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Ammonia volatilization from nitrogen fertilizers applied to sugarcane straw[1]

Volatilização de amônia de fertilizantes nitrogenados aplicados sobre palhada de cana-de-açúcar

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ABSTRACT - Maintenance of crop residues over soil surface under conservational systems limits incorporation of nitrogen fertilizers into the soil. Application of urea over crop residues enhance N-NH_3 volatilization losses, justifying the usage of urease inhibitors or N sources less susceptible to volatilization under such conditions. This study aimed to evaluate volatilization losses from N sources applied over sugarcane straw. A field trial was carried out in a sugarcane field in Iracemapolis, Sao Paulo on a Typic Kandiudox in June 2014. We used a complete block experimental design, with seven treatments and four replications. Treatments included Control [CO], ammonium nitrate [AN], NS30™ (ammonium nitrate-75% and ammonium sulfate-25% fused mixture) [NS30™], ammonium nitrate plus ammonium sulfate (ammonium nitrate-75% and ammonium sulfate-25% physical mixture) [AN-AS], urea [UR], urea treated with 0.4% Cu and 0.15% B [UR-CuB], urea treated with 530 mg kg^{-1} of NBPT [UR-NBPT]. Treatments were applied at rate of 100 kg ha^{-1} N (except CO). Volatilization losses were quantified up to 30 days after fertilization (DAF). Maximum N-NH_3 occurred 16 DAF for UR and UR-CuB and 20 DAF for UR-NBPT. Accumulated N-NH_3 losses ranged from 20% (UR), 17% (UR-CuB), and 14% (UR-NBPT) of applied N; non-amidic sources showed losses lower than 1%. Adding urease inhibitor to urea shows potential in reducing volatilization losses even under application over large amounts of straw.

Key words: Urea. NBPT. NS 30™. Green cane.

RESUMO - A manutenção da palha na superfície do solo dificulta a incorporação mecânica dos fertilizantes nitrogenados no solo. A aplicação de ureia na superfície nestas condições favorece as perdas de N-NH_3 por volatilização, tornando necessário o uso de inibidores de urease ou fontes menos sujeitas à volatilização. Avaliou-se a volatilização de NH_3 de fontes de N aplicadas sobre palhada de cana-de-açúcar. O experimento foi realizado em Nitossolo Vermelho eutrófico no município de Iracemápolis-SP em junho de 2014. O delineamento experimental foi em blocos aleatorizados, com sete tratamentos e quatro repetições. Os tratamentos foram controle [CO], nitrato de amônio [NA], NS30™ (fusão entre nitrato de amônio-75% e sulfato de amônio-25%) [NS30™], mistura física de sulfato de amônio (75%) e nitrato de amônio (25%) [NA-SA], ureia [UR], ureia recoberta com 0,4% Cu e 0,15% B [UR-CuB] e ureia tratada com 530 mg NBPT kg^{-1} [UR-NBPT]. Todos os tratamentos (exceto controle) foram aplicados na dose de 100 kg ha^{-1} de N. As perdas de N-NH_3 foram avaliadas até 30 dias após adubação (DAA). As máximas perdas de N-NH_3 ocorreram aos 16 DAA para UR e UR-CuB e aos 20 DAA para UR-NBPT. As perdas acumuladas de N-NH_3 foram 20, 17 e 14% para UR, UR-CuB e UR-NBPT, respectivamente; para as fontes não amídicas as perdas foram inferiores a 1% do N aplicado. A adição de inibidores de urease tem potencial em reduzir perdas por volatilização da ureia mesmo em condições de elevada quantidade de palha sobre o solo.

Palavras-chave: Ureia. NBPT. NS 30™. Cana-crua.

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INTRODUCTION

The estimated area cultivated with sugarcane in Brazil in the 2015/16 season was nine million hectares, of which 52% was in the state of São Paulo (CONAB, 2015), where harvesting is mainly mechanised with no burning. In this system, the amount of straw that remains on the surface varies from 10 to 20 t ha^{-1} dry weight (DW) (LEAL *et al*., 2013; THORBORNE *et al*., 2012), making it difficult to incorporate fertilizers into the soil mechanically.

