Volatilization of ammonia from conventional sources of nitrogen and compacted urea under controlled conditions

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ABSTRACT: Urea is the most used nitrogen fertilizer in tropical agriculture, but when applied to the soil surface, it can promote nitrogen (N) losses by volatilization of ammonia (NH3). The present study aimed to evaluate, under controlled laboratory conditions, the N-NH3 losses from conventional N sources and compacted urea. Fertilizers were applied on the surface of a eutrophic Red Latosol of clayey texture (Oxisol), previously moistened to 60% of its maximum water-retention capacity. Conduction of the experiment was in a completely randomized design with six replicates. The treatments were four N sources in doses equivalent to 100 kg ha⁻¹ of N (urea, urea + N-(N-butyl) thiophosphoric triamide (NBPT), ammonium nitrate and urea compacted with additives and polymers), and the additional control groups (soil with no fertilizer and empty chamber). We evaluated the N-NH3 losses by volatilization for a period of 20 days with the aid of hermetically sealed chambers. The results demonstrated the importance of using compacted urea for reducing nitrogen losses via volatilization. These results suggest that choosing the N source can reduce its volatilization and thus improve the harnessing of N from the nitrogen fertilization, when performed with a urea basis.

Key words: nitrogen fertilization; N-NH3 losses; nutritional efficiency

Volatilização de amônia de fontes convencionais de nitrogênio e ureia compactada sob condições controladas

RESUMO: A ureia é o fertilizante nitrogenado mais utilizado na agricultura tropical, mas quando aplicada na superfície do solo pode apresentar perdas de nitrogênio (N) via volatilização da amônia (NH3). O presente estudo objetivou avaliar as perdas de N-NH3 de diferentes fontes de N. Os fertilizantes utilizados foram aplicados na superfície de um Latossolo Vermelho eutrófico, textura argilosa, previamente umedecido a 60% da capacidade máxima de retenção de água. Os tratamentos foram quatro fontes de N em dose equivalente a 100 kg ha⁻¹ de N (ureia, ureia + N-(N-butil) tiофосфориқ триамид (NBPT), nitroso de amônia e ureia compactada com aditivos e polímeros) e os controles adicionais (solo sem fertilizante e câmara vazia). Foram avaliadas as perdas de N-NH3 por volatilização por um período de 20 dias com o auxílio de câmaras hermeticamente fechadas. Os resultados demonstraram a importância do uso de ureia compactada na redução das perdas de N via volatilização. Esses resultados sugerem que a escolha da fonte de N pode reduzir sua volatilização e melhorar o aproveitamento de N da adubação nitrogenada, quando realizada a base de ureia.

Palavras-chave: fertilização nitrogenada; perdas de N-NH3; eficiência nutricional
Volatilization of ammonia from conventional sources of nitrogen and compacted urea under controlled conditions

Introduction

Synthesis of ammonia (NH₃) from the reaction of nitrogen gas (N₂), present in the atmosphere, with hydrogen (H₂), under conditions of high pressure and temperature and in the presence of iron (Yamamoto et al., 2016; Guelfi, 2017), is considered the greatest technological advance in the nitrogen fertilizer sector. From the synthesis of ammonia, the large-scale production of the main nitrogen fertilizers used in world agriculture was possible, with urea among these.

Due to its chemical characteristics and the hydrolyzation ease, losses due to the NH₃ volatilization compose one of the main factors responsible for the low efficiency of urea in supplying N to crops (Cantarella, 2007; Frazão et al., 2014; Silva et al., 2017). Top-dressing urea can promote some quite significant N losses, ranging from 40 to 60% (Frazão et al., 2014; Lana et al., 2018).

One alternative in reducing N losses due to NH₃ volatilization is mechanically incorporating the fertilizer into the soil or through the water depth from rain or irrigation (Cantarella, 2007). Additionally, the urease inhibitors, substances that reduce the conversion rate of urea to NH₃, have been efficiently used as a second option in an attempt of reducing nitrogen losses by volatilization (Sanz-Cobena et al., 2011; Frazão et al., 2014). In addition to this, several substances have been studied aiming to reduce N losses due to ammonia volatilization, including NBPT (N-(N-buty1) thiophosphoric triamide) among them, copper plus boron and acrylic polymers (Timilsena et al., 2014).

