

Division - Soil Use and Management | Commission - Lime and Fertilizer

Controlled-release nitrogen fertilizers: characterization, ammonia volatilization, and effects on second-season corn

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ABSTRACT: The development of new fertilizer technologies to reduce nitrogen (N) losses from an agricultural system and to increase nitrogen use efficiency (NUE) is a global research objective. Controlled-release nitrogen fertilizers have shown great potential for reducing N losses and synchronizing N release according to crop demand, thereby improving the NUE. The objective of this study was to characterize controlled-release nitrogen fertilizers and compare them with conventional nitrogen sources in terms of N release, N loss via NH₃ volatilization, and fertilizer effects on second-season corn. The field experiment was performed on an Ultisol in a randomized block design. The treatments consisted of two conventional nitrogen sources (urea and ammonium sulfate) and three brands of polymer-coated urea (PCU; Agrocote[®], FortBlen[®], and Kimcoat[®]). The variables N release and N loss by NH₃ volatilization were subjected to nonlinear regression analysis using a logistic model and the Korsmeyer-Peppas model, respectively. Leaf N content and dry matter yield were subjected to the Tukey test, and the morphologies of the PCUs were observed by scanning electron microscopy (SEM). Electron micrographs revealed differences in the number of layers and the thickness of the coatings of the studied PCUs. FortBlen®, containing granules with single- or double-layer coatings with thicknesses ranging from 34.53 to 50.34 µm, promoted more gradual N release and reduced N-NH₃ losses by 36.4 % compared with those observed with uncoated urea. Kimcoat® released approximately 98 % of the applied N within 24 hours, resulting in N-NH₃ volatilization, and the responses in second-season corn were similar to those with uncoated urea. Although no benefits were observed in second-season corn for PCUs over uncoated nitrogen sources, some PCUs promoted more gradual N release and reduced N-NH₃ volatilization, providing a promising alternative for environments prone to N loss.

Keywords: polymer-coated urea, N release, coating characteristics, scanning electron microscopy.

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INTRODUCTION

Corn is the grain with the highest global production, which was estimated at 1.09 billion tons for the 2018/19 crop (USDA, 2019). The nutrient with the highest requirement in corn is nitrogen (N), with 14.4 kg required for each ton of grain produced (Pauletti and Motta, 2019). Provided to supply N to crops, urea $[CO(NH_2)_2]$ is the most commonly used fertilizer in the world, with an estimated increase in global demand of 1.6 % per year expected until 2022 (IFA, 2018). Its high concentration of N (45 to 46 %), low cost per N unit, high market availability, high solubility, and high compatibility with most fertilizers explain why urea is widely used in agriculture (Chien et al., 2009).

The N in urea, when applied on the soil surface, can be lost by denitrification, leaching, and ammonia (NH $_3$) volatilization. In some cases, losses of N in the form of ammonia (N-NH $_3$) may represent more than 50 % of the N applied (Tasca et al., 2011). The magnitude of the loss of NH $_3$ varies because it depends on the technology used to apply the fertilizer (Stafanato et al., 2013; Silva et al., 2017), the soil properties (Rochette et al., 2009; Sunderlage and Cook, 2018), and the environmental conditions (Holcomb et al., 2011; Otto et al., 2017).

After being applied to the soil surface, urea is hydrolyzed by the action of the enzyme urease, producing ammonium, carbon dioxide, and hydroxyl ions (Trenkel, 2010). This reaction results in increased pH around the fertilizer granules, altering the balance between the ammonia and ammonium in the soil ($NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$) and favoring the transformation of $N-NH_4^+$ into $N-NH_3$ and its subsequent loss to the atmosphere (Rochette et al., 2009).

The N-NH₃ losses can reduce crop yield and nitrogen use efficiency (NUE) (Abalos et al., 2014), thereby having negative economic consequences for farmers (Good and Beatty, 2011). In addition to the productivity and economic impacts, N-NH₃ losses from agricultural areas affect air quality and contaminate terrestrial and aquatic ecosystems (Liu et al., 2013).

The use of new fertilizer technologies to reduce N losses from an agricultural system and to increase NUE is a global research objective. In this sense, fertilizers whose release is controlled by a physical barrier have shown great potential and have been designated by the Association of American Plant Food Control Officials (AAPFCO) as controlled-release fertilizers (CRFs) (Trenkel, 2010). The use of polymer- or resin-coated urea (PCU) as a CRF can decrease volatilization and leaching losses and synchronize nutrient release according to crop demand, thereby improving the NUE (Cahill et al., 2010; Trenkel, 2010).

The PCU production is carried out by coating urea granules with one or more layers. Each layer contains a water-permeable material that regulates nutrient release (Trenkel, 2010). The CRF release mechanism involves nutrient transfer from the fertilizer-polymer interface to the polymer-soil interface, driven by water (Azeem et al., (2014). According to the same authors, the parameters governing the release mechanism are: (i) diffusion/swelling, (ii) degradation of the polymer coating, and (iii) fracture or dissolution.

The PCUs on the market differ in their coating material chemistry and coating thickness and cost 1.3 to 12 times more than conventional urea (Wilson et al., 2009; Trenkel, 2010). Studies comparing PCU and uncoated urea have shown conflicting results. Some studies indicate advantages for the use of PCU (Noellsch et al., 2009; Ye et al., 2013; Zhao et al., 2013), whereas others have noted inefficiency of PCUs when compared to uncoated urea (Cahill et al., 2010; Civardi et al., 2011; Prando et al., 2013).

The divergence between the results in the literature reveals a lack of information on this subject, especially information on the association of the coating characteristics with the dynamics of N and the effects on crops. Thus, the characterization and



understanding of nutrient release from these fertilizers are important for defining strategies to increase the NUE.

