Comissão 3.2 - Corretivos e fertilizantes

AMMONIA VOLATILIZATION FROM COATED UREA FORMS[1]

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SUMMARY

Nitrogen fertilization is a major component of the cost of agricultural production, due to the high cost and low efficiency of fertilizers. In the case of urea, the low efficiency is mainly due to losses by volatilization, which are more pronounced in cultivation systems in which plant residues are left on the soil. The objective of this work was to compare the influence of urea coated with sulfur or boric acid and copper sulfate with conventional N fertilizers on N volatilization losses in sugar cane harvested after stubble burning. The sources urea, sulfur-coated urea, urea coated with boric acid and copper sulfate, as well as nitrate and ammonium sulfate, were tested at amounts containing N rates of 120 kg ha^{-1} N. The integration of new technologies in urea fertilization can reduce N losses by volatilization. These losses were most reduced when using nitrate and ammonium sulfate. The application of a readily acidified substance (boric acid) to urea was more efficient in reducing volatilization losses and nutrient removal by sugar cane than that of a substance with gradual acidification (elemental sulfur).

Index terms: elemental sulfur, boric acid, copper sulfate, sugarcane, harvest without burning.

RESUMO: *VOLATILIZAÇÃO DE AMÔNIA ORIUNDA DE UREIA EM RAZÃO DE SEUS RECOBRIMENTOS*

A adubação nitrogenada é um dos principais componentes na formação do custo de produção, por causa do elevado preço e da baixa eficiência dos fertilizantes. No caso da ureia, a baixa eficiência deve-se principalmente às perdas por volatilização, que se intensifica em

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sistemas de cultivo com preservação de restos culturais sobre o solo. Objetivou-se com este trabalho comparar a influência da ureia recoberta com enxofre, com acido bórico e sulfato de cobre e com fertilizantes nitrogenados convencionais sobre as perdas de nitrogênio (N) por volatilização, em cana-de-açúcar colhida sem queima prévia da palhada. As fontes estudadas para fornecer dose de N igual a 120 kg ha^{-1} foram: ureia, ureia revestida com enxofre, ureia revestida com acido bórico e sulfato de cobre, nitrato e sulfato de amônio. A agregação de novas tecnologias à ureia resultou na redução das perdas de N por volatilização de amônia. Entretanto, as menores perdas de N por volatilização de amônia foram encontradas com uso de nitrato e sulfato de amônio. A adição de substância prontamente acidificante (ácido bórico) à ureia foi mais eficiente na diminuição das perdas por volatilização e na exportação de nutriente pela cana-de-açúcar, em relação à adição de substância com ação gradual de acidificação (enxofre elementar).

Termos de indexação: enxofre elementar, ácido bórico, sulfato de cobre, cana-de-açúcar, sem queima.

INTRODUCTION

Environmental laws encourage the adoption of harvest forms of sugarcane that dispense the previous burning of the crop stubble, which reflects back on the fertilization practices, not only in terms of amounts but also of sources and application forms. Commonly, sugar cane fertilizers are water-soluble and consequently readily available to the crop. Among the most typical nitrogen fertilizers are urea, sulfate and ammonium nitrate (Cantarella et al., 2007, Vitti et al., 2008).

Nitrogen (N) is a very dynamic element in the soil and as such can get lost by one or several processes, e.g., volatilization, leaching, denitrification, runoff, and crop removal (De Datta, 1981).

The losses of ammonia nitrogen (NH_3-N) from urea applied to the surface are significant in soils with tropical and subtropical climate, due to the climatic conditions such as high temperatures, winds and high relative air humidity (Oliveira et al., 2007).

The straw left on the soil surface in the green cane system facilitates ammonia (NH_3) losses by evaporation from amidic ammonia sources not incorporated into the soil (Trivelin et al., 1998). In a study by Cantarella et al. (1999), 12 and 30 %, respectively, of the NH_3 -N of the urea fertilizer applied on sugarcane straw, at 50 and 100 kg ha^{-1} N, was lost by volatilization. Costa et al. (2003) and Vitti et al. (2007a) reported losses of more than 30 % of the N applied to straw cane.

