



# Ammonia volatilization and nitrogen status in second-season corn after lime and gypsum application in no-till

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**ABSTRACT.** In no-till (NT), liming and urea fertilization are performed on the soil surface, which can increase nitrogen (N) losses via ammonia volatilization. On the basis of N fertilization management, gypsum application provides a promising alternative for improving N uptake by plants. Therefore, the objective of this study was to evaluate the N behavior loss by NH<sub>3</sub>-N volatilization, the soil pH at a depth of 0 – 0.05 m, leaf N content, and N uptake by second-season corn after lime and gypsum application in a Rhodic Ferralsol under NT. Overall, the treatments consisted of a 4 × 4 factorial arrangement with four lime rates (0, 2.6, 5.4, and 8.1 Mg ha<sup>-1</sup>) and four gypsum rates (0, 4, 8, and 12 Mg ha<sup>-1</sup>). During the study period, second-season corn was cultivated for two years and fertilized with urea, for which the N losses through ammonia volatilization, soil pH, leaf N content, and N uptake values were quantified. The losses through ammonia volatilization were subjected to nonlinear regression using a logistic model, and the other variables were subjected to linear regressions. The lime applied by broadcasting on the soil surface in the NT increased the pH of the topsoil and increased N losses via NH<sub>3</sub>-N volatilization in the second-season corn. Further, the N losses in the NT treated with lime accounted for 58% of the applied N, which increased by 2.3 to 2.5% for each Mg ha<sup>-1</sup> of lime applied. Therefore, lime or gypsum application did not improve the status of N in second-season corn in soils with low acidity and no S deficiency.

**Keywords:** nonlinear models; soil acidity; N uptake; soil pH.

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## Introduction

No-till (NT) has been adopted on approximately 180 million hectares worldwide (Kassam, Friedrich, & Derpsch, 2018). This system is considered a global strategy for conservation agriculture as it is an effective approach for managing agro-ecosystems for improved and sustainable crop productivity, and increases profits and food security while preserving and enhancing environmental and social resources (Pittelkow et al., 2015).

Tropical soils with low pH and base saturation associated with the presence of reactive aluminum (Al<sup>3+</sup>) have acidity related problems that restrict root growth and, consequently, decrease the yield of sensitive crops (Singh et al., 2017). Soil pH correction, which is considered a global agricultural practice, is required to alleviate these problems. In NT, soil pH correction is mainly performed via lime application to the soil surface without incorporation, thereby raising the topsoil pH (Caires, Haliski, Bini, & Scharr, 2015).

In addition to acidity limitations, tropical soils generally have low levels of organic matter and available N, and therefore require supplemental N fertilization to achieve satisfactory yields. In NT, urea [CO(NH<sub>2</sub>)<sub>2</sub>] is the fertilizer most used to meet the N requirement of crops (IFA, 2018). Overall, its characteristics of high N concentration (45 to 46%), low cost/N unit, high market availability, high solubility, and good compatibility with most fertilizers have popularized the use of urea in agriculture (Chien, Prochnow, & Cantarella, 2009). However, when urea is applied to the soil surface, it can be lost by denitrification, leaching, and ammonia (NH<sub>3</sub>-N) volatilization (Gillette et al., 2017), the latter of which is the main route of N loss in agricultural systems, accounting for more than 50% of the applied N (Tasca, Ernani, Rogeri, Gatiboni, & Cassol, 2011). After it is applied on the soil surface, urea is hydrolyzed via enzyme urease actions, consuming H<sup>+</sup>, producing ammonium and carbonic gas, and increasing the pH around the fertilizer granules (Trenkel, 2010).