Nitrogen fertilization is important for the adequate nutrition and productivity of sugarcane (FRANCO *et al*., 2011, THORBORNE *et al*., 2011). The most commonly used nitrogen fertilizer in agriculture is urea (45% N), which generally has a lower price per unit of nutrient compared to other nitrogen fertilizers, such as ammonium sulfate and ammonium nitrate. After being applied to the soil, urea [$CO(NH_2)_2$] is hydrolyzed by the enzyme urease, which can result in a significant loss of N-NH_3 by volatilization if the fertilizer is not properly incorporated into the soil. These losses occur due to the consumption of H^+ ions during the process of enzymatic hydrolysis, resulting in an increase in pH near the fertilizer granules, which even in acid soils favors the transformation of NH_4^+ into NH_3 (CANTARELLA; MONTEZANO, 2010). In a system of green cane harvesting (where there is no burning), the loss of NH_3 through volatilization after the surface application of urea is greater due to the presence of straw on the ground, which, besides being a source of urease and promoting its high activity, makes it difficult to incorporate the fertilizer into the soil (TRIVELIN *et al*., 2002).

Fertilizers that are more efficient are a new way of reducing fertilizer consumption and environmental damage (MACHADO *et al*., 2011). A number of strategies have been evaluated for increasing the efficiency of urea, including the addition of urease inhibitors (CANTARELLA *et al*., 2008), organic compounds (GIOACCHINI *et al*., 2006), rock dust (KAOOSI, 2007), metals and boron (FARIA *et al*., 2014; GROHS *et al*., 2011; NASCIMENTO *et al*., 2013). N-(n-Butyl) thiophosphoric triamide (NBPT) is a class of compounds that have proved to be efficient in inhibiting urease (CANTARELLA *et al*., 2008), usually for 3 to 15 days after their application to the soil (CANTARELLA; MONTEZANO, 2010).

Certain micronutrients can also act as urease inhibitors. Grohs *et al*. (2011) found that urea coated with Cu and B both delayed and reduced the loss of N-NH_3 in relation to common urea at different intervals of water input under irrigated rice cultivation. Stafanato *et al*. (2013) and Nascimento *et al*. (2013) also obtained similar results in a controlled environment and in an area cultivated with sugarcane respectively. Other nitrogen fertilizers have appeared on the market, such as the double salt, ammonium nitrate with ammonium sulfate (brand name, NS30™), obtained from the reaction between ammonia, nitric acid and sulfuric acid, and then homogenized and granulated.

Despite the existence in Brazilian market of commercial products containing urea treated with NBPT, or urea treated with Cu and B, sugarcane producers have preferred to use sources that are less susceptible to losses through volatilization for application to the straw, due to uncertainty of the effectiveness of these treatments, both in reducing volatilization and on productivity.

The aim of this work was to evaluate the volatilization of N-NH_3 from conventional nitrogen fertilizers (urea and ammonium nitrate), stabilized fertilizers (urea with NBPT or with Cu and B) and the double salt, ammonium nitrate and ammonium sulfate (NS30™), when applied to sugarcane straw.

