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Urease Inhibitor and Irrigation Management to Mitigate Ammonia Volatilization from Urea in No-Till Corn

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ABSTRACT: High nitrogen (N) losses by ammonia (NH_3) volatilization from urea can compromise nitrogen fertilization efficiency and corn yield. The purpose of this study was to assess the effects of irrigation management and the addition of the urease inhibitor *N*-(*n*-butyl)thiophosphoric triamide (NBPT) on NH_3-N losses from urea and on corn yield. To this end, two experiments were carried out in the 2011/12 crop season on a sandy clay loam Acrisol in the Central Basin region of Rio Grande do Sul, southern Brazil. Experiment I consisted of two different N sources (urea and urea plus the inhibitor) at a rate of 200 kg ha^{-1} N and two corn sowing times [viz., an early time (Sept. 3, 2011) and an intermediate time (Oct. 3, 2011)]. Experiment II considered a combination of three irrigation management systems (viz., without irrigation on the fertilization day and on the next 7 days; 20 mm of water immediately before N fertilization; and 20 mm water after N fertilization) and two N sources (urea and urea plus the inhibitor) at 150 kg ha^{-1} N. A control treatment without topdressed N fertilization was also performed in parallel with the two experiments. The NH_3-N losses from common urea increased with increasing soil moisture in Experiment I (25 % applied N), and with irrigation before N fertilization in Experiment II (27 % applied N). The inhibitor reduced NH_3-N losses from urea by 46 to 80 %. Also, irrigation after fertilization reduced ammonia volatilization by 83 % on average, with little effect from the inhibitor. The effects of the inhibitor and post-fertilization irrigation on the mitigation of NH_3 losses by volatilization from urea were not additive; in addition, they led to no increase in corn yield.

Keywords: *Zea mays*, nitrogen, NBPT.

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INTRODUCTION

An adequate supply of nitrogen (N) by topdressing fertilization is crucial with a view to obtaining high corn grain yields (Fontoura and Bayer, 2009). In Brazil, N is supplied largely in the form of urea. However, high N losses by ammonia (NH_3) volatilization have considerably diminished the agronomic efficiency of this nitrogen fertilizer (Sangoi et al., 2016). The NH_3-N losses from urea are usually intensified by the presence of crop residues on the soil surface in no-till systems (Rojas et al., 2012). This may be one of the origins of average yields as low as 40 % of the productive potential of field crops (Menegati, 2013; Emater, 2016).

Ammonia volatilization has been extensively studied in different regions of Brazil, where reported NH_3-N losses range from 5 to 78 % of N applied as urea depending on the particular environmental conditions (Lara Cabezas et al., 1997; Cantarella et al., 2008; Rojas et al., 2012; Soares et al., 2012; Viero et al., 2014; Viero et al., 2015). The addition of a urease inhibitor such as *N*-(*n*-butyl) thiophosphoric triamide (NBPT) to urea has proved to be an effective, technically feasible method to reduce NH_3-N losses from common urea and increase the efficiency of topdressed N fertilization in corn (Cantarella et al., 2008; Soares et al., 2012; Viero et al., 2015).

The inhibitor can reduces NH_3-N losses by as little as 15 % to as much as 78 % under especially favorable environmental conditions (Cantarella et al., 2008). High air temperature and moisture and also high wind speed and soil moisture increase volatilization losses by facilitating urea hydrolysis, and do not favor NH_4^+ diffusion in soil (Holcomb III et al., 2011; Viero et al., 2015). Although the inhibitor efficiently reduces NH_3-N losses, it does not always lead to increased grain yields (Abalos et al., 2014; Mota et al., 2015). Whether this is a result of an expressive contribution of mineralized N from soil organic matter to crop yield or a result of using N application rates that exceed the response potential of the crop is unclear. For example, Pereira et al. (2009) found the urease inhibitor to reduce NH_3-N losses from 65 to 7.6 % of applied N, and to increase grain yield by only 6.5 %.

Additional variables potentially influencing NH_3-N losses by volatilization are the time of sowing and irrigation regime. An early corn sowing date (August/September) in southern Brazil may result in N topdressing being applied when the air temperature is more moderate compared to later sowing (October/November). Early sowing may thus reduce NH_3-N losses because ammonia volatilization is a temperature-dependent process (Bouwmeester et al., 1985; Tasca et al., 2011; Viero et al., 2014). Rainfall or irrigation shortly after application of urea-based fertilizers can reduce NH_3 volatilization, whereas similar events before fertilization can intensify this volatilization (Viero et al., 2015). Increased volatilization by the effect of irrigation before fertilization is at least partly due to the increased soil moisture facilitating hydrolysis of the fertilizer, and of the resulting NH_4^+ and OH^- ions not diffusing in the soil (Overrein and Moe, 1967).