The objective of this study was to characterize controlled-release nitrogen fertilizers and compare them with conventional nitrogen sources in terms of the loss of N-NH₃ and their effects on second-season corn.

MATERIALS AND METHODS

Experimental site and treatments

The field experiment was conducted in Maringá (23° 25′ S; 51° 57′ W), Paraná State, Brazil, at 550 m a.s.l. The climate was classified as subtropical humid mesothermic (Cfa) according to the Köppen-Geiger Classification System (Peel et al., 2007). The soil is a sandy-clay loam *Argissolo Vermelho* (Santos et al., 2018), which correspond to an Ultisol (Soil Survey Staff, 2014). Soil chemical and granulometric analyses of the 0.00-0.20 m layer yielded the following results: 14.2 g dm⁻³ organic matter, pH(H₂O) 5.4, 20.9 mg dm⁻³ P (Mehlich-1), 1.03 cmol_c dm⁻³ Ca²⁺, 0.36 cmol_c dm⁻³ Mg²⁺, 0.28 cmol_c dm⁻³ K⁺, 6.63 cmol_c dm⁻³ cation exchange capacity, 230 g kg⁻¹ clay, 10 g kg⁻¹ silt, and 760 g kg⁻¹ sand.

The experimental design consisted of randomized blocks, with six replicates for each treatment. The treatments consisted of two conventional nitrogen sources (urea and ammonium sulfate) and three PCUs (Agrocote®, FortBlen®, and Kimcoat®). The experimental units consisted of 7 rows that were 10 m long and spaced 0.45 m apart, totaling 31.5 m² in area. Hybrid DKB-285 Pro 2 corn was sown on February 28, 2017, with basic fertilization of 30, 45, and 45 kg ha¹ N, P_2O_5 , and K_2O , respectively, on a population of 60,000 plants ha¹. Nitrogen fertilizers were applied by broadcasting at stage V3/V4 at a rate of 60 kg N ha¹ 48 h after 60 mm of precipitation.

Ammonia capture and determination of ammonia volatilization

Immediately after nitrogen application, the capture of ammonia began for the determination of nitrogen loss through ammonia volatilization. As NH $_3$ volatilized, the capture method described by Araújo et al. (2009) was implemented using a semi-opened static chamber constructed in a PET bottle with an area of 0.007854 m². A 2.5 cm wide and 25 cm long strip of filter paper hung inside the chamber, with the bottom edge of the filter paper submerged in a 50 cm³ bottle containing 20 mL of $\rm H_2SO_4$ 0.05 mol $\rm L^{-1}$ + 2 % v/v glycerin solution. The sampling was carried out by changing the bottles containing the strips and solutions on predetermined dates. After each collection, the chambers were rotated within the plot to minimize the environmental factors that could influence NH $_3$ volatilization. After sampling, the samples were refrigerated, and the amount of volatized N-NH $_3$ was determined with UV/VIS spectrophotometry by using the salicylate-hypochlorite method (Bower and Holm-Hansen, 1980). The N-NH $_3$ losses were summed over each sampling period to determine the cumulative loss over time. During the experimental period, no irrigation was performed, and the daily data on rainfall, air relative humidity and maximum and minimum air temperatures were recorded.

N release and characterization

Nitrogen release from the PCUs was examined using the pouch method (Carson and Ozores-Hampton, 2012). A 5 g sample of PCU was placed into a pouch (10×10 cm) made of nylon mesh that allowed moisture to contact the PCUs. The pouches were taken to the field and distributed on the soil surface along with the plots. After 3, 9, 13, 18, 23, and 27 days, the pouches were removed from the field and weighed, and the remaining N content was determined by the Kjeldahl method. Cross-sectional morphologies of the PCUs were observed via scanning electron microscopy (SEM) using a Quanta 250 FEG microscope. Samples were sputter-coated with gold before observation.



Corn nutritional status and dry matter production

The nutritional status of the corn was evaluated by the leaf N content. The leaf below and opposite the ear of corn were collected at the phenological stage R2. After being dried and ground, the leaves were subjected to sulfuric acid digestion and N determination using the Kjeldahl method. Dry matter was evaluated at physiological maturity (R6) on the material manually harvested from $8.1~\text{m}^2$. Moisture was determined, and dry matter production was corrected to obtain the mass in kilograms per hectare.

Statistical analysis

The treatments were submitted to nonlinear regression analysis using a logistic model (Equation 1) to assess the variable ammonia volatilization. This logistic model is traditionally used to estimate plant growth (Seber and Wild, 2003), and more recently, it was used in a study to estimate cumulative ammonia volatilization (Soares et al., 2012; Vale et al., 2014; Silva et al., 2017).

$$Y = \frac{\alpha}{1 + \exp^{[-\gamma \text{ (time-}\beta)]}}$$
 Eq. 1

in which Y is the amount of volatilized nitrogen accumulated in the form of NH_3 in kilograms per hectare at a given time; α is the asymptotic value, indicating the stabilized value of cumulative volatilization in relation to time (maximum volatilization); β is the time when α reaches half of its maximum value and corresponds to the curve inflection point (the day when the maximum daily loss of N-NH $_3$ occurs); and γ is a relative index used to obtain the maximum daily loss of N-NH $_3$ (MDL) according to equation 2.

$$MDL = \gamma \left(\frac{\alpha}{4}\right)$$
 Eq. 2

The controlled-release data were submitted to nonlinear regression analysis using the Korsmeyer-Peppas model (Equation 3), which is used to analyze release from polymeric systems over time (Korsmeyer et al., 1983).

$$\frac{M_1}{M_m} = \alpha t^n$$
 Eq. 3

in which M_1/M_∞ is the percentage of N released over time; α is a kinetic constant that incorporates the structural and geometric characteristics of the form released in a controlled manner; t is the time in days; and n is the release exponent of the controlled-release fertilizer. The release mechanism was classified according to the n exponent as follows: quasi-Fickian diffusion (n <0.5), Fickian diffusion (n = 0.5), anomalous (non-Fickian) diffusion (0.5< n <1.0), and case II diffusion (n = 1.0) (Ritger and Peppas, 1987; Peppas and Brannon-Peppas, 1994; Siepmann and Peppas, 2012).