The growth and quality of plants are mainly due to the amount of water and fertilizer. It is therefore very important to improve the use of water and fertilizer nutrients. However, about 40-70, 80-90 and 50-70 % of the applied amount of N, P and K fertilizer, respectively, is normally lost to the environment and cannot be absorbed by plants, causing great economic and resource losses, aside from environmental pollution (Lara Cabezas et al., 1999; Trivelin et al., 2002; Costa et al., 2003; Wu & Liu, 2008).

Fertilizers with higher efficiency represent a new trend to maintain fertilizer consumption and minimize environmental pollution (Du et al., 2008; Tang et al., 2009; Machado et al., 2011).

With the aim of increasing the use efficiency of urea, several studies tested various polymers with different principles of action, urease and nitrification inhibitors (Cantarella et al., 2008; Bhatia et al., 2010), rock dusts and organic compounds (Gioacchini et al., 2006; Kaoosi, 2007), micronutrients and some metals (Grohs et al., 2011), and sulfur (Girardi & Mourão Filho, 2004; Shaviv, 2005).

The purpose of this study was to compare the influence of urea coated with sulfur or with boric acid and copper sulfate, and of conventional nitrogen fertilizers on nitrogen losses by volatilization in sugarcane harvested without previous stubble burning.

MATERIAL AND METHODS

The experiment was conducted in the sugarcane region of Piracicaba, São Paulo (South Latitude: 22° 40'; West Longitude: 47° 53') in a ratoon cane plantation harvested without burning, on sandy soil (chemical properties see table 1). The experimental design in randomized blocks consisted of six treatments: CT (control), UR (urea), AN (ammonium nitrate), UBC (urea coated with boric acid and copper sulfate), AS (ammonium sulfate), and SU (sulfur-coated urea), with four replications All treatments were fertilized with N, K_2O and P_2O_5 corresponding to 120, 100 and 30 kg ha^{-1}, respectively.

The NH_3 -N losses by volatilization were recorded (2, 4, 6, 8, 10, 12, 14, 16, 18, 20, and 22 days) after N fertilization. To estimate N losses by ammonia volatilization from soil after N fertilization, we used the direct method with semi-open collectors (Nômmik, 1973) in a dynamic mode, i.e., changing the chamber of the collectors to the subsequent bases (PVC rings by which collectors are fixed to the ground) and the integration of correction factors proposed by Lara Cabezas et al. (1999). At each base, 15 g of N was applied in the fertilizer forms under study, in an amount proportional to the diameter of the collectors (15 cm).

Two pieces of foam (density 0.02 g cm^{-3}) were fixed within each semi-open collector, soaked in 50 mL of phosphoric acid solution (0.25 mol L^{-1}) and glycerin (3 % v/v) prior to installation, to absorb the ammonia. The upper foam was fixed (31 cm above the ground) to capture atmospheric ammonia, and to isolate the lower foam (15.5 cm above the ground), which hasd the function of capturing NH_3-N from the soil surface (Lara Cabezas & Trivelin, 1990). For each sampling period, the foam soaked in phosphoric acid was replaced.

The upper foams were discarded and the ones beneath stored under refrigeration (5 °C) until analysis. Each foam was placed on a porcelain funnel equipped with a vacuum pump, and the foam was washed with approximately 400 mL of deionized water. From the solution extracted from each foam, a 50 mL aliquot was taken for NH_3-N distillation and determination by the Kjeldahl method. At the time of fertilizer application and collector installation, the moisture content of the soil and straw were 6 and 20 %, respectively.