Increasing the efficiency of topdressed N fertilization in no-till corn requires devising new, more effective methods to mitigate NH_3-N losses by volatilization. Our starting hypothesis was that in the early sowing time, due to the mild air temperatures, the NH_3-N losses from common urea are reduced in comparison to the warmer periods in the intermediate sowing time; and urease inhibitor and adequate irrigation management are efficient alternatives to decrease NH_3-N losses from urea and to increase corn yield. The primary purpose of this study was to assess the N volatilization from topdressing common urea applied to corn in different sowing times and the potential of a urease inhibitor and of irrigation management for reducing NH_3-N losses by volatilization and increasing corn grain yields in a sandy clay loam Acrisol from the Central Basin region of Rio Grande do Sul, southern Brazil.

MATERIALS AND METHODS

Site and experiments

Two field experiments were conducted in the 2011/12 crop season at the Agronomic Experimental Station of the Federal University of Rio Grande do Sul (30° 51' S, 51° 39' W, 42 m a.s.l.), in the municipality of Eldorado do Sul, Rio Grande do Sul, southern Brazil. The regional climate is subtropical humid (Cfa) as per the Köppen classification system, with temperature ranging from 9 °C in the coldest month to 25 °C in the warmest (mean 19.4 °C). The average annual rainfall is 1,440 mm, with short periods of water deficit in the summer (Bergamaschi et al., 2003). The soil was a sandy clay loam Acrisol (WRB, 2014), or *Argissolo Vermelho Distrófico típico* according to the Brazilian classification system (Santos et al., 2013) with 540 g kg^{-1} sand, 240 g kg^{-1} silt, and 220 g kg^{-1} clay (Bayer et al., 2000). Soil samples from the 0.00-0.20 m layer were found to contain 22 g kg^{-1} organic matter, 34 mg dm^{-3} available P (Mehlich-1), and 172 mg dm^{-3} available K (Mehlich-1), and to have a pH(H_2O) of 5.7 and 59 % base saturation. The experimental sites had been cultivated with white oat (*Avena sativa L.*) and vetch (*Vicia sativa* L.) in autumn-winter, and with corn (*Zea mays L.*) in rotation with soybean (*Glycine max L.*) in summer under no-tillage for 20 years.

Experiment I followed a randomized block design with split plots and three replicates. The main plots (12 × 5 m) were sown at two different times, namely: (a) an early sowing time (Sept. 3, corresponding to the beginning of the recommended period); and (b) an intermediate sowing time (Oct. 3). The sub-plots (4 × 5 m) were supplied with N in two different forms (common urea and urea plus a urease inhibitor) at a single rate (200 kg ha^{-1} N) by topdressing the corn crop. Corn was sown 30 (early sowing time) or 60 days (intermediate time) after vetch desiccation and rolling. Topdressed N fertilization was applied at the V5 (early sowing) and V7 stage (intermediate sowing time) of corn (Ritchie et al., 1993). A control treatment without N application was also run in parallel.

Experiment II followed a randomized block design with split plots and four replicates. The main plots (12 × 5 m) were placed under three different irrigation regimes, namely: (a) without irrigation on the day of fertilization and the next 7 days; (b) 20 mm of water immediately before N fertilization, and (c) 20 mm of water immediately after N fertilization. The sub-plots (4 × 5 m) were supplied with N in the form of common urea or urea plus urease inhibitor at a single rate (150 kg ha^{-1} N). The potential effects of rain and dew on the treatment without irrigation were minimized by using metal structures covered with plastic tarps at night and when rain was forecast. Corn was sown on Oct. 3, 60 days after a white oat crop was desiccated. The N sources were applied by hand at the V7 stage of corn (Ritchie et al., 1993). A control treatment without N fertilization was also conducted in parallel.