In soils under NT, it has been recommended the management of acidity with correctives such as lime associated or not with soil conditioners such as gypsum, both of which are applied on the soil surface, where nitrogen fertilizers

such as urea are also deposited. The increase in the soil pH as a result of lime dissolution and urea hydrolysis changes the balance between ammonia and ammonium in the soil, thereby favoring the transformation of  $\text{NH}_4^+$ -N into  $\text{NH}_3$ -N, which can be lost to the atmosphere (Rochette et al., 2009). N losses as ammonia ( $\text{NH}_3$ -N), are very important because can reduce crop yield and N use efficiency (NUE) (Abalos, Jeffery, Sanz-Cobena, Guardia, & Vallejo, 2014), and causing negative economic effects for farmers (Good & Beatty, 2011). Further, reducing  $\text{NH}_3$ -N volatilization rates also has environmental benefits. Specifically, the volatilized  $\text{NH}_3$  can be deposited nearby or transported over long distances when reacted with acids to form ammonium aerosols, such as  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{HSO}_4$  (Galloway et al., 2004), consequently affecting air quality and contaminating ecosystems (Liu et al., 2013).

Intended to improve N fertilization management, gypsum application is a promising alternative, especially in acidic soils. When applied to the soil surface, gypsum moves down the soil profile during drainage and increases the  $\text{Ca}^{2+}$  supply while reducing the levels of toxic  $\text{Al}^{3+}$ , thereby improving root development in the deep soil layers (Zoca & Penn, 2017). The deepening of root systems improves the N uptake by plants, especially  $\text{NO}_3^-$  that has moved to the subsoil, which might otherwise be lost (Caires, Zardo Filho, Barth, & Joris, 2016). In addition, gypsum is a sulfur (S) source that is also involved in the metabolism of N (Marschner, 2012), and its presence thereby increases N uptake and NUE (Arata, Lerner, Tranquilli, Arrigoni, & Rondanini, 2017; Salvagiotti & Miralles, 2008).

Although the effects of pH on ammonia volatilization and S in improving the nutritional status of N are known, few field studies have demonstrated the effects of lime, in the presence and absence of gypsum, on N losses and nutritional status of N in NT.

Therefore, this study was conducted to test the following hypotheses: i) liming applied on the soil surface in NT will increase N losses by  $\text{NH}_3$ -N volatilization, thereby decreasing N uptake in second-season corn, and ii) gypsum increases N uptake by second-season corn under the NT. The aim of this research was to evaluate N loss behavior due to  $\text{NH}_3$ -N volatilization, soil pH, leaf N content, and N uptake by second-season corn after lime and gypsum application in a Rhodic Ferralsol soil under NT more than 20 years old.

## Material and methods

### Site description and soil

Field research was conducted in Floresta (23°35' S, 52°04' W), Paraná State, Brazil, at 395 m above sea level. The climate in the study area is classified as subtropical humid mesothermic (Cfa) according to the Köppen-Geiger System (Peel, Finlayson, & McMahon, 2007), in which the average temperatures in the coldest and hottest quarters are 17°C and 28°C, respectively, with annual rainfall ranging from 1400 to 1600 mm. The soil of the study site was classified as LATOSSOLO VERMELHO Distroférico (Santos et al., 2018), which corresponds to a Rhodic Ferralsol soil (FAO, 2015), and has existed under NT for more than 20 years. During this time, the soil has been cultivated with wheat, black oat, or corn in the winter and soybean or corn in the summer. Table 1 lists the results of the chemical characterization and particle size distribution analyses at different soil depths in June 2014 before the start of this research.