Nitrogen diffusion from controlled-release fertilizer coatings was calculated as proposed by Ritger and Peppas (1987) and Peppas and Brannon-Peppas (1994) (Equation 4).

$$\frac{M_1}{M_{\infty}} = 4 \left[\frac{Dt}{\pi l^2} \right]^{0.5}$$
 Eq. 4

Equation 4 was rearranged to give equation 5.

$$D = \frac{\pi l^2}{16t} \left(\frac{M_1}{M_m} \right)^2 \times 10^{12}$$
 Eq. 5

in which D is the diffusion of the released nutrient in μm^2 day⁻¹; I is the thickness of the fertilizer coating layer in μm ; t is the time in days; and M_1/M_{∞} is the percentage of N released over time, as determined by equation 3.



The leaf N content and dry matter in corn were submitted to variance homogeneity tests (Bartlett), an error normality test (Shapiro Wilk), and analysis of variance with a comparison of means by the Tukey test ($\alpha = 0.10$).

RESULTS

The electron micrographs revealed the cross-sectional morphology of each fertilizer, indicating the presence of a coating in two of the three PCUs evaluated (Figure 1). FortBlen® consists of two types of granules: the first has inner and outer layer thicknesses of 35.88 and 34.53 μ m, respectively (Figure 1a), and the second has a single layer with a thickness of 50.34 μ m (Figure 1b). Only one coating layer of 8.11 μ m thickness was observed for Agrocote® (Figure 1c), and no coating was detected for Kimcoat® (Figure 1d).

The N release over time was different for each fertilizer (Figure 2a), with 100, 97.8, and 86.6 % N released from Kimcoat[®], Agrocote[®], and FortBlen[®], respectively, at 27 days after application. One day after fertilizer application, Kimcoat[®] had released 98.7 % N, whereas 81.0 and 52.9 % N had been released from Agrocote[®] and FortBlen[®], respectively.

Estimating the N diffusion for the Kimcoat® fertilizer was not possible, as this parameter depends on the presence of a coating layer that completely covers the granule. For the other PCUs, the Korsmeyer-Peppas model demonstrated that these fertilizers exhibit quasi-Fickian N release behavior, as FortBlen® and Agrocote® yielded n values of 0.0571 and 0.1492, respectively (Figure 2a). As shown in figure 2b, diffusion decreased dramatically in the first five days after fertilizer application and stabilized over time. On the first day after fertilizer application, diffusion was 220.91 and 8.48 μ m² day⁻¹, decreasing to 21.80 and 0.46 μ m² day⁻¹ after 27 days for FortBlen® and Agrocote®, respectively.

The cumulative volatilization of NH₃ (kg ha⁻¹) followed a sigmoidal pattern, increasing gradually at first and then at a high rate before the rate of increase gradually slowed, with

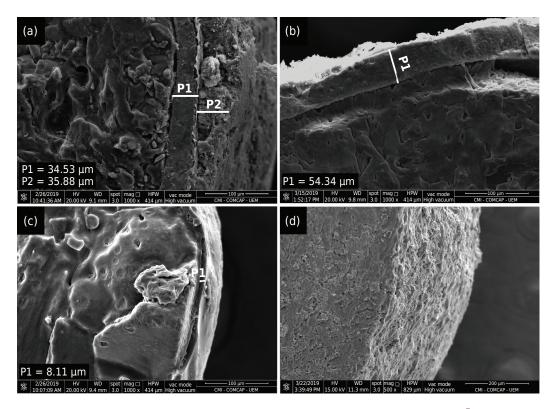


Figure 1. Electron micrographs of the PCUs used as N sources for corn. FortBlen® with double coating (a); FortBlen® with single coating (b); Agrocote® with single coating (c), and Kimcoat® without coating (d).



the volatilization stabilizing at the maximum (Figure 3a). The maximum and minimum temperatures in the first 76 hours after nitrogen fertilizer application were 31.9 and 20.1 °C, respectively, and the relative humidity was above the critical relative humidity of urea (80 % at 20 °C) (Figure 3b) (Adams and Merz, 1929). According to the adjusted model, the maximum volatilization of N-NH₃ decreased as follows: urea (26.4 kg N ha⁻¹; 44 % of the applied N), Kimcoat® (26.1 kg N ha⁻¹; 43.5 % of the applied N), Agrocote® (20.1 kg N ha⁻¹; 33.5 % of the applied N), FortBlen® (16.8 kg N ha⁻¹; 28 % of the applied N), and ammonium sulfate (1.9 kg N ha⁻¹; 3.2 % of the applied N) (Table 1). FortBlen®, Agrocote®, and Kimcoat® reduced the N-NH₃ losses by 36.4, 23.6, and 1.0 %, respectively, compared with that from urea.