The corn hybrid P30F53 (Dupont Pioneer) was planted at a density of 8 plants per m^2, using a 0.5 m spacing between rows in both experiments. Fertilization at sowing was projected to provide a grain yield of 15.0 Mg ha^{-1} (CQFS-RS/SC, 2004) with application of N, P_2O_5, and K_2O at rates of 30, 120, and 120 kg ha^{-1}, respectively. The urease inhibitor used was *N*-(*n*-butyl)thiophosphoric triamide (NBPT), commercially available as SuperN®, at a concentration of 0.05 % . After volatilization was assessed, the corn was sprinkler irrigated in all treatments when the water potential fell below - 0.04 MPa. Weeds and pests were controlled by using registered products in accordance with the technical specifications for the crop (Rodrigues and Silva, 2011).

Sampling and quantification of ammonia losses

The NH_3-N losses were quantified by using a semi-open collector (Nömmik, 1973), rotated according to Cantarella et al. (2003). The collector consisted of a transparent acrylic chamber 0.15 m in diameter and 0.35 m high, supported on a PVC base that was inserted to a depth of 2.5 cm in the soil and protected from rainfall. Sampling was done on a rotational basis, using eight bases per sub-plot. After each sampling, the chamber was transferred to the next base, thereby allowing the soil and applied N fertilizer to be exposed to the environmental conditions (rain, wind, temperature) in order to minimize the impact of the presence of the chamber (Cantarella et al., 2008).

The bases were covered with plastic film when N fertilizer was applied. Immediately after fertilization, chambers containing two polypropylene discs (2 cm thick, density = 28 g dm^{-3}) were installed, soaked in 60 mL of phosphoric acid (50 mL L^{-1}) and glycerin (40 mL L^{-1}) solution. The discs were placed 0.15 and 0.30 m, respectively, from the soil. One disc was used to capture NH_3-N from the soil and the other to avoid contamination with atmospheric ammonia.

The bottom disc was changed each sampling day, stored in a plastic bag and refrigerated at 5 °C until analysis. The N retained on the disc was extracted by washing with KCl (1.0 mol L^{-1}) five times and the total volume of washing solution collected made for 500 mL in a volumetric flask. A 20 mL aliquot of washing solution was then supplied with 0.2 g of MgO and steam-distilled in a semi-micro Kjeldahl system (Tedesco et al., 1995). The amount of NH_3-N volatilized was calculated from the total volume of solution used to wash the disc (500 mL), and the results were expressed as daily rates (kg ha^{-1} d^{-1}), NH_3-N cumulative losses (kg ha^{-1}), and percent NH_3-N losses in relation to the applied N rate (% applied N).

Grain yield

Corn grain yield was determined in an area of 10 m^2 in the center of the sub-plots following correction of grain moisture to 13 %.

Statistical analysis

The NH_3-N cumulative loss and grain yield data were subjected to analysis of variance using Proc Mixed in the SAS software package (SAS, 2016). In Experiment I, sowing time and N source were used as the fixed effects, and blocks as the random effects. In Experiment II, irrigation treatment and N source were the fixed effects, and blocks were the random effects. Treatment means were calculated using *LSMeans* and differences between means with Tukey's test at the 5 % significance level.

RESULTS AND DISCUSSION

Daily rates and NH_3-N cumulative losses

In Experiment I, the highest daily rates of NH_3-N volatilization from common urea were observed on the second day after N fertilization. Rates peaked at 24 kg ha^{-1} d^{-1} with early sowing and at 12 kg ha^{-1} d^{-1} with sowing at the intermediate time (Figure 1a). With the urease inhibitor, NH_3-N volatilization peaked later (7-9 days after fertilization) and at a lower level: 4 kg ha^{-1} d^{-1}.

The N source used significantly influenced NH_3-N cumulative losses at both corn sowing times (Table 1). Thus, common urea resulted in increased NH_3-N losses with early sowing (25 % applied N) relative to the intermediate sowing time (13 % applied N) (Figure 1b and Table 2). In contrast, urea in combination with the urease inhibitor led to similar NH_3-N losses at both sowing times (a mean of 6.0 % applied N).