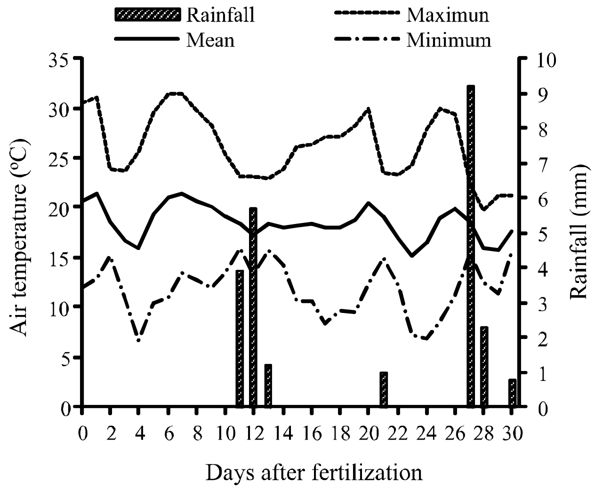
MATERIAL AND METHODS

The experiment was carried out from June 27 to July 27, 2014, in a commercial area cultivated with the RB855453 variety of sugarcane, grown in a eutrophic Red Nitosol (SANTOS *et al*., 2013) in the municipality of Iracemápolis, State of São Paulo (22°35'18.0" S and 47°31'30.2" W). Chemical characterization and texture of the soil were carried out at a depth of 0-20 cm as per the methodologies proposed by Raij *et al*. (2001) and Camargo *et al*. (1986) respectively. The soil displayed a pH $CaCl_2$ of 5.5, organic matter of 35 g dm^{-3}, phosphorus of 40 mg dm^{-3}, sulfur of 7 mg dm^{-3}, potassium of 3.2 mmol$_c$ dm^{-3}, calcium of 44 mmol$_c$ dm^{-3}, magnesium of 19 mmol$_c$ dm^{-3}, aluminum of 0, H+Al of 38 mmol$_c$ dm^{-3}, sum of bases of 66.2 mmol$_c$ dm^{-3}, cation exchange capacity of 104.2 mmol$_c$ dm^{-3}, base saturation of 64%, clay of 708 g kg^{-1}, silt of 130 g kg^{-1} and sand of 161 g kg^{-1}.

Air temperature and rainfall data during the 30 days of the experiment were collected from a weather station near the experimental area, and can be seen in Figure 1.

The fertilizers were applied to the straw about 15 days after harvesting the third ratoon. The DW and moisture of the straw covering the soil were estimated by collecting the straw found in an area of 1 m^2 at 10 random locations in the experimental area. After obtaining the weight of the wet straw (precision of 0.1 g), a sub-sample was oven dried (65 °C) for 72 h to determine the moisture. The DW of the straw was 14 t ha^{-1} and the moisture content was 12%, i.e. within the values normally found for areas of green cane (LEAL *et al*., 2013; THORBURN *et al*., 2012).

Figure 1 - Rainfall, and maximum, mean and minimum air temperatures during the experiment



The experimental design was of randomized blocks, with seven treatments and four replications, giving a total of 28 experimental units, comprising 5 rows of sugarcane, 10 m in length and spaced 1.5 m apart. The treatments were: 1. Control [CO]; 2. Ammonium nitrate (32% N) [AN]; 3. NS30™ (a blend of ammonium nitrate - 75% and ammonium sulfate - 25%, of 30% N and 7.0% S) [NS30™]; 4. A physical mix of ammonium sulfate and ammonium nitrate (75% ammonium sulfate and 25% ammonium nitrate, with 30% N and 7.0 % S) [AN-AS]; 5. Urea (45% N) [UR]; 6. Urea coated with 0.4% Cu and 0.15% B (44% N) [UR-CuB]; and 7. Urea treated with NBPT - 530 mg kg^{-1} (45% N) [UR-NBPT].

All the sources were applied at a dose of 100 kg N ha^{-1} by surface application in a band close to the ratoon row (<30 cm), to simulate ratoon fertilization of the sugarcane. For the treatments NS30™, UR-CuB and UR-NBPT, the commercial fertilizers NS30™, FH Nitromais™ and SuperN™ were used respectively. Potassium chloride was applied to all the plots at a dose of 100 kg K_2O ha^{-1}.

N loss through volatilization was determined by the semi-open collector method used by Nascimento *et al.* (2013). The collectors consisted of a cylindrical acrylic structure mounted on PVC supports with a diameter of 15 cm. Five bases were used per experimental unit, on which the collectors were periodically rotated. The bases were spaced 20 cm apart, and 25 cm from the row of sugarcane. Each collector had supports in its interior to hold two foam pads; one 15 cm from the ground, and the other 15 cm from the first pad to retain the N-NH_3 from the atmosphere, avoiding contamination of the lower foam pad, which captured N-NH_3 from the nitrogen sources and the soil.

Foam pads used were 2 cm thick and 15 cm in diameter. The pads were washed by sequential immersion in the following solutions: water, 1 mol L^{-1} KOH solution, 1 mol L^{-1} H_3PO_4 solution, and deionized water (twice). After each immersion, the pads were firmly squeezed by hand. At the end of the process, they were air-dried. Treatment of the pads was carried out by immersion in a 1 mol L^{-1} solution of H_3PO_4 + 40 g L^{-1} glycerine. After treatment, each pad was squeezed to remove the excess solution. The amount of solution retained in each pad was about 60 mL, evaluated by weighing the dry and the soaked pads. The treated pads were placed into individual plastic bags and kept frozen until use. Before being used in the field, the foam pads were unfrozen.