The products that have promoted the best results are urea analogs, especially the NBPT, commercialized since 1996 in the United States and more recently in Brazil. NBPT is today the only urease inhibitor with great commercial and practical importance in agriculture, marketed in over 70 countries (Timilsena et al., 2014; Guelfi, 2017). Stabilization of N urea by adding substances for this purpose has, as its main benefit, the delaying of the volatilization peak. This, in turn, provides: a) a greater number of days after the nitrogen fertilization for its incorporation by the waters from rains or irrigation; b) reduction of N losses by volatilization due to excessive urea hydrolysis on the soil surface; c) increased N absorption, yield, N fertilization efficiency and crops quality (Guelfi, 2017).

Companies all over the world now commercialize urea previously treated with NBPT, Cu + B, polymers and additives with the N-stabilizing function by inhibiting the reaction of the urease enzyme activity in the soil (Cantarella, 2007; Guelfi, 2017). However, there are questions about these inhibitors stability after their application, mainly because the products have variable efficiency in function to their storage and the edaphoclimatic conditions at the application period (Cantarella, 2007; Mota et al., 2015).

Therefore, new technologies have been developed in order to bring results with greater predictability and stability. For this reason, urea compacted with additives and acrylic polymers can be an alternative in reducing N losses through volatilization, delaying peak losses and, consequently, increasing the using efficiency of the fertilizer. Hence, the objective of this research was to evaluate, under controlled laboratory conditions, the N-NH₃ losses from conventional N sources and from urea compacted with additives and polymers.

Materials and Methods

Experimental area and cultivation conditions

The experiment conduction was in the municipality of Olímpia - São Paulo - Brazil, in a laboratory located at the Kimberlit Agroscience Research Center in a partnership with the São Paulo State University (Unesp), School of Agricultural and Veterinary Studies, Jaboticabal Campus, during the period from 09/01/2017 to 28/01/2017.

We employed the completely randomized experimental design, with the following five treatments: 1 - urea (45% of N); 2 - urea + NBPT; 3 - ammonium nitrate (33% of N) and 4 - urea compacted with additives and polymers (33% of N), in a dose equivalent to 100 kg ha⁻¹ of N. In addition, the control (absence of N sources) was used to certify the absence of nitrogen contamination and thus the absence of volatilization. We conducted the treatments (N sources) with six (6) replicates. The soil used was collected in the 0-20 cm layer, from a cultivated area with no vegetation coverage, classified as a eutrophic Red Latosol (Oxisol) with clayey texture, with 526 g kg⁻¹ of clay, 189 g kg⁻¹ of silt and 285 g kg⁻¹ of sand. After collection, the soil sample went under air-drying followed by a sieve (2 mm mesh) for homogenization and then subjected to the chemical analysis, as according to the methodology described by Raji et al. (2001). The obtained values were as it follows: pH (water) 6.2 OM = 22 g dm⁻³; P (resin) = 48 mg dm⁻³; H+Al = 25 mmol dm⁻³; K = 6.8 mmol dm⁻³; Ca²⁺ = 42 mmol dm⁻³; Mg²⁺ = 18 mmol dm⁻³; CEC = 91.8 mmol cm⁻³ and V = 73%.

Production flowchart of the compacted urea source

The compacted urea, 33-00-00 + 3% of Ca (calcium carbonate) + 3% of S (elemental sulfur) and 0.3% of B (ulexite), with hardness of 3.5 kg, was obtained by compacting the urea powder, adding nutrients and additives that inhibit the urease enzyme, hailing from an acrylic polymer (Figure 1).