The increased NH_3-N loss from common urea with early sowing contradicts our starting hypothesis that anticipating corn sowing would reduce NH_3-N volatilization by the effect of the milder prevailing temperatures. However, the difference in mean air temperature between the two sowing times was less than 2 °C (Figure 1c). Therefore, the determining factor for the increased NH_3-N losses observed with early sowing was the increased soil moisture on the day that N fertilizer was applied (0.22 g g^{-1} on the early sowing date and 0.13 g g^{-1} on the intermediate date) (Figure 1d). Although the increased soil moisture

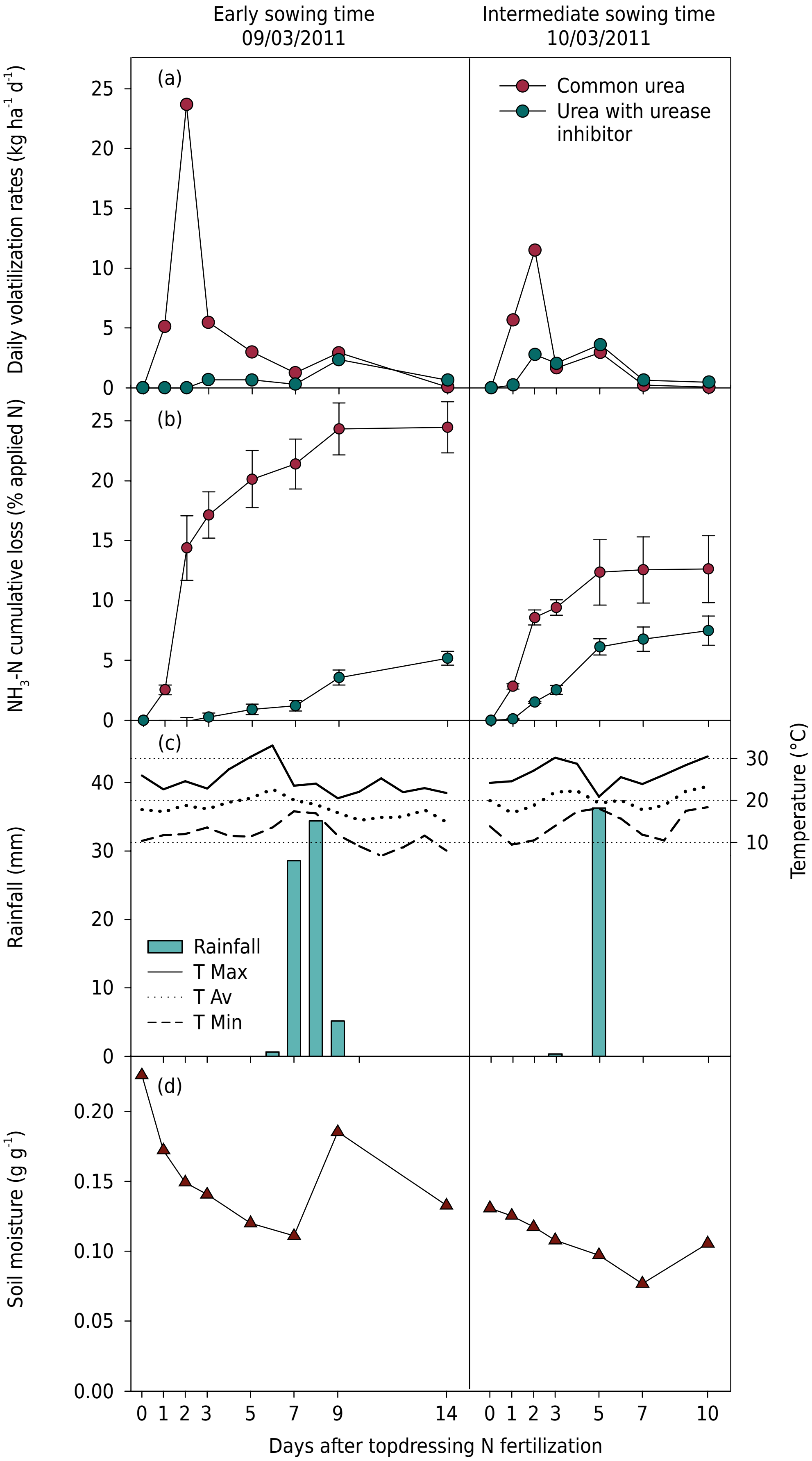

Figure 1. Daily volatilization rates (a) and NH_3-N cumulative losses (b) from common urea and urea with a urease inhibitor applied to corn at two different sowing times (early and intermediate). Rainfall and daily air temperature [maximum (T Max), average (T Av), and minimum (T Min)] (c), and soil moisture (d) in Experiment I. Vertical bars represent mean standard errors.