The highest $N-NH_3$ losses were observed between 4.2 and 4.9 days after fertilizer application (Table 1). For FortBlen®, Agrocote®, and Kimcoat® to lose the same amount of $N-NH_3$ as that lost from urea 4.2 days after application, an additional 2.9, 1.7, and 0.3 days, respectively, were required (Table 1). Urea, ammonium sulfate, Agrocote®

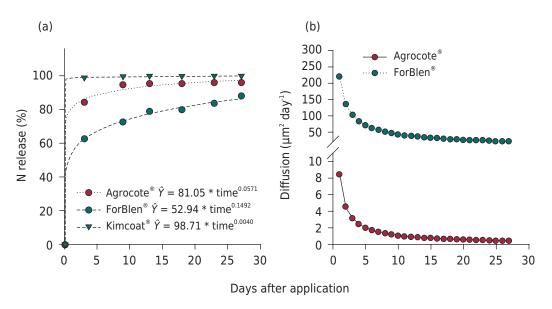


Figure 2. Nitrogen released (a) and N diffusion (b) through the coating of the PCUs over time.

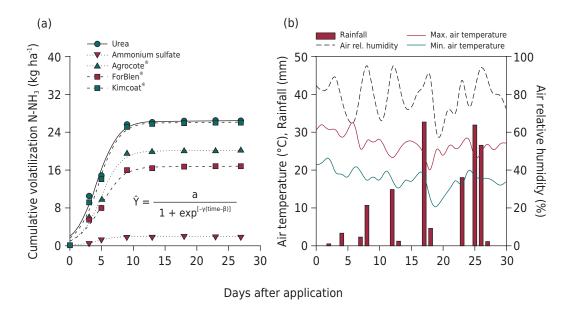


Figure 3. Cumulative volatilization N-NH₃ (a) and climatic conditions (b), after broadcast applications of urea, ammonium sulfate, and PCUs.



Table 1. Parameters of the sigmoid regression adjusted for the cumulative losses of NH₃. Time span for fertilizer-controlled release to lose 10, 20, or 50 % of the maximum losses of NH₃ by volatilization that occurred with urea (26.4 % of the N applied)

Treatments	Parameter				MDL	Time for volatilization of 10, 20, or 50% of the maximum losses observed for uncoated urea		
	α	β	γ	R ²		10 % (day)	20 % (day)	50 % (day)
	kg ha ⁻¹ N-NH ₃	day			kg ha ⁻¹ day ⁻¹ N-NH ₃			
Urea	26.4	4.2	0.59	0.98	3.9	0.5	1.9	4.2
Amm. Sulf.	1.9	4.3	0.79	0.99	0.4	-	-	-
Agrocote [®]	20.1	4.9	0.62	0.99	3.1	1.8	3.2	5.9
FortBlen®	16.8	4.9	0.57	0.98	2.4	1.9	3.5	7.1
Kimcoat [®]	26.1	4.5	0.60	0.99	3.9	0.9	2.2	4.5

 α : asymptotic value (maximum volatilization); β : day when α reaches half of its maximum value and day when the curve inflection point occurs (maximum daily loss of N-NH₃); γ : relative index and MDL: maximum daily loss of N-NH₃.

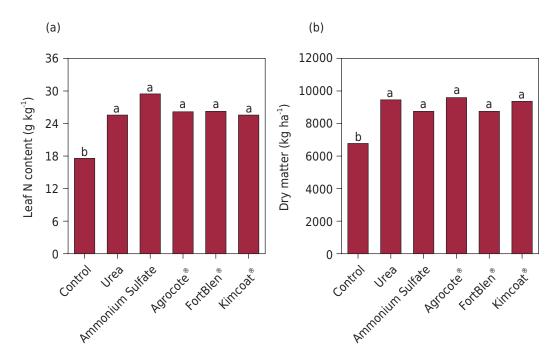


Figure 4. Leaf nitrogen content (a) and dry matter of corn (b), after broadcast fertilization with 60 kg ha⁻¹ using urea, ammonium sulfate, and PCUs.

FortBlen $^{\circ}$, and Kimcoat $^{\circ}$ had maximum daily losses of N-NH $_3$ equal to 3.9 kg ha $^{-1}$ (6.5 % of the applied N), 0.4 kg ha $^{-1}$ (0.7 % of the applied N), 3.1 kg ha $^{-1}$ (5.2 % of the applied N), 2.4 kg ha $^{-1}$ (4.0 % of the applied N), and 3.9 kg ha $^{-1}$ (6.5 % of the applied N), respectively (Table 1).

The application of PCUs to corn did not change the leaf N content or dry matter production compared to those with urea and ammonium sulfate application (Figure 4). However, nitrogen fertilization resulted in average increases of 51.2 and 36.3 % in the leaf N content and dry matter, respectively, compared to those of maize not receiving N fertilization.

DISCUSSION

N release and diffusion from the CRFs

The higher coating thickness of the FortBlen® fertilizer promoted longer N release than that observed with the other PCUs. Similar results were reported by Chagas et al.



(2016), who studied granular urea coated with elemental sulfur and an organic polymer and observed gradual N release over a longer period for fertilizers with higher coating thicknesses. Similarly, Azeem et al. (2016), who studied urea coated with biopolymer, observed that the duration of N release increased with the increase in coating thickness. According to Guertal (2009) and Trenkel (2010), the N release from coated fertilizers may occur as a function of temperature, soil moisture, microbial activity, coating thickness, and the combined action of these factors.

The inefficient control over N release observed with Kimcoat® was due to the absence of a coating (Figure 1d). Martins et al. (2014) evaluated the dissolution of Kimcoat® and conventional urea and observed that both dissolved simultaneously and completely after 4.5 min of exposure to water. The results obtained by Martins et al. (2014) corroborate those obtained in this paper, which suggest that Kimcoat® is subject to the same physical, chemical, and biological phenomena as conventional urea. Petean et al. (2019) studied organic polymer latex-based fertilizers and observed the release of 94.1 to 97.8 % of the applied N by 74 days after application; that is, with Kimcoat®, N was released 74 times faster than N was released from the other fertilizers studied by Petean et al. (2019).