Analysis and volatilization of ammonia

In order to conciliate the volatilization rate, we used semi-open chambers to capture the ammonia, as previously described by Gurgel et al. (2016) (Figure 2). In a nutshell, the chamber are basically glass-made cylindrical containers with 68 cm² of basal area, a hermetically lid and capacity for 1.5 L, with two holes opened on opposite sides, 5 cm below the lid, for placing two glass tubes, one for air inlet and the other for the air outlet. Inside the chamber, in front of the air inlet tube, we placed a rigid plastic barrier to enable the air circulation before it left the chamber. The empty space volume in the chamber was close to 500 ml – between the lid and the soil (Figure 2).

Each soil sample, placed in its respective chamber, filled the volume up to 2 cm below the air inlet and outlet holes, which
corresponded to 1200 g of soil. The ambient temperature during the experiment kept at 26 °C and we moistened the soil one week prior to starting the experiment, in order to recompose the microbial activity. The water amount was equivalent to 60% of the maximum water-retention capacity, determined by the water volume percolated after adding 100 ml of water in 100 ml of soil, in a glass percolation tube. No replacement of water in the soil occurred during the experiment in order to avoid a possible incorporation of urea into the water with a consequent reduction in the N-NH$_3$ volatilization. After the NH$_3$ volatilization, the moisture content in the soil was close to 30% of the maximum water-retention capacity.

Treatments application and ammonia collection

The weighting of the fertilizers was on an analytical balance with precision of 0.1 mg and we applied them to the soil surface contained inside the chambers, with a dose equivalent to 100 kg ha$^{-1}$. The air, coming from a compressor, had its pressure regulated by a manometer at 2.4 kgf cm$^{-2}$ and passed through a solution of H$_2$SO$_4$ 0.05 mol L$^{-1}$ to eliminate traces of NH$_3$ and then through a flask containing deionized water to keep humidified. Subsequently, the air passed through the PVC tubes into the volatilization chambers, where the individual records controlled the airflow and a flow meter at a rate of 1.5 L min$^{-1}$ regulated it. The air from the chambers then passed through 0.5 cm diameter glass tubes, into flasks containing 150 ml of the collecting solution, in which it was continuously vented in order to retain the NH$_3$ dragged from the chambers.

The collecting solution was made with 20 g L$^{-1}$ of boric acid and the indicators of pH change were methyl red (0.044 g L$^{-1}$) and bromocresol green (0.066 g L$^{-1}$), with pH close to 5.0, adjusted with NaOH (0.1 mol L$^{-1}$). We replaced the flasks containing collecting solutions and daily analyzed the NH$_3$, until the losses by NH$_3$ volatilization ceased or its rates stabilized at a level close to the limit of the method detection. Determination of the ammonia was by the potentiometric titration with a standardized 0.005 mol L$^{-1}$ H$_2$SO$_4$ solution, according to the methodology described by Cantarella & Trivelin (2001).
Results and Discussion

In order to identify the pattern of the efficiency loss from nitrogen sources in relation to the urea volatilization, we compared the different sources by measuring their rate in percentage of daily N-NH$_3$ loss (Figure 3). As expected, conventional urea had greater N loss when compared to the other sources. Moreover, the conventional urea has this loss anticipated, with its maximum peak on the fourth day after applying the fertilizer, amassing losses of up to 18.15% of total N applied (Figure 3, Table 1). N-NH$_3$ losses were concentrated in the first 12 days for all N sources, since the ammonia volatilization stabilized after that period. The control treatment (absence of N), as expected beforehand, did not show any volatilization, thus ensuring the experimental efficiency. Our results are in agreement with previous studies developed by Oliveira et al. (2014), where these authors observed that the volatilization of urea compacted with sulfur and bentonite in a controlled environment is significantly lower in comparison to the conventional urea. In contrast to this, both NBPT-treated urea and compacted urea peaked on the eighth day, corresponding to the daily N-NH$_3$ volatilization of 4.13% and 3.22% of the N applied, respectively. Comparing the peaks of fertilizer volatilization, N-NH$_3$ losses were reduced in 81 and 77%, for compacted urea and NBPT-treated urea respectively, in relation to the conventional urea (fourth day after applying the fertilizer).