Table 1. Analysis of variance of the results of Experiments I and II

Fixed effect	DF	NH_3-N cumulative loss		Grain yield	
		F	p	F	p
			Experiment I		
Nitrogen source (N)	1	35.65	0.0269	0.30	0.6395
Sowing time (S)	1	5.45	0.0799	5.48	0.0792
N × S	1	49.45	0.0022	0.00	0.9562
			Experiment II		
Irrigation regime (I)	2	153.00	<0.0001	2.24	0.1881
Nitrogen source (N)	1	146.52	<0.0001	1.63	0.2335
I × N	2	71.72	<0.0001	1.64	0.2470

DF: degrees of freedom. F-value. p-value.

Table 2. The NH_3-N cumulative losses by volatilization and corn grain yield as affected by N source and corn sowing time in Experiment I

N source	Corn sowing time	
	Early	Intermediate
	NH_3-N cumulative loss (% applied N)	
Common urea	25 Aa*	13 Ba
Urea with urease inhibitor	5 Ab	7 Ab
	Grain yield (Mg ha^{-1})	
Common urea	15.3^{NS}	13.9
Urea with urease inhibitor	15.5	14.2

* Different letters indicate that the means of the treatment were different as per Tukey's test at the 5 % level. Uppercase letters compare corn sowing times for the same N source (in the line) and lowercase letters compare N sources for the same corn sowing time (in the column). NS: not significant. Note: Corn yield in the control treatments was 11.3 Mg ha^{-1} with early sowing time (September 3) and 14.5 Mg ha^{-1} in the intermediate sowing time (October 3).

facilitated hydrolysis of urea, the absence of rain in the five days following application of the fertilizer hindered diffusion of NH_4^+ and OH^- ions in the soil. Thus, the fertilizer remained on the soil surface and intensified NH_3-N losses by increasing alkalinity near its granules (Overrein and Moe, 1967).

The rainfall effects on cumulative NH_3-N losses were negligible in the Experiment I, even though rainfall was 40 mm more in the early sowing time. The NH_3-N losses were probably so similar between the two corn sowing times because the difference in rainfall arose after the five-day period following N fertilization - the first five days after N fertilization is a critical period in which 80 % of NH_3-N losses occurred (Figure 1b). This is consistent with previously reported results (Da Ros et al., 2005; Rojas et al., 2012; Viero et al., 2014) and suggests that any strategy intended to efficiently reduce NH_3-N losses should be used during this short period following N fertilizer application.

Adding the urease inhibitor to urea efficiently reduced ammonia volatilization; thus, it decreased NH_3-N cumulative losses by 46 % at early sowing and 80 % at the intermediate sowing time (Figure 1b). According to Cantarella et al. (2008), the efficiency of the inhibitor in decreasing NH_3-N losses from urea is limited to the 15-78 % range. As can be seen from table 2, the efficiency of the inhibitor peaked when the environmental conditions favored volatilization and NH_3-N losses from common urea were highest. With the inhibitor, NH_3-N losses by volatilization were low, irrespective of the climatic conditions. Therefore, its apparently high efficiency relative to the treatment with common urea alone was only observed when the environmental conditions facilitated high NH_3-N losses.

In Experiment II, the daily rates of NH_3-N loss from common urea differed between irrigation regimes. Thus, applying common urea to dry soil (viz., soil that was not irrigated before fertilization and was protected from dew and rain for 7 days after N application) led to a peak NH_3-N loss of 9.0 kg ha^{-1} d^{-1} on the second day after N fertilization (Figure 2a). In contrast, applying urea to soil (viz., soil supplied with 20 mm of water immediately before N fertilization) increased NH_3-N losses on the second day after fertilization to 17 kg ha^{-1} d^{-1}. However, applying N fertilizer immediately before irrigation caused the daily rate of volatilization to fall below 2.0 kg $ha^{-1}d^{-1}$.

Consistent with the results of Experiment I, the difference in soil moisture between the treatment without irrigation (0.13 g g^{-1}) and that involving irrigation immediately before fertilization (0.17g g^{-1}) (Figure 3b) had a strong influence on NH_3-N losses. According to Rochette et al. (2009), soil moisture directly influences urease activity, which is lower in dry soils and increases as soil moisture increases, thus also increasing N losses. In a laboratory study, Tasca et al. (2011) examined the effect of soil moisture on NH_3-N losses and found approximately 30 % of common urea to be lost by volatilization when applied to the surface of a soil with 10 % moisture. Losses decreased to 15 % when common urea was applied to soil with 5 % moisture. These results reinforce the assumption that high soil moisture can intensify NH_3-N losses through volatilization of ammonia.