The quasi-Fickian diffusion observed with Agrocote® and FortBlen® indicates that mineral elements partially diffuse through an expanded polymer matrix with water-filled pores (Alharbi et al., 2018). Quasi-Fickian diffusion is governed by Fick's laws and polymeric matrix swelling and relaxation but features a lower granule diffusion rate than that during polymeric matrix swelling and relaxation. According to Lopes et al. (2005), the swelling and relaxation of the polymeric matrix involve a transition from a semirigid state to a more flexible state. When this phenomenon occurs in the PCUs, in addition to the diffusion that occurs, expansion and, consequently, relaxation of the granule coating layer occurs during N release.

The diffusion was highest with FortBlen® (Figure 2b) because it has a thicker coating layer than Agrocote®, thus requiring more intense swelling and relaxation of the polymeric matrix to release the N. The reduction in diffusion over time observed with Agrocote® and FortBlen® demonstrate that N release occurred due to the differences in concentration between the matrix and dissolution medium, which tend to reach phase equilibrium (Van Milligen et al., 2005).

N-NH₃ volatilization with the conventional and CRFs

The air relative humidity in the first 72 h after the application of the fertilizers exceeded the critical relative humidity of urea, a condition that triggers fertilizer dissolution (Skujins and McLaren, 1971). Fertilizer dissolution provides favorable conditions for volatilization. The observed sigmoidal model of cumulative N-NH $_3$ volatilization results from an increase in urease enzyme activity (Vale et al., 2014), through which protons are consumed by urea hydrolysis, thereby increasing the soil pH around fertilizer granules to as much as 8.7 and changing the balance between NH $_4$ and NH $_3$ (Rochette et al., 2009). After achieving maximum loss, the NH $_3$ volatilization flux decreased over time due to the gradual reduction in pH and the stabilization of N in the form of N-NH $_4$ instead of N-NH $_3$ (Otto et al., 2017).

Kimcoat® inefficiently reduced N-NH₃ losses because of its lack of coating and behaved similarly to conventional urea in terms of N losses, as mentioned by Martins et al. (2014). In turn, the coatings of Agrocote® and FortBlen® contributed to the reduction in gaseous N-NH₃ emissions. Several studies have shown the promising potential of coating urea to decrease the N loss that occurs through volatilization (Pereira et al., 2009; Zhao et al., 2013; Nash et al., 2015; Pan et al., 2016; Ke et al., 2017; Kaneko et al., 2019). In the study performed by Zhao et al. (2013) and in the present study, the N-NH₃ losses ranged from 78.8 to 46.5 % and were lower in the PCU treatments than in the common fertilizer treatments. In a meta-analysis, Pan et al. (2016) observed that coated urea fertilizers,



such as thermoplastic resin-coated urea, sulfur-coated urea, and polyolefin-coated urea, significantly reduced NH₃ volatilization by 82.7, 78.4, and 69.4 %, respectively.

The 36.4 % reduction in N-NH $_3$ losses observed with FortBlen 8 compared with those for uncoated urea was similar to the 37 % reduction found by Cancellier et al. (2016) when using polymer-sulfur-coated urea. Similarly, Kaneko et al. (2019) observed a 22.7 % reduction in N-NH $_3$ losses under field conditions when using PCU compared with those for uncoated urea.

Although some PCUs have been found to reduce $N-NH_3$ volatilization, no delay of the peak in ammonia volatilization has been observed with PCUs. However, Ke et al. (2017), studying different CRFs, reported that PCUs had the potential to reduce ammonia volatilization mainly because of a delay in the peak ammonia volatilization to 20 days. The divergence between these results demonstrates the complexity of the environmental and intrinsic factors affecting each fertilizer, the N losses, and the dynamics of the cropping system.

Nitrogen content and dry matter production

In this study, PCUs were not efficient in improving the leaf N content or dry matter yield compared to those for readily soluble sources. The leaf N content was within the suitable range for second-season corn only with the use of ammonium sulfate; the other amidic sources tested resulted in N contents that were close to the lower limit, ranging from 27 to 35 g kg⁻¹ N (Pauletti and Motta, 2019). These results are similar to those observed by Zavaschi et al. (2014), whose use of PCUs did not increase the leaf N concentrations or grain yield relative to those obtained with uncoated urea. Similarly, Rubin et al. (2016) showed that at a rate of 180 kg N ha⁻¹, no difference existed in corn yield among PCU, urea with urease and nitrification inhibitors, and a 50/50 blend of PCU and urea averaged across 12 site-years. Other studies also point to the inefficiency of PCUs in improving crop yields when compared to uncoated urea (Pereira et al., 2009; Cahill et al., 2010; Civardi et al., 2011; Prando et al., 2013).

Some studies have suggested that PCUs significantly increase yield and NUE compared to uncoated urea (Noellsch et al., 2009; Ye et al., 2013; Zhao et al., 2013). Zhao et al. (2013), studying the effect controlled-release fertilizer on NUE in summer corn, observed that the grain yield, NUE and N recovery were higher with the PCU than with the common compound fertilizer. Nevertheless, these authors suggest that the increase in grain yield and NUE with the PCU was generally attributable to the higher photosynthetic rate and lower ammonia volatilization than those with common fertilizer.

