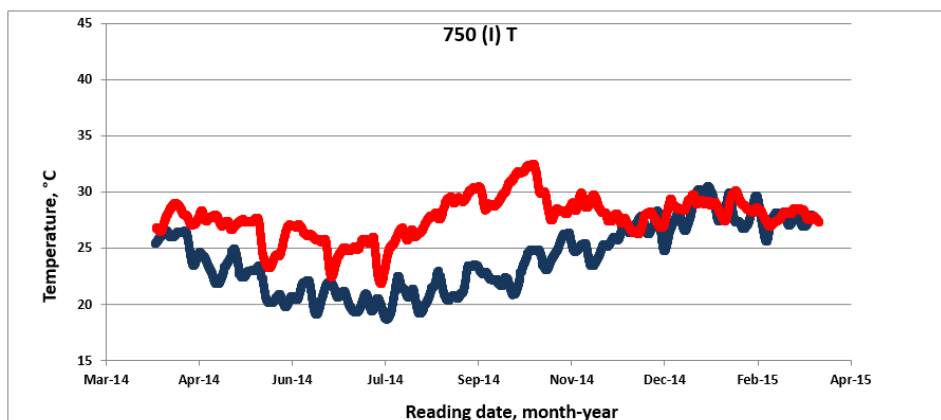


Figure 2. Temperature recordings during 1 year inside the 750 kg bags of urea stored at Paranaguá (blue line) and Rondonópolis (red line).

Conclusion

Urea treated with NBPT and stored in Paranaguá maintained the effectiveness of the urease inhibitor for over nine months, although the residual concentration of the inhibitor declined with time. Thus, the degree of NBPT degradation on urea stored under conditions similar to Paranaguá gives a relatively long shelf-life of 9-12 months, whereas the shelf-life is reduced in a hotter site.

Samples of NBPT-treated urea that contained around 500 mg NBPT/kg urea after storage had similar performances in reducing NH_3 volatilization losses as freshly prepared NBPT-treated urea (prepared with 560 mg NBPT/kg), supporting this concentration as adequate to reduce NH_3 losses from a Latosol. However, storage at a high temperature caused a more rapid degradation of NBPT on treated urea. Using a higher rate of NBPT in places where temperatures are relatively high (tropical climate) may be an alternative to prolong the shelf-life of urea fertilizers treated with NBPT, although it is safer to restrict storage time in hot places.

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