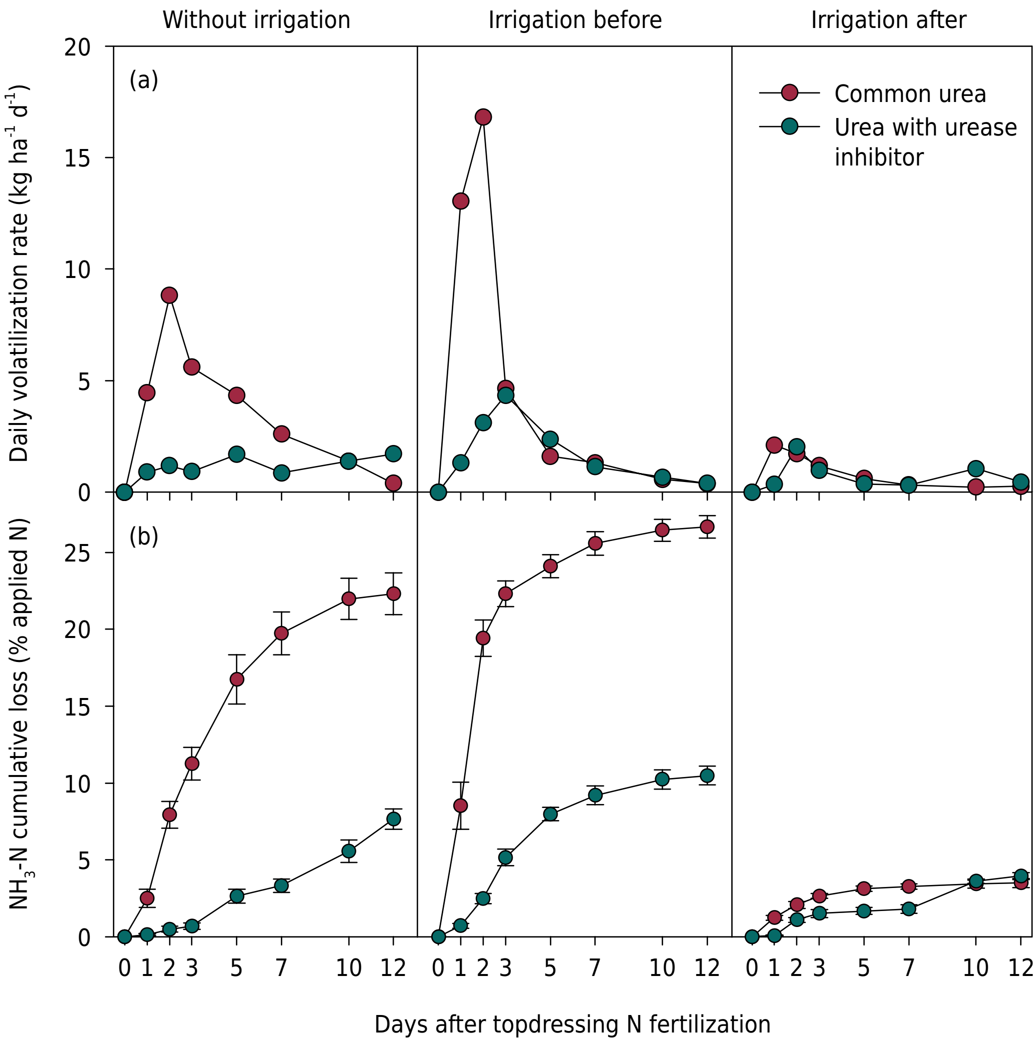

Figure 2. Daily volatilization rates (a) and NH_3-N cumulative losses (b) from common urea and urea with a urease inhibitor applied to no-till corn under three different irrigation regimes, namely: without irrigation (the plots were protected from rain and dew on the day of fertilization and for 7 days after N fertilization), irrigation before (20 mm of water immediately before N fertilization), and irrigation after (20 mm water immediately after N fertilization). Vertical bars indicate mean standard errors.