The volatilized ammonia nitrogen was calculated with the volumes of sulfuric acid used for titration in the blank tests and samples, according to equation (1).

$$N = (Vs\text{-}Vb) \times f \qquad (1)$$

Where N = nitrogen captured in the collector, Vs = volume of acid used for sample titration, Vb = volume of acid spent for titration of the control; and f = 0.7 (factor of acid molarity, the volume of the aliquot and of the extract from the flask). Subsequently, the results were corrected according to the equations proposed by Lara Cabezas et al. (1999). The daily and accumulated volatilization rates were calculated as the sum of daily losses.

After the analysis of variance and confirmation of the significance of the F test, the means were partitioned by Tukey's test at a significance level of 5 %, using the statistical software SAS version 9.01 (SAS, 2004).

RESULTS AND DISCUSSION

N losses by volatilization during the 22-day evaluation did not exceed 10 % of the applied N, regardless of the source (Figure 1). This was probably a result of the high precipitation (> 50 mm) on the first days after fertilization (Figure 2). According to Lara Cabezas et al. (1997), when there is enough water to dilute the hydroxyl (OH^-) concentration around the urea granules produced in the hydrolysis reaction, the urea is not only leached into the soil, but ammonia volatilization is also reduced. According to Cantarella et al. (1999), the incorporation of urea to a depth of ≥ 5 cm is sufficient to control the NH_3 loss.

Cantarella et al. (1999) observed that the rain maintained the level of volatilization low and concluded that loss rates were more pronounced when rainfall was insufficient to leach urea into the soil. Costa et al. (2003) also observed a reduction in the NH_3-N loss rate after precipitation events.

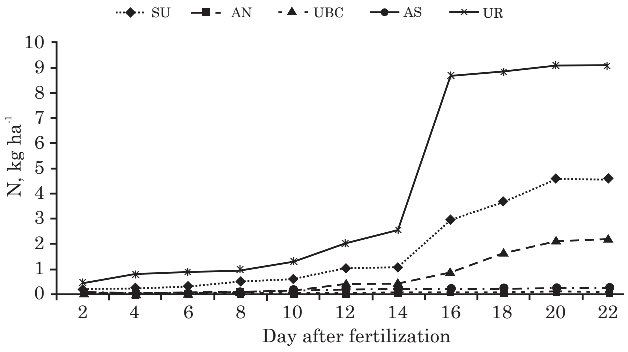
These losses peaked between 15 and 16 days after fertilization, due to a lack of moisture to hydrolyze urea, because there was no rain until the 12th day. The process of urea hydrolysis started after rain fell on the 14th. According to Cantarella (2007), the losses can peak even on the first day if the soil is covered with plant residues. However, discrepant results of the duration of this period are reported in the literature: Gava (1999) observed the greatest losses on the 11th day while Costa et al. (2003), Pereira et al. (2009) and Tasca et al. (2011) mentioned a peak in the first six days. This variation is due to many factors that influence volatilization losses, among them moisture (Da Ros et al., 2005).

Nitrogen losses by volatilization were statistically higher when uncoated urea (UR) was used. Urea coating causes a statistically significant reduction of NH_3-N losses in relation to UR, and losses from sulfur-coated urea (SU) were higher than from urea coated with boric acid and copper sulphate (UBC). However, regardless of the coating material, volatilization losses were not reduced to the level of losses from soils fertilized with nitrate (AN) and ammonium sulfate (AS) as nitrogen sources (Figure 1). The NH_3-N losses from the different sources in the evaluation period can thus be ranked as follows: UR>US>UBC>AN=AS.

The higher losses from conventional urea (UR) in relation to the other sources are due to the action of urease, since the conditions for the action of the enzyme in the soil, microorganisms and plant residues were favorable. The influence of the enzyme on volatilization losses is greater when urea is applied on a soil surface covered with crop residues in an environment with insufficient moisture for fertilizer incorporation (Figure 1).