After applying the fertilizers, the foam pads were replaced in each collector at 2, 4, 6, 8, 10, 12, 16, 20, 25 and 30 days after fertilization (DAF). The two pads (upper and lower) were removed from the collector with the use of tweezers. The lower pad was stored in a plastic bag, identified and taken to the laboratory. The upper pad was discarded. The collector was rotated to the next base, and two more foam pads were then placed into the collector, using rubber gloves.

In the laboratory, each foam pad was extracted separately in a beaker, by the addition of around 400 ml of deionized water. The pad was firmly squeezed, and its weight (wet) was then recorded. The volume of solution was obtained by weighing the beaker containing the extractor solution and adding the amount of residual solution in each pad (subtracting the weight of the wet pad from the dry pad). An aliquot of around 80 mL was transferred to a plastic vial and stored in a freezer until analysis.

To determine the N content of the solution, an aliquot of the extract was analyzed by steam distillation using 10 mL of 5 mol L^{-1} NaOH solution, and then titrated with a 0.025 mol L^{-1} H_2SO_4 solution to quantify the ammonium (BREMNER, 1996). For each collection, the quantity of volatilized N (in mg collector^{-1}) was divided by the amount of N applied (mg collector^{-1}) to obtain the loss by volatilization (in % of the applied dose). Daily losses of N-NH_3 through volatilization were calculated by dividing the cumulative loss for the period by the number of days in the period (2, 4 or 5 days, depending on the collection). The accumulated loss of N-NH_3 was also calculated by summing the losses for each period. During the experimental period, daily temperature and rainfall data were recorded.

The daily and accumulated losses were subjected to analysis of variance (ANOVA) in a design of randomized blocks, in arrangement of split-plot in time. The plots consisted of the sources, and the split-plots comprised the collection periods. The ANOVA F-test was highly significant ($P<0.01$) for source and time, and also for the interaction source x time, for both the daily and accumulated losses. In this case, the mean values were compared by Tukey test ($P<0.05$). Analysis was carried out using the ExpDes package of the R software (FERREIRA; CAVALCANTI; NOGUEIRA, 2013; R DEVELOPMENT CORE TEAM, 2015). The graphs were adjusted using the SigmaPlot 12.5 software.

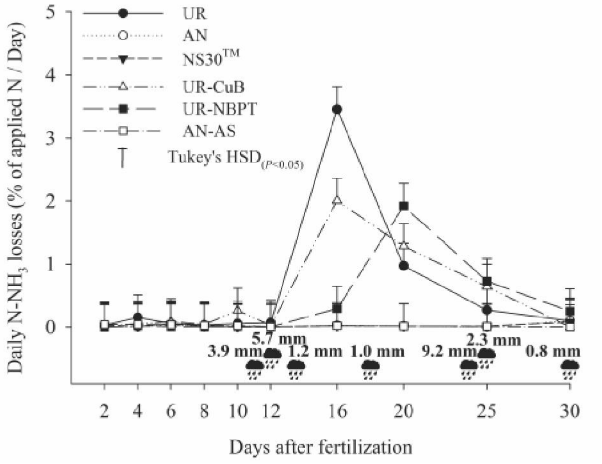
RESULTS AND DISCUSSION

Daily losses of N-NH_3 were practically nil for all sources for the first 12 DAF (Figure 2), possibly due to the low soil moisture and the absence of rainfall during this period (Figure 2). These results agree with the observations of Rochette *et al*. (2009), who found a decrease in urea hydrolysis in the absence of soil moisture. Duarte *et al*. (2007) also observed the absence of ammonia volatilization in dry soil. However, the results of this study indicate an interesting phenomenon of dissolution of the urea granules but with no losses through volatilization during the first twelve days of evaluation. The relative humidity, dew, and straw moisture made dissolution of the urea granules possible in the first days after application of the fertilizers, since in the field evaluations it was not possible to see fertilizer granules on the straw. However, this relatively low volume of moisture together with the low air temperatures may not have been sufficient to trigger the process of urea hydrolysis, or the drag of NH_3 intense enough to promote significant losses during the first 12 days. Dissolution of the urea is therefore not synonymous with the start of loss through volatilization, possibly due to the low activity of the enzyme urease under conditions of low soil moisture (ROCHETE *et al*., 2009).