Although the benefits of PCUs are usually realized when the environmental conditions are causing substantial N loss (Ruark et al., 2018), in our study, reducing the N-NH₃ losses with the use of PCUs did not result in an increase in the leaf N content or dry matter yield compared to those with uncoated urea. It is possible that N release from fertilizers was not "slow" enough to supply N to corn in the final stages of the growth cycle since even the fertilizer with the slowest release (FortBlen®) released 70 % of the N by 7 days after N fertilization (Figure 2a). In addition, the N supplied by the soil, plus the N supplied at planting and broadcast application (even in the urea treatment) were enough to satisfy the demand of the plants, explaining the lack of significant difference among the N sources. Silva et al. (2017) demonstrated that in environments in which N is not a limiting factor, the N retained because of reduced NH₃ loss is less likely to influence yield. In the same vein, Cantarella et al. (2018) reported that, in many cases, most of the N uptake by crops comes from the soil, and N from the fertilizer, although important, is complementary.

New studies evaluating N dynamics and crop performance are needed to prove the effectiveness of this technology in agriculture.



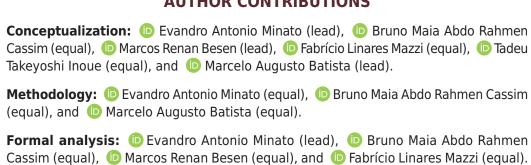
CONCLUSION

Polymer-coated urea fertilizers that have more layers and thicker coatings release N more gradually and over a longer period, reducing $N-NH_3$ losses by 36.4 % over those with uncoated urea.

Kimcoat $^{\circ}$ was not effective at controlling N release and released approximately 98 % of the N applied within 24 hours, ultimately resulting in accumulated N-NH $_{3}$ volatilization and responses in second-season corn similar to those achieved with uncoated urea.

Although no benefits were observed in second-season corn for PCUs over uncoated nitrogen sources, the technology employed in Agrocote $^{\otimes}$ and FortBlen $^{\otimes}$ promoted more gradual N release and reduced N-NH $_3$ volatilization, thereby providing promising alternatives for environments prone to N loss.

AUTHOR CONTRIBUTIONS



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Writing - review and editing: Devandro Antonio Minato (equal), Devandro Maia Abdo Rahmen Cassim (equal), Devandro Renan Besen (equal), Fabrício Linares Mazzi (equal), Devandro Takeyoshi Inoue (equal), and Devandro Augusto Batista (equal).

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Funding acquisition: De Tadeu Takeyoshi Inoue (equal) and De Marcelo Augusto Batista (equal).

REFERENCES

Abalos D, Jeffery S, Sanz-Cobena A, Guardia G, Vallejo A. Meta-analysis of the effect of urease and nitrification inhibitors on crop productivity and nitrogen use efficiency. Agr Ecosyst Environ. 2014;189:136-44. https://doi.org/10.1016/j.agee.2014.03.036

Adams JR, Merz AR. Hygroscopicity of fertilizer materials and mixtures. Ind Eng Chem. 1929;21:305-7. https://doi.org/10.1021/ie50232a003

Alharbi K, Ghoneim A, Ebid A, El-Hamshary H, El-Newehy MH. Controlled release of phosphorous fertilizer bound to carboxymethyl starch-g-polyacrylamide and maintaining a hydration level for the plant. Int J Biol Macromol. 2018;116:224-31. https://doi.org/10.1016/j.ijbiomac.2018.04.182



Araújo ES, Marsola T, Miyazawa M, Soares LHB, Urquiaga S, Boddey RM, Alves BJR. Calibração de câmara semiaberta estática para quantificação de amônia volatilizada do solo. Pesq Agropec Bras. 2009;44:769-76. https://doi.org/10.1590/S0100-204X2009000700018

Azeem B, KuShaari K, Man Z. Effect of coating thickness on release characteristics of controlled release urea produced in fluidized bed using waterborne starch biopolymer as coating material. Procedia Engineer. 2016;148:282-9. https://doi.org/10.1016/j.proeng.2016.06.615

Azeem B, Kushaari KZ, Man ZB, Basit A, Thanh TH. Review on materials & methods to produce controlled release coated urea fertilizer. J Control Release. 2014;181:11-21. https://doi.org/10.1016/j.jconrel.2014.02.020

Bower CE, Holm-Hansen T. A salicylate-hypochlorite method for determining ammonia in seawater. Can J Fish Aquat Sci. 1980;37:794-8. https://doi.org/10.1139/f80-106

Cahill S, Osmond D, Weisz R, Heiniger R. Evaluation of alternative nitrogen fertilizers for corn and winter wheat production. Agron J. 2010;102:1226-36. https://doi.org/10.2134/agronj2010.0095

Cancellier EL, Silva DRG, Faquin V, Gonçalves B de A, Cancellier LL, Spehar CR. Ammonia volatilization from enhanced-efficiency urea on no-till maize in Brazilian Cerrado with improved soil fertility. Cienc Agrotec. 2016;40:133-44. https://doi.org/10.1590/1413-70542016402031115

Cantarella H, Otto R, Soares JR, Silva AGB. Agronomic efficiency of NBPT as a urease inhibitor: A review. J Adv Res. 2018;13:19-27. https://doi.org/10.1016/j.jare.2018.05.008.