On the fourth day after applying the fertilizer (peak of untreated urea), the ammonia loss from conventional urea was significantly higher than the other N sources (Table 1). On the eighth day (peaks of treated urea), until the sixteenth day after applying the fertilizers, the N-NH$_3$ loss by compacted urea was significantly lower than that NBPT-treated one. NH$_3$ losses by ammonium nitrate were small, attaining a maximum value of only 0.18% of the N applied. Ammonium nitrate has an acid reaction in the soil, with its NO$_3^-$ anion acting as an accompanying ion and favoring the NH$_4^+$ mobility in the vertical soil profile direction, reducing the volatilization (Lara Cabezas et al., 1997). Corroborating with our results under greenhouse conditions, lower N-NH$_3$ losses were also observed in the field study. According to Otto et al. (2017), fertilization with ammonium nitrate in sugarcane had N losses by volatilization of less than 1%. Similar results were also observed in the coffee crop (Dominghetti et al., 2017), where, as a result, the authors observed that conventional urea is able to lose up to 35% N, reducing the soil pH.

For the NBPT-treated urea, these results are explained by the delay in the activity of the enzyme urease caused by using this substance, leading to lower conversion rates of N in the amidic form (N-NH$_3$) to the ammoniac form (N-NH$_4$) (Timilsena et al., 2014). In the case of compacted urea, the decrease in N-NH$_3$ losses due to volatilization may be related to the effect of adding urease-inhibiting acrylic polymers as well as the presence of elemental sulfur in its composition. Elemental sulfur decreases the rate of both the hydrolysis and hygroscopicity of urea (Gueffi, 2017). The presence of two mechanisms for controlling the N volatilization in compacted urea, compared to only using NBPT, may be the main reason for the lower losses in this fertilizer type. However, the greater N-NH$_3$ losses by conventional urea are due to the greater saturation of the sites of action from the urease enzyme, considering the greater ammonium availability in the soil from this fertilizer type, as Silva et al. (2017) observed.

Urea is rapidly hydrolyzed during its first post-application week, making itself susceptible to high losses due to the N-NH$_3$ volatilization (Soares 2011; Soares et al., 2012). Hence, it is exactly during this period that the NBPT performance is more evident, delaying the hydrolysis and consequently keeping the volatilization rate low (Soares et al., 2012; Lana et al., 2018). NBPT is able to inhibit the enzymatic degradation of urea for up to 14 days, providing a lesser N-NH$_3$ loss (Okumura & Cinque, 2012).

Table 1. Analysis of variance and means comparison test (Tukey) for the daily volatilization of ammonia (NH$_3$) after applying fertilizers in the volatilization chamber.
Another explanation for the greater volatilization would be the greater saturation of the sites of action from the urease enzyme, given the greater ammonium availability in the soil coming from untreated urea, as observed by Silva et al. (2017). The rate of urea hydrolysis by the urease enzyme is more expressive during the first two to three days after the fertilization, with number highly dependent on the soil temperature, moisture and the volume of urea applied per area (Soares et al., 2012; Silva et al., 2017). Mota et al. (2015) reinforce the importance of delaying the urea hydrolysis for 7 days, as there may be enough rainfall precipitation to incorporate the fertilizer into the soil, significantly reducing the NH₃ loss by volatilization.

Accumulations of the daily N-NH₃ losses stabilized after the tenth day in regards to the conventional urea, and after the twelfth day for the treated ureas (Figure 4).