Table 1. Soil chemical properties prior to the experiment

Depth	pH ($CaCl_2$)	MO	P	S	K^+	Ca^{2+}	Mg^{2+}	Al^{+3}	H+Al	CTC	V	m
cm		g dm^{-3}	mg dm^{-3}		mmol$_c$ dm^{-3}						%	
0-10	4.7	13	6	9	1.0	10	5	3	31	47.4	34	16



	SU	AN	UBC	AS	UR
kg ha^{-1} of NH_3-N	4.56 b	0.190 d	2.19 c	0.105 d	9.090 a

Figure 1. Concentration of accumulated NH_3-N at each sampling after fertilization. UR: conventional urea, AS: ammonium sulfate, AN: ammonium nitrate, UBC: urea coated with boric acid and copper sulfate; SU: sulfur-coated urea. Means followed by the same letter do not differ statistically at 5 % probability by the Tukey test.

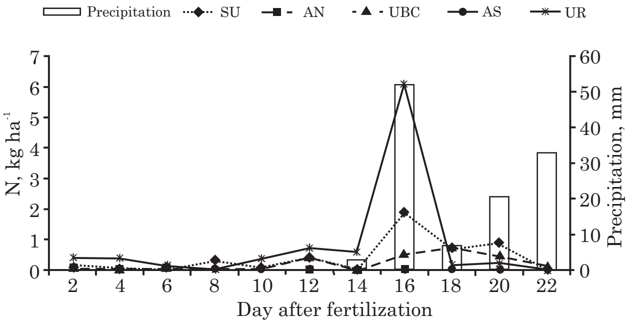


Figure 2. Daily precipitation and volatilization losses of NH_3-N as a function of days after fertilization. UR: conventional urea, AS: ammonium sulfate, AN: ammonium nitrate, UBC: urea coated with boric acid and copper sulfate; SU: sulfur-coated urea.

The straw left on the soil surface in the "green cane" harvest system facilitates NH_3 volatilization losses from amidic and ammoniacal fertilizers not incorporated into the soil (Trivelin et al., 1998) since apart from hampering the incorporation of urea into the soil, straw contains high amounts of urease. Cantarella et al. (1999) reported NH_3-N volatilization losses of 12 and 30 %, respectively, from urea applied on sugarcane straw at 50 and 100 kg ha^{-1} N, while Costa et al. (2003) and Vitti et al. (2007a) observed losses of more than 30 % of the N applied on cane residues.

With the use of sulfur-coated urea (SU), NH_3-N losses were reduced by 50 % compared to conventional urea (UR), due to the physical protection of the layer of elemental sulfur in the SU. Volatilization began to increase after a rainfall of only 2 mm (Figure 2), which was probably not enough rain to solubilize the elemental sulfur coating. In a study with urea treated with a urease inhibitor, Cantarella et al. (2008) observed the beginning of volatilization after a rainfall of 2.6 mm, in an experiment with sugarcane harvested without previous stubble burning.

The coating with elemental sulfur may also have acted as a barrier against the ureolytic action of residues on the ground. Vitti et al. (2007b) emphasized that the waste on the soil increases volatilization losses when urea is the N source, since the straw not only contributes to the amount of urease, but also forms a physical barrier preventing the soil-fertilizer contact, which reduces NH_4^+ adsorption to soil colloids. According to Silva et al. (1995), an increased contact between fertilizer and soil particles increases NH_4^+ adsorption to negatively charged soil, hampering the transformation into NH_3, the form in which N is lost by volatilization.

Although the losses by UR and SU volatilization were statistically different, after the beginning of volatilization, a rainfall of over 50 mm reduced volatilization losses to almost zero. One can therefore not infer that coating with elemental sulfur would have the same effect under loss-prone conditions over a longer period (Figure 1). The dissolution of urea in soil solution occurs after the hydrolytic and microbial degradation of the protective sulfur coating, facilitated by micropores and imperfections, cracks and incomplete coating, and urea unprotected by sulfur is subject to the same losses (Shaviv, 2005; Cantarella, 2007; Trenkel, 2010).

