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## Ammonia volatilization losses from urea coated with copper, boron, and selenium

# Perdas por volatilização de amônia de ureia com cobre, boro e selênio

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## **Highlights:**

Urea exhibited a 50.32% N loss by volatilization.

Urea coated with B and Cu reduced N losses by volatilization.

Selenium added to the urea coating of B and Cu had no effect on N volatilization.

## **Abstract**

Urea coated with copper and boron may be a vehicle for selenium fertilization in grazing systems to improve both forage and animal productivity, and consequently, the nutritional quality of milk and meat. Urea is the most often used form of N fertilizer in Brazil; however, it can experience high losses by volatilization, primarily in pastures with high amounts of senescent biomass. The goal of this study was to evaluate losses by ammonia volatilization from urea coated with Cu, B, and Se. The fertilizer was applied to the soil surface under forage straw residues in cylindric glass chambers under controlled laboratory conditions. The treatments were urea (UR), urea coated with boric acid and copper sulfate (UBC), urea coated with boric acid, copper sulfate, and selenium (UBCS), and ammonium sulfate (AS). Measurements were recorded at regular intervals after fertilizer application for 27 days. High losses occurred from ammonia volatilization of amidic-N sources in the initial days after fertilizer application. The total loss of N by ammonia volatilization according to fertilizer treatment was UR > UBC = UBCS > AS. Urea lost by ammonia volatilization accounted for up to 50% of the N applied, although losses from coated urea treatments UBC and UBCS were 11.45% lower than that of urea. The Cu and B in the coated urea reduced losses by ammonia volatilization and the inclusion of Se had no effect. It is suggested that Se may be added to the Cu and B coating of urea to reduce ammonia volatilization.

Key words: Biofortification. Pasture. Sodium selenate. Straw residue.

### Resumo

O revestimento de ureia com Cu e B pode ser um veículo para a adubação com selênio (Se) em pastagens melhorando a produtividade da forragem e animal e, consequentemente a

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qualidade nutricional de leite e carne. A ureia é a fonte de N mais utilizada no Brasil, porém pode apresentar elevadas perdas por volatilização, principalmente em pastagens com altas quantidades de biomassa senescente. O objetivo foi avaliar as perdas por volatilização de amônia em ureia revestida com Cu, B e Se aplicado em superfície sob resíduos de palhada de forragem em câmaras cilíndricas de vidro sob condições controladas em laboratório. Os tratamentos foram ureia revestida com ácido bórico e sulfato de cobre (UBC), ureia revestida ácido bórico, sulfato de cobre e selênio (UBCS), e sulfato de amônio (AS) e medidas nos dias após aplicação dos fertilizantes. Altas perdas por volatilização de amônia a partir das fontes amídicas ocorreram nos primeiros dias após a aplicação dos fertilizantes. As perdas totais de N por volatilização de amônia comparando os fertilizantes foi de UR>UBC=UBCS>AS. A ureia perdeu amônia por volatilização em até 50% do N aplicado, enquanto as perdas com as ureias revestidas UBC e UBCS foram 11,45% menores que a ureia. O Cu e o B no revestimento da ureia reduzem as perdas por volatilização de amônia e a inclusão do Se não apresenta influência.

Palavras-chave: Biofortificação. Pastagem. Selenato de sódio. Palhada.

Selenium application along with fertilizer is an agricultural process for biofortification that has been proposed as a strategy to increase the dietary Se intake for animals and humans (Wu et al., 2015). The consumption of Se-fertilized forage provides better incorporation into ruminal microorganisms (Galbraith et al., 2015), consequently promoting higher concentration in animal muscle and milk (Davis et al., 2008). Selenium along with urea at doses of 20 to 80 g ha<sup>-1</sup> yielded positive effects in increasing Se content and truly degraded organic matter *in vitro* of *Brachiaria brizantha* 'Marandu' (Faria et al., 2018).

Urea is the most widely used nitrogen source to improve productivity of pastures, primarily because of its low cost; however, it has a high susceptibility to ammonia losses by volatilization depending on factors, such as the management and condition of soil moisture, temperature, soil pH, wind velocity, soil organic carbon and N, and even the rate of N-urea application.

Losses by ammonia volatilization occurred on the initial days after N fertilizer side dressing (Cancellier et al., 2016) reaching 94% by day 14 (Faria, Nascimento, Vitti, Luz, & Guedes, 2013; Oliveira, Gava, Vitti, Bendassoli, & Trivelin, 1997) when applied to a straw-covered soil surface. This

occurs because the urea granule does not rapidly diffuse into the surrounding soil (Fenn & Richards, 1986); consequently, urea is hydrolyzed by urease on the soil surface.