From 11 to 13 DAF, the accumulated rainfall was 12 mm, enough to raise the soil moisture and increase urease activity (ROCHETTE *et al*., 2009), but not to incorporate the fertilizer into the soil (Figure 2). Lara Cabezas, Korndorfer and Motta (1997) found that 28 mm of water was necessary to incorporate the fertilizer when straw was present. For that reason, the loss of N-NH_3 from the amide sources was seen from 12 DAF (Figure 2). The remaining sources continued to display low N-NH_3 loss.

N-NH_3 losses peaked at 16 DAF for UR and UR-CuB, with UR showing a greater daily loss than UR-CuB during this period (Figure 2). On the other hand, UR-NBPT showed peak loss at 20 DAF, and was therefore more effective than UR-CuB in delaying hydrolysis of the enzyme urease. From this peak, the amide sources displayed a reduction in daily loss, so that at 25 and 30 DAF the three sources had similar losses of N-NH_3. This reduction in loss through volatilization after reaching maximum loss can be explained by a decrease in hydroxyl concentrations around the urea granules, causing a gradual fall in pH and stabilization of the N in the form of N-NH_4^+ instead of N-NH_3.

Figure 2 - Average daily losses of N-NH_3 through volatilization from 0 to 30 days after fertilization (DAF)

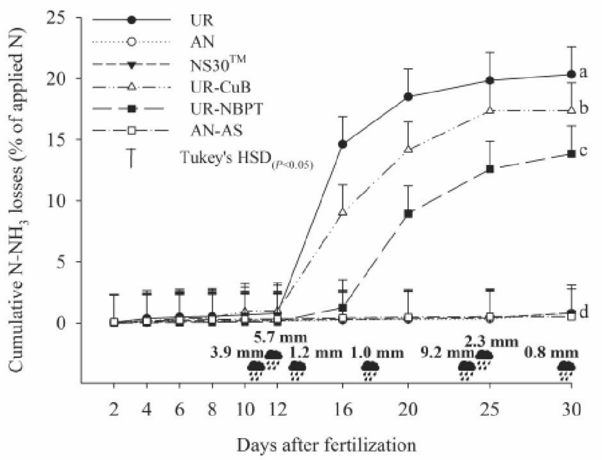


The results presented in Figure 2 show that the treatment of urea with urease inhibitors, such as Cu and B, and NBPT, results in a reduction, but not the elimination, of N-NH_3 loss through volatilization. In other words, the inhibitors were able to reduce, but not eliminate, the activity of the enzyme urease, possibly due to the high amount of this enzyme in areas with the presence of straw (TRIVELIN *et al*., 2002). One of the advantages of using these products is the possibility of rainfall occurring during the period of urease inhibition, thereby resulting in low N-NH_3 losses from amide sources. Incorporation of the urea by the rain promotes increased contact between the fertilizer and the soil particles, with a consequent increase in the adsorption of N-NH_4^+ to the negatively-charged particles of soil, hampering its transformation into N-NH_3 (SILVA *et al*., 1995), and reducing losses through volatilization (LARA CABEZAS; KORNDORFER; MOTTA, 1997).

At 30 DAF, losses were similar for all sources of N. The sources AN, AN-AS, and NS30™ showed low NH_3 loss during the 30 days of the evaluation (Figure 2) due to the absence of N in amide form in these sources. Both AN-AS and NS30™ showed very low daily losses of N-NH_3 and, despite the difference in the production process of these sources, they can be considered similar from the point of view of their potential for loss through volatilization.

The accumulated loss of N-NH_3 from the UR totaled 20% of the applied N (Figure 3). These results are within the range of values obtained by Cantarella *et al*. (2008) in seven areas of green cane in the State of São Paulo. Those authors saw losses of NH_3 in the urea ranging from 1.1% (when rainfall occurred immediately after application) to 25% under conditions conducive to such losses. Faria *et al*. (2013) found losses of N-urea of the order of 14 to 18% of the N applied to soybean and maize straw respectively. In turn, Stafanato *et al*. (2013) observed greater losses of N-urea through volatilization, which reached 47% of the applied N.