Conventional urea had maximum losses of 43.60% of the N applied. In contrast to this, treatments with the addition of urease inhibitors and acrylic polymers to the urea resulted in lower N losses when compared to the conventional urea: 10.38% and 8.45% of N applied, for the fertilizers urea + NBPT and compacted urea, respectively. At the experiment conclusion, N-NH₃ losses regarding the compacted fertilizer were significantly lower than the verified for other sources, except for ammonium nitrate (Table 2), which is mainly due to the lower volatilizations in the eighth, twelfth and sixteenth days after applying the fertilizers. However, under laboratory conditions, the current literature has demonstrated that applying conventional urea can lead to losses of up to 60% of all N applied via N-NH₃ volatilization under controlled conditions and to temperature increases from 45 to 50 °C. However, the mean values found in the tests conducted in the field and the greenhouse demonstrated a mean from 20 to 30%, under experimental conditions (Cantarella et al., 2008; Soares et al., 2012).

In light of the foregoing challenging agriculture scenario, several natural or synthetic compounds have been developed in order to minimize the nutrients loss when applied to the soil, be either by reducing the volatilization, leaching or the complexation with other ions (Guelfi, 2017). Among these technologies, using coating in fertilizers has been an alternative that has increased the fertilization efficiency, resulting in higher yields in different crops such as coffee (Abranches, 2019) and maize (Zavaschi et al., 2014). Among the used natural polymers are starch, algins, wheat gluten, rubber and latex (Guelfi, 2017). Several synthetic compounds have also been prepared for coating fertilizers, such as polyolefins, polyurethane, polyacrylic, polycrylamide, polysulfonate, polylvin chloride, polystyrene, polyacetate and polydopamine (Guelfi, 2017). Considering our results, the fertilizer compacted with additives and polymers increased the efficiency in reducing the NH₃ volatilization in the same proportion of the urea treated with NBPT, a urease inhibitor. Both treatments effectively reduced the volatilization losses by up to 30% when compared to the conventional urea. The increased efficiency of the compacted fertilizer is justified by the composition of the additives and polymers inserted in the urea coating, since these substances act by delaying the urease enzyme activity, in addition of acting also on the N-releasing dynamics into the soil solution, decreasing the NH₃ concentration as well as the pH value in the fertilizer application area and, consequently, also reducing the NH₃ volatilization (Stafanato et al., 2013; Oliveira et al., 2014).

**Table 2. Analysis of variance and means comparison test (Tukey) for the accumulated volatilization of ammonia (NH₃) after applying fertilizers in the volatilization chamber.**

<table>
<thead>
<tr>
<th>Days after the fertilizers application</th>
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</tr>
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<tbody>
<tr>
<td></td>
<td>4</td>
<td>8</td>
<td>12</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td><strong>% of N applied</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>31.81 a</td>
<td>41.51 a</td>
<td>42.89 a</td>
<td>43.45 a</td>
<td>43.60 a</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>0.01 c</td>
<td>0.32 d</td>
<td>0.61 d</td>
<td>0.77 d</td>
<td>0.88 d</td>
</tr>
<tr>
<td>Compacted urea</td>
<td>0.54 b</td>
<td>6.01 c</td>
<td>7.71 c</td>
<td>8.29 c</td>
<td>8.45 c</td>
</tr>
<tr>
<td>Urea + NBPT</td>
<td>0.63 b</td>
<td>7.57 b</td>
<td>9.58 b</td>
<td>10.25 b</td>
<td>10.38 b</td>
</tr>
<tr>
<td>F test</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>DMS</td>
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<td>0.33</td>
<td>0.34</td>
<td>0.33</td>
<td>1.34</td>
</tr>
<tr>
<td>C.V. (%)</td>
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<td>1.51</td>
<td>1.40</td>
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<td>1.34</td>
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<td>Mean</td>
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<td>13.85</td>
<td>15.20</td>
<td>15.69</td>
<td>15.83</td>
</tr>
</tbody>
</table>

**significant at 1% of probability (p < 0.01).**

**Figure 4.** Accumulated NH₃ volatilization by the surface application of urea, ammonium nitrate, compacted urea and urea + NBPT over 20 days from the experiment implementation.
Program in Agronomy (Crop Production) of the São Paulo State University (Unesp), School of Agricultural and Veterinary Studies, Jaboticabal Campus.

Literature Cited