In the plots with UBC as N source, NH_3-N volatilization losses were on average 75 and 52 % lower than when using UR and SU, respectively. The reason is the reductive effect of boric acid on the pH around the urea granule, thus reducing the conversion of NH_4^+ to NH_3. According to Cantarella (2007), the reaction of urea hydrolysis consumes H^+ protons and raises the pH around the particles, inducing a H^+ deficit that hampers the persistence of N in the form of NH_4^+. However, the hydrolysis of UBC generates protons by the dissociation of H_3BO_3, thus meeting the H^+ demand for the maintenance of N in its reduced form.

The reduction of N volatilization losses by acidification of the medium has been studied for many years, mainly based on mixtures of urea with other acidifying N sources (Lara Cabezas et al., 1997; Costa et al., 2003; Lara Cabezas & Souza, 2008). However, because the ammonium sulfate is hygroscopic, mixing with urea tends to reduce the critical moisture and flowability of the mixture, and depending on the exposure time of the mixture in the field, can affect its application (Vitti et al., 2002). Furthermore, the unit price of N will increase with the mixture of sources, since the concentration of N in ammonium sulfate is lower than in urea.

Thus, it is more feasible to use compounds such as boric acid as acidifying agents in the region around the granules, because this acid releases H^+ when in contact with water. To provide the same amount of protons as by the H_3BO_3 system, a three-fold amount of ammonium sulfate would be required. Sulfate is less efficient, due to the need of converting SO_4^{-2} to H_2SO_4 for posterior donation of protons from the system.

Another explanation for the lower N volatilization from UBC is the toxicity caused by heavy metals such as Cu, Zn and Ag, affecting the urease activity in the soil. Chaperon & Sauvé (2007) demonstrated a reduction of urease activity in the soil due to the increase of metal concentration in the soil, including Cu.

Stuczynski et al. (2003) reported an inhibitory effect of Zn on the activity of a group of soil enzymes, especially of urease. Tabatabai (1977) reported an inhibitory effect of Cu^{+2} on urease activity in the soil, and that this effect was only lower than that of Ag^+ and Hg^+. With the application of UBC, Grohs et al. (2011) obtained a reduction of approximately 50 % of ammonia volatilization compared to UR, in tilled soil.

Almost no NH_3-N volatilization losses were observed from plots fertilized with ammonium nitrate (AN) (Figure 2) and ammonium sulfate (AS) as N source, which can be explained by the chemical species in which the nutrient was applied to the crop. Similar results were obtained by Cantarella et al. (2003), Vitti et al. (2005), and Lara Cabezas & Souza (2008).

For the occurrence of volatilization losses, N must be in the form of NH_3 which, under normal temperature and pressure conditions, is in gaseous form due to its low boiling point (-38 °C). Ammonia is only formed when the pH of the medium is high, due to the removal of H^+ protons from ammonium. This situation only occurs when fertilizers are applied to soil with a basic pH (a rare case in tropical soils) or when the dissolution of the particular nitrogen source favors the increase of OH^- around the granule (Cantarella, 2007).

When NH_4^+ in the forms of AN and AS is applied to aerated soil, it tends to be rapidly oxidized to nitrate in soil with low available C, incorporated into microbial biomass, as in the case of soil where sugarcane is harvested without previous burning, or absorbed by plants. The NO_3^- is reduced, incorporated into the soil biomass or absorbed by plants (Cantarella, 2007). It is worth noting that in the transformation chain of nitrogen in tropical soil, both N sources resulted in the formation of only negligible amounts of ammonia, contrary to when urea was applied (Vitti et al., 2005; Lara Cabezas & Souza, 2008).

CONCLUSIONS

1. In this study, the integration of new technologies in urea fertilizers resulted in the reduction of nitrogen losses by volatilization. These losses were lowest with the use of nitrate and ammonium sulfate.

2. The application of a readily acidified substance (boric acid) to urea was more efficient in reducing volatilization losses and nutrient removal by sugar cane than that of a substance with gradual acidification (elemental sulfur).

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