Figure 3 - Cumulative losses of $N\text{-}NH_3$ through volatilization in nitrogen fertilizers from 0 to 30 days after fertilization (DAF)



UR-CuB displayed an accumulated loss that was lower than that of UR (Figure 3). The accumulated $N\text{-}NH_3$ loss was 17% for UR-CuB, slightly less than the 20% seen with UR. Results from the literature differ as to the effectiveness of Cu and B in reducing loss through the volatilization of N-urea. Nascimento *et al*. (2013) saw a reduction in volatilization in the treatment of urea with Cu and B in relation to urea, however in that study the losses were very low due to the rainfall that occurred soon after fertilization. Stafanato *et al*. (2013) found a reduction in loss for both urea tablets with Cu and B, and urea coated with Cu and B. Faria *et al*. (2013) found no reduction in the loss of urea through volatilization with Cu and B compared to urea. In that work, losses of N-urea varied from 14 to 18%, while for urea with Cu and B, they varied from 14 to 16%, with no statistical differences. Similar results were seen by Faria *et al*. (2014), who did not find any statistical difference between $N\text{-}NH_3$ loss for urea or urea coated with Cu and B.

The loss of $N\text{-}NH_3$ with UR-NBPT reached 14% and was statistically lower than losses in the treatments with UR and Cu-CuB (Figure 3). In addition to delaying the peak loss (Figure 2), NBPT allowed a reduction of around 21% in $N\text{-}NH_3$ loss compared to UR. In areas of green cane, Cantarella *et al.* (2008) saw reductions of 15 to 78% in loss through volatilization when urea was treated with NBPT. Stafanato *et al.* (2013) found that NBPT reduced the loss of N-urea from 47 to 7%. In that study, NBPT was much more effective in reducing loss than the addition of Cu and B to the urea.

Although UR-CuB and UR-NBPT reduced losses compared to UR, they were relatively high (of the order of 17% and 14% of the applied N for UR-CuB and UR-NBPT respectively). This corroborates results obtained in Brazil, which show that these inhibitors are not capable of completely controlling the loss of $N\text{-}NH_3$ that occurs when urea is applied to the soil surface (CANTARELLA *et al*., 2008). On the other hand, for the non-amide sources evaluated in the present study, the accumulated losses of $N\text{-}NH_3$ were similar and less than 1% of the total N dose applied (Figure 3). These results are very close to those obtained by Cantarella *et al.* (2008) and Faria *et al.* (2013).

The results of this study show the potential of fertilizers stabilized with the use of urease inhibitors for reducing loss through the volatilization of $N\text{-}NH_3$ in urea, even when applied over large amounts of straw in the dry season. However, losses of $N\text{-}NH_3$ from these sources were of the order of 14 and 17% of the applied N, far greater than losses seen with the other sources. While the use of non-amide sources is safe for surface application in areas of green cane in the dry season, sources produced from urea with inhibitors should be evaluated with caution, considering the price of these fertilizers compared to non-amide sources, and their effects on productivity, which were not evaluated in this study.

The use of urea-based fertilizers has economic and operational advantages. However, for the large-scale adoption of stabilized fertilizers, new strategies to increase the effectiveness of inhibitors may be necessary, especially under conditions which are favorable to loss, such as in systems with large amounts of straw covering the soil and little probability of rainfall after fertilization.

CONCLUSIONS

1. Maximum $N\text{-}NH_3$ loss through volatilization occurred at 16 (urea and urea treated with copper and boron) or 20 days after fertilization (urea treated with NBPT) on sugarcane straw;
2. Accumulated $N\text{-}NH_3$ losses through volatilization totaled 20, 17 and 14% respectively for urea, urea treated with copper and boron, and urea treated with NBPT;

3. The fertilizers ammonium nitrate, and the physical mix or blend of ammonium nitrate and ammonium sulfate presented N-NH_3 losses through volatilization of less than 1%.

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