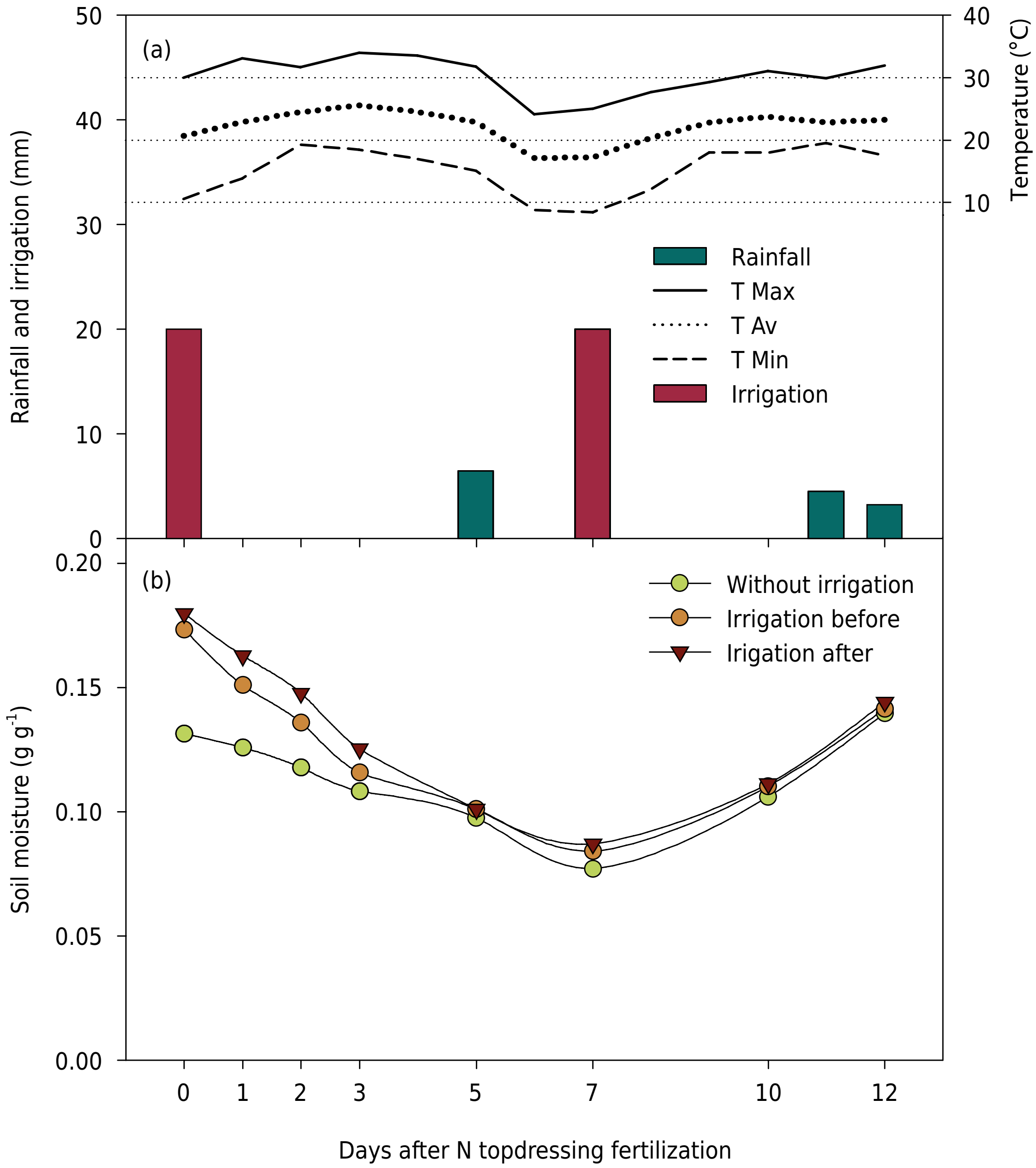

Figure 3. Rainfall, irrigation and daily air temperature [maximum (T Max), average (T Av) and minimum (T Min)] (a); and soil moisture (b) over a period of 12 days (sampling) following N application under three different irrigation regimes.

Despite the strong effect of soil moisture, irrigation can have an even stronger influence on NH_3-N losses from common urea. This is clearly apparent from the difference in NH_3-N cumulative losses from urea applied immediately before or after irrigation. Although soil moisture was similar in both cases (0.17 and 0.18 g g^{-1}, respectively) (Figure 3b), ammonia volatilization was roughly 80 % lower when the soil was irrigated immediately after fertilization. Therefore, soil moisture sufficed to hydrolyze urea in both treatments, but irrigation after fertilization significantly reduced NH_3-N losses - probably through its effect of incorporating fertilizer into the soil (Rochette et al., 2013). Adsorption of NH_4^+ by negative soil charges and buffering of a rise in soil pH around granules (Holcomb III et al., 2011) strongly decreased volatilization rates: from 17 to 2 kg ha^{-1} d^{-1} on the second day after N fertilization (Figure 2a). A similar effect was previously reported by Holcomb III et al. (2011): irrigation with 21.6 mm water reduced NH_3-N losses from 53.4 to 2.8 % applied N, which they ascribed to incorporation of N into the soil.