Carson LC, Ozores-Hampton M. Methods for determining nitrogen release from controlled-release fertilizers used for vegetable production. HortTechnology. 2012;22:20-4. https://doi.org/10.21273/HORTTECH.22.1.20

Chagas WFT, Guelfi DR, Caputo ALC, Souza TL, Andrade AB, Faquin V. Ammonia volatilization from blends with stabilized and controlled-released urea in the coffee system. Cienc Agrotec. 2016;40:497-509. https://doi.org/10.1590/1413-70542016405008916

Chien SH, Prochnow LI, Cantarella H. Recent developments of fertilizer production and use to improve nutrient efficiency and minimize environmental impacts. Adv Agron. 2009;102:267-322. https://doi.org/10.1016/s0065-2113(09)01008-6

Civardi EA, Silveira Neto AN, Ragagnin VA, Godoy ER, Brod E. Ureia de liberação lenta aplicada superficialmente e ureia comum incorporada ao solo no rendimento do milho. Pesq Agropec Trop. 2011;41:52-9. https://doi.org/10.5216/pat.v41i1.8146

Good AG, Beatty PH. Fertilizing nature: a tragedy of excess in the commons. PLoS Biol. 2011;9:e1001124. https://doi.org/10.1371/journal.pbio.1001124

Guertal EA. Slow-release nitrogen fertilizers in vegetable production: a review. HortTechnology. 2009;19:16-9. https://doi.org/10.21273/HORTSCI.19.1.16

Holcomb JC, Sullivan DM, Horneck DA, Clough GH. Effect of irrigation rate on ammonia volatilization. Soil Sci Soc Am J. 2011;75:2341. https://doi.org/10.2136/sssaj2010.0446

International Fertilizer Association - IFA. Fertilizer outlook 2018-2022 - Production & International Trade and Agriculture Services. In: 86th IFA Annual Conference; June 18-20, 2018; Berlin, Germany. Berlin: IFA; 2018. Available from: https://www.fertilizer.org/images/Library_ Downloads/2018_IFA_Annual_Conference_Berlin_PIT_AG_Fertilizer_Outlook.pdf

Kaneko FH, Ferreira JP, Leal AJF, Buzetti S, Reis AR, Arf O. Ammonia volatilization in response to coated and conventional urea in maize crop field. Biosci J. 2019;35:713-22. https://doi.org/10.14393/bj-v35n3a2019-41772

Ke J, Xing X, Li G, Ding Y, Dou F, Wang S, Liu Z, Tang S, Ding C, Chen L. Effects of different controlled-release nitrogen fertilizers on ammonia volatilization, nitrogen use efficiency and yield of blanket-seedling machine-transplanted rice. Field Crop Res. 2017;205:147-56. https://doi.org/10.1016/j.fcr.2016.12.027

Korsmeyer RW, Gurny R, Doelker E, Buri P, Peppas NA. Mechanisms of solute release from porous hydrophilic polymers. Int J Pharm. 1983;15:25-35. https://doi.org/10.1016/0378-5173(83)90064-9



Liu X, Zhang Y, Han W, Tang A, Shen J, Cui Z, Vitousek P, Erisman JW, Goulding K, Christie P, Fangmeier A, Zhang F. Enhanced nitrogen deposition over China. Nature. 2013;494:459-62. https://doi.org/10.1038/nature11917

Lopes CM, Lobo JMS, Costa P. Formas farmacêuticas de liberação modificada: polímeros hidrifílicos. Rev Bras Cienc Farm. 2005;41:143-54. https://doi.org/10.1590/S1516-93322005000200003

Martins IS, Cazetta JO, Fukuda AJF. Condições, modos de aplicação e doses de ureia revestida por polímeros na cultura do milho. Pesq Agropec Trop. 2014;44:271-9. https://doi.org/10.1590/s1983-40632014000300010

Nash P, Motavalli P, Nelson K, Kremer R. Ammonia and nitrous oxide gas loss with subsurface drainage and polymer-coated urea fertilizer in a poorly drained soil. J Soil Water Conserv. 2015;70:267-75. https://doi.org/10.2489/jswc.70.4.267

Noellsch AJ, Motavalli PP, Nelson KA, Kitchen NR. Corn response to conventional and slow-release nitrogen fertilizers across a claypan landscape. Agron J. 2009;101:607-14. https://doi.org/10.2134/agronj2008.0067x

Otto R, Zavaschi E, Souza Netto GJM, Machado BA, Mira AB. Ammonia volatilization from nitrogen fertilizers applied to sugarcane straw. Rev Cienc Agron. 2017;48:413-8. https://doi.org/10.5935/1806-6690.20170048

Pan B, Lam SK, Mosier A, Luo Y, Chen D. Ammonia volatilization from synthetic fertilizers and its mitigation strategies: a global synthesis. Agr Ecosyst Environ. 2016;232:283-9. https://doi.org/10.1016/j.agee.2016.08.019

Pauletti V, Motta ACV. Manual de adubação e calagem para o estado do Paraná. 2 ed. Curitiba: Núcleo Estadual Paraná da Sociedade Brasileira de Ciência do Solo - NEPAR SBCS; 2019.

Peel MC, Finlayson BL, McMahon TA. Updated world map of the Köppen-Geiger climate classification. Hydrol Earth Syst Sci Discuss. 2007;4:439-73.