Urease is an enzyme produced by microorganisms that accumulates in soil colloids and organic substances resulting in high activity (Paulson & Kurtz, 1969); that is affected by vegetation type (Longo & Melo, 2005). UBC has shown potential in the reduction of the volatilization loss of ammonia (Faria et al., 2013). Some chemical elements, including trace elements, have potential as urease inhibitors (Tabatabai, 1977). The use of urease inhibitors to coat urea grains could aid in increasing the efficient use of this N source by avoiding losses by volatilization (Chagas, Gouveia, Costa, Barbosa, & Alves, 2017).

Nitrogen fertilization of pastures is a method to increase beef productivity in Brazil; as well as a possible vehicle to increase Se content in forage. Hence, the goal of this study was to evaluate the losses by ammonia volatilization from urea coated with Cu, B, and Se applied to the soil surface under forage straw residues.

The research was conducted in volatilization chambers under controlled laboratory conditions (Soares, Cantarella, & Menegale, 2012) in a

complete randomized block experimental design in a factorial scheme of  $4 \times 11$  with eigth replicates. The treatments were urea (UR), urea coated with boric acid and copper sulfate (UBC), urea coated with boric acid, copper sulfate, and selenium (UBCS), and ammonium sulfate (AS) and measurements were recorded at 1, 2, 3, 4, 7, 9, 11, 14, 17, 21, and 27 days after fertilizer application.

The experimental unit was comprised of a cylindric glass chamber with a basal area of 100 cm<sup>2</sup> containing 1.3 kg of dry soil. A control without N was conducted under the same conditions during the experimental period and served as a correction factor in the calculation of ammonia losses from fertilizer, as measured by ammonia collectors.

The soil was collected from the 0–0.2 m top layer of a sandy loam soil classified as Typic Hapludox at Piracicaba-SP, Brazil. Soil characterization was 180 g kg<sup>-1</sup> clay, 20 g kg<sup>-1</sup> silt, and 800 g kg<sup>-1</sup> sand; pH 4.6 (CaCl<sub>2</sub>); 5 mg dm<sup>-3</sup> S-SO<sub>4</sub><sup>2-</sup>, 12 mg dm<sup>-3</sup> P; 0.3 mmolc dm<sup>-3</sup> of K; 10 mmolc dm<sup>-3</sup> Ca; 8 mmolc dm<sup>-3</sup> Mg; 38 mmolc dm<sup>-3</sup> H + Al; 0 mmolc dm<sup>-3</sup> Al. The cation-exchange capacity was 56.3 mmolc dm<sup>-3</sup> and base saturation was 33%. Other characteristics included 0.24 mg dm<sup>-3</sup> B, 0.6 mg dm<sup>-3</sup> Cu, 97 mg dm<sup>-3</sup> Fe, 7.9 mg dm<sup>-3</sup> Mn, 1.4 mg dm<sup>-3</sup> Zn, less than 4 mg dm<sup>-3</sup> Na, and a low Se level (0.5 mg dm<sup>-3</sup>).

The soil was limed with 2 Mg CaCO<sub>3</sub> ha<sup>-1</sup> equivalents and its surface was covered with 4.4 g straw residues of *Brachiaria brizantha* containing senescent leaves, stems, and sheaths corresponding to 442 g m<sup>-2</sup> as measured under natural conditions in a rotational grazing system. The soil was moistened to 60% of the maximum water retention capacity for an incubation period of 10 days to recompose the microbial and enzymatic activities prior to the application of the fertilizer treatments.

The coating fertilizers were prepared using a precision scale balance. Prior to coating, a mixture of boric acid and copper sulfate was prepared to supply 0.4 g kg<sup>-1</sup> B and 0.14 g kg<sup>-1</sup> Cu (Faria et al., 2013). Treatment with Se was prepared with sodium selenate added into the mixture of Cu and B. All mixtures were homogenized with a mortar and pestle before coating the urea granules (average weight of granules 8.9 mg). Quantities of N and Se were calculated in equivalence to the chamber area surface with the application of 34.5 g Se ha<sup>-1</sup> (Faria et al., 2018) and 100 kg N ha<sup>-1</sup>.

The fertilizer treatments were applied to the surface of the straw residues. Volatilized ammonia was swept and transferred to a flask containing a boric acid solution to trap the gas. It was then measured by titration with a standardized H<sub>2</sub>SO<sub>4</sub> solution (Cantarella & Trivellin, 2001).