Similar to Experiment I, the urease inhibitor was efficient in reducing NH_3-N losses. Thus, in both dry soil (viz., soil without irrigation until 7 days after N fertilization) and humid soil (viz., soil irrigated immediately before fertilization), it reduced NH_3-N losses by 64 and 59 %, respectively, relative to common urea (Figure 2b and Table 3). These results

Table 3. NH_3-N cumulative losses by volatilization and corn grain yield as affected by N source and irrigation regime in Experiment II

N source	Irrigation systems		
	Without irrigation[(1)]	Irrigation before	Irrigation after
	NH_3-N cumulative losses (% applied N)		
Common urea	22 Aa*	27 Aa	4 Ba
Urea with urease inhibitor	8 Bb	11 Ab	4 Ba
	Grain yield (Mg ha^{-1})		
Common urea	11.6[NS]	10.9	10.9
Urea with urease inhibitor	11.8	10.7	11.7

[(1)] Without irrigation: the plots were protected from rain and dew on the day of fertilization and for 7 days after topdressing N fertilization. Irrigation before: 20 mm water immediately before N fertilization. Irrigation after: 20 mm water immediately after N fertilization. * Different letters indicate that the means of the treatment were different as per Tukey's test at the 5 % level. Uppercase letters compare irrigation regimes for the same N source (in the line) and lowercase letters compare N sources for the same irrigation regime (in the column). NS: not significant. Note: Corn yield in the control treatment was 8.9 Mg ha^{-1}.

are consistent with those of Cantarella et al. (2008) and Pereira et al. (2009). However, with irrigation after fertilization - which resulted in a substantial reduction in NH_3-N losses by volatilization - the urease inhibitor had no influence on N losses (Table 3).

Grain yield

Nitrogen source and sowing time had no effect on corn grain yield in Experiment I (Table 1). In Experiment II, the reduction in NH_3-N losses observed in the treatments, including the treatment in which the N fertilizer contained the urease inhibitor and was applied before irrigation, led to no increase in corn yield (Table 3). Some authors (Pereira et al., 2009; Abalos et al., 2014) have shown the inhibitor to reduce NH_3-N losses from common urea by approximately 50 % while increasing grain yield by less than 7.5 %. For example, Pereira et al. (2009) found the inhibitor reduced NH_3-N losses from 65 to 7.6 % of applied N (80 kg ha^{-1}) and increased grain yield by only 6.5 %.

The less expressive effect on grain yield from the treatments that reduced NH_3-N losses by volatilization may have at least partly been due to the high N availability in the soil. This idea is supported by the high yield of the control treatment, where grain yield was 8.9 Mg ha^{-1} (Experiment II). Corroborating our study, Fontoura and Bayer (2010) found no substantial increase in corn yield in the south-central region of Paraná as a result of reduced NH_3-N losses by the addition of a urease inhibitor to urea. They ascribed this result to the high N content of the soil and/or the amount of N exceeding the requirements of the crop for maximum yield. Therefore, our similar results in this respect may have been a consequence of N being incorporated by the winter cover crop (vetch in Experiment I) and by the soil, as reflected in the high grain yield obtained in the control treatments, which excluded N application (11.3 Mg ha^{-1} with early sowing and 14.5 Mg ha^{-1} with sowing at an intermediate time). Although NH_3-N losses were up to 25 % of N applied as urea, N was not a limiting factor for corn crop development.

CONCLUSIONS

The main factor that determine the NH_3-N loss from common urea was the soil moisture and not the air temperature, as our starting hypothesis. The high soil moisture intensified NH_3-N loss from urea in the early sowing time. The urease inhibitor N-(n-butyl)thiophosphoric triamide (NBPT) very efficiently reduced NH_3-N losses by volatilization from urea applied to a dry or humid soil. Irrigation (or rainfall) immediately after N fertilization reduced NH_3-N losses. The effects of the urease inhibitor and of irrigation after fertilization (viz., decreased NH_3-N losses by volatilization) were not additive. Also, reducing NH_3-N losses had no impact on corn yield.

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