Peppas NA, Brannon-Peppas L. Water diffusion and sorption in amorphous macromolecular systems and foods. J Food Eng. 1994;22:189-210. https://doi.org/10.1016/0260-8774(94)90030-2

Pereira HS, Leão AF, Verginassi A, Carneiro MAC. Ammonia volatilization of urea in the out-of-season corn. Rev Bras Cienc Solo. 2009;33:1685-94. https://doi.org/10.1590/s0100-06832009000600017

Petean CC, Teixeira Filho MCM, Galindo FS, Buzetti S, Malmonge JA, Malmonge LF. Polímeros orgânicos com ureia dissolvida e doses de nitrogênio no milho. Rev Cienc Agr. 2019;62:1-9. https://doi.org/10.22491/rca.2019.2761

Prando AM, Zucareli C, Fronza V. Características produtivas do trigo em função de fontes e doses de nitrogênio. Pesq Agropec Trop. 2013;2013:34-41. https://doi.org/10.1590/S1983-40632013000100009

Ritger PL, Peppas NA. A simple equation for description of solute release II. Fickian and anomalous release from swellable devices. J Control Release. 1987;5:37-42. https://doi.org/10.1016/0168-3659(87)90035-6

Rochette P, MacDonald JD, Angers DA, Chantigny MH, Gasser M-O, Bertrand N. Banding of urea increased ammonia volatilization in a dry acidic soil. J Environ Qual. 2009;38:1383-90. https://doi.org/10.2134/jeq2008.0295

Ruark MD, Soratto RP, Rosen CJ. Merits and limitations of enhanced efficiency fertilizers. In: Lal R, Stewart BA, editors. Soil nitrogen uses and environmental impacts. Boca Raton: CRC Press; 2018. p. 289-314.

Rubin JC, Struffert AM, Fernández FG, Lamb JA. Maize yield and nitrogen use efficiency in upper midwest irrigated sandy soils. Agron J. 2016;108:1681-91. https://doi.org/10.2134/agronj2015.0552

Santos HG, Jacomine PKT, Anjos LHC, Oliveira VA, Lumbreras JF, Coelho MR, Almeida JA, Araújo Filho JC, Oliveira JB, Cunha TJF. Sistema brasileiro de classificação de solos. 5. ed. rev. ampl. [e-book]. Brasília, DF: Embrapa; 2018.



Seber GAF, Wild CJ. Nonlinear regression. New Jersey: John Wiley & Sons; 2003.

Siepmann J, Peppas NA. Modeling of drug release from delivery systems based on hydroxypropyl methylcellulose (HPMC). Adv Drug Deliv Rev. 2012;64:163-74. https://doi.org/10.1016/j.addr.2012.09.028

Silva AGB, Sequeira CH, Sermarini RA, Otto R. Urease inhibitor NBPT on ammonia volatilization and crop productivity: a meta-analysis. Agron J. 2017;109:1-13. https://doi.org/10.2134/agronj2016.04.0200

Skujins J, McLaren AD. Urease reaction rates at low water activity. Space Life Sci. 1971;3:3-11. https://doi.org/10.1007/BF00924209

Soares JR, Cantarella H, Menegale MLC. Ammonia volatilization losses from surface-applied urea with urease and nitrification inhibitors. Soil Biol Biochem. 2012;52:82-9. https://doi.org/10.1016/j.soilbio.2012.04.019

Soil Survey Staff. Keys to soil taxonomy. 12th ed. Washington, DC: United States Department of Agriculture, Natural Resources Conservation Service; 2014.

Stafanato JB, Goulart RS, Zonta E, Lima E, Mazur N, Pereira CG, Souza HN. Volatilização de amônia oriunda de ureia pastilhada com micronutrientes em ambiente controlado. Rev Bras Cienc Solo. 2013;37:726-32. https://doi.org/10.1590/S0100-06832013000300019

Sunderlage B, Cook RL. Soil property and fertilizer additive effects on ammonia volatilization from urea. Soil Sci Soc Am J. 2018;82:253-9. https://doi.org/10.2136/sssaj2017.05.0151

Tasca FA, Ernani PR, Rogeri DA, Gatiboni LC, Cassol PC. Volatilização de amônia do solo após a aplicação de ureia convencional ou com inibidor de urease. Rev Bras Cienc Solo. 2011;35:493-502. https://doi.org/10.1590/S0100-06832011000200018

Trenkel ME. Slow- and controlled-release and stabilized fertilizers: an option for enhancing nutrient use efficiency in agriculture. Paris: International Fertilizer Industry Association; 2010.

United States Department of Agriculture - USDA. World corn production; 2019 [cited 2019 Aug 17]. Available from: http://www.worldofcorn.com/#world-corn-production-metric.

Vale MLC, Sousa RO, Scivittaro WB. Evaluation of ammonia volatilization losses by adjusted parameters of a logistic function. Rev Bras Cienc Solo. 2014;38:223-31. https://doi.org/10.1590/s0100-06832014000100022

Van Milligen BP, Bons PD, Carreras BA, Śnchez R. On the applicability of Fick's law to diffusion in inhomogeneous systems. Eur J Phys. 2005;26:913-25. https://doi.org/10.1088/0143-0807/26/5/023

Wilson ML, Rosen CJ, Moncrief JF. Potato response to a polymer-coated urea on an irrigated, coarse-textured soil. Agron J. 2009;101:897-905. https://doi.org/10.2134/agronj2008.0192x

Ye Y, Liang X, Chen Y, Liu J, Gu J, Guo R, Li L. Alternate wetting and drying irrigation and controlled-release nitrogen fertilizer in late-season rice. Effects on dry matter accumulation, yield, water and nitrogen use. Field Crop Res. 2013;144:212-24. https://doi.org/10.1016/j.fcr.2012.12.003

Zavaschi E, Faria LA, Vitti GC, Nascimento CAC, Moura TA, Vale DW, Mendes FL, Kamogawa MY. Ammonia volatilization and yield components after application of polymer-coated urea to maize. Rev Bras Cienc do Solo. 2014;38:1200-6. https://doi.org/10.1590/S0100-06832014000400016

Zhao B, Dong S, Zhang J, Liu P. Effects of controlled-release fertilizer on nitrogen use efficiency in summer maize. PLoS ONE. 2013;8:e70569. https://doi.org/10.1371/journal.pone.0070569