Data obtained were subjected to statistical analysis using SAS® v.9.2 (Statistical Analysis System Institute, Cary NC, USA). Fertilizers and measurement dates were used as fixed effects in the analysis of variance (ANOVA). Significant effects of fertilizer treatments were compared using orthogonal contrasts and the Tukey's test with a 5% level of significance.

Uniform fertilization with urea coated with sodium selenate was attained with no influence of Se on losses by ammonia volatilization (Table 1). The AS treatment was used as a standard because of its stability under experimental conditions, whereas N amidic from urea showed large N losses by ammonia volatilization. The urea treatment lost up to 50% of applied N by ammonia volatilization. Losses of N from coated urea fertilizer UCB and UCBS were 11.45% lower than that of urea.

Table 1
Orthogonal contrasts and significance of total volatilized N-NH<sub>3</sub>

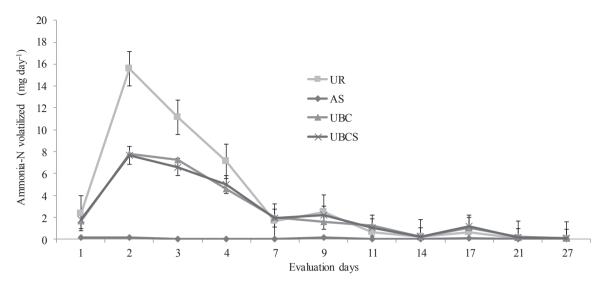
Treatments	N-NH <sub>3</sub> volatilized mg vessel <sup>-1</sup> (100 mg of N applied)
Ammonium Sulfate (AS)	1.38
Urea (UR)	50.32
Urea coated with B and Cu (UBC)	38.73
Urea coated with B, Cu, and Se (UBCS)	38.99
CV (%)	26
Contrasts	F Test
AS vs UR + UBC + UBCS	-41.29**
UR vs UBC + UBCS	11.45**
UBC vs UBCS	-0.26 <sup>ns</sup>

ns: non-significant; \* and \*\*: significant at 5% and 1% by the F test, respectively.

The total loss of N by ammonia volatilization comparing the fertilizers was UR > UBC = UBCS > AS. Amidic-N sources (e.g., urea) had higher losses of N than did AS, whereas coated urea with urease inhibitors showed intermediate losses. The reduction of ammonia losses by volatilization from urea by B and Cu have been previously observed (Faria et al., 2013), because of the potential of metals to function as a urease inhibitor (Tabatabai, 1977). Similarly, Se was a potential inhibitor for urease activity; however, its inhibition was observed only for doses of Se greater than those utilized in this experiment, which could be harmful to grazing animals.

Higher losses of ammonia volatilization from amidic-N sources were observed in the initial days after fertilizer application, and urea exhibited high peaks through the 4<sup>th</sup> day (Figure 1). The curve of losses by ammonia volatilization in amidic-N

sources decreased and were similar from the 7th day to the 21st day, reaching nearly zero by day 27. Urea losses by ammonia volatilization were at 96.7% of the total amount of ammonia volatilized within the first 7 days (Cancellier et al., 2016). The experimental environment provided favorable conditions for ammonia volatilization, primarily in the initial days after N fertilization. The straw residues on the soil surface were favorable for urease activity. Furthermore, the insufficient humidity hampered the rapid incorporation of fertilizer, allowing the higher and continuous losses from amidic-N sources, mainly from urea with no urease inhibitor. Low water content in the soil increased the losses by ammonia volatilization because of the higher content of ammonium and nitrate in the solution were favorable for gas formation from the ammonia (Silva et al., 2017).



**Figure 1.** Ammonia volatilization losses as a function of days after fertilization. UR: urea, AS: ammonium sulfate, UBC: urea coated with boric acid and copper sulfate; UBCS: urea coated with boric acid, copper sulfate, and sodium selenite.

Soil surface in pastures is covered by large amounts of senescent biomass along with losses during the grazing period, even with the utilization of efficient management systems. Therefore, the presence of the senescent plant biomass negatively affects soil fertilizer incorporation, as well as proportionates a high urease activity, which consequently increases the losses of amidic-N sources by ammonia volatilization. However, rainfall of more than 50 mm reduces volatilization losses to almost zero, even in no tillage systems (Nascimento, Vitti, Faria, Luz, & Mendes, 2013). Cu and B in the coating of urea also reduced losses by ammonia volatilization, while the Se inclusion had no effect on ammonia volatilization.

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