**Table 1.** Chemical characterization and particle size distribution analyses of different depths in June 2014.

Analysis	Soil depth (m)		
	0.0 – 0.20	0.20 – 0.40	0.40 – 0.60
pH $\text{CaCl}_2$	4.9	5.1	5.0
pH $\text{H}_2\text{O}$	5.5	5.8	5.6
H+Al (mmol <sub>c</sub> dm <sup>-3</sup> )	52.5	46.1	46.1
Organic C (g dm <sup>-3</sup> )	10.28	7.13	5.92
P (mg dm <sup>-3</sup> )	7.5	2.26	2.16
$\text{Ca}^{2+}$ (mmol <sub>c</sub> dm <sup>-3</sup> )	37.5	33.1	28.3
$\text{Mg}^{2+}$ (mmol <sub>c</sub> dm <sup>-3</sup> )	16.0	14.7	14.5
K <sup>+</sup> (mmol <sub>c</sub> dm <sup>-3</sup> )	1.55	0.63	0.43
$\text{Al}^{3+}$ (mmol <sub>c</sub> dm <sup>-3</sup> )	0.63	0	0
S- $\text{SO}_4^{2-}$ (mg dm <sup>-3</sup> )	10.2	11.7	20.0
CEC (mmol <sub>c</sub> dm <sup>-3</sup> )	108.1	94.53	89.33
Base saturation (%)	50.89	51.23	48.39
Clay (g kg <sup>-1</sup> )	760	770	800
Silt (g kg <sup>-1</sup> )	90	80	80
Sand (g kg <sup>-1</sup> )	150	150	120

pH 1:2.5, soil:solution; H+Al was determined by the Shoemaker-McLean-Pratt (SMP) method; organic C content was determined using the Walkley and Black method; Ca, Mg, and Al contents were extracted by KCl 1 mol L<sup>-1</sup>; P and K contents were extracted by Mehlich-1; CEC: cation exchange capacity =  $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + \text{K}^+ + \text{H}^+ + \text{Al}$ ; base saturation =  $100 (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ / \text{CEC})$ ; and particle size distribution was determined using the densimeter method.

### Experimental design, treatments, and crop studies

A randomized complete block design was employed with four replications in a split-plot arrangement. The plot size was  $40 \times 5$  m, and the subplot sizes were  $10 \times 5$  m. The treatments consisted of a  $4 \times 4$  factorial arrangement with four lime rates (0, 2.6, 5.4, and  $8.1 \text{ Mg ha}^{-1}$ ) in a plot and four gypsum rates (0, 4, 8, and  $12 \text{ Mg ha}^{-1}$ ) in the subplots. The dolomitic lime used contained  $207 \text{ g kg}^{-1}$  Ca,  $114 \text{ g kg}^{-1}$  Mg, and 90% effective calcium carbonate equivalent. The gypsum used was a sub-product of the phosphoric acid industry and contained  $180 \text{ g kg}^{-1}$  Ca and  $150 \text{ g kg}^{-1}$  S. Both the lime and gypsum were rate corrected on a dry basis according to the moisture level determined in the laboratory and were applied to the soil surface in October 2014.

Second-season corn was sown in March 2015 and February 2017 (6 and 29 months after the application of lime and gypsum) at a distribution of  $4.2 \text{ seeds m}^{-1}$  and row spacing of 0.7 m. At the sowing time,  $16.5 \text{ kg N ha}^{-1}$  and  $77 \text{ kg P}_2\text{O}_5 \text{ ha}^{-1}$  were applied as monoammonium phosphate (MAP), and after 15 days, a topdressing of  $60 \text{ kg K}_2\text{O ha}^{-1}$  was applied using potassium chloride (KCl). In the V4 corn stage, when four fully developed leaves were present, and one day after a rainfall event (Figure 1),  $100 \text{ kg N ha}^{-1}$  was applied by broadcast to the soil surface using urea (45% N) as the source.

To determine the leaf N content, 15 leaves were collected from the middle third of the leaf opposite and below the corn cob during the tasseling stage (Pauletti & Motta, 2019). After sampling, the leaves were washed in distilled and deionized water, dried in a forced air circulation oven at  $65^\circ\text{C}$  for 72h, and then ground. Corn grains were harvested at a rate of  $10.5 \text{ m}^2$  for each plot (using a 5 m length of the middle three rows), and the yield was corrected on a dry weight (0% moisture) basis. Then, the grain samples were ground to determine the grain N content. The grain and leaf N content analyses were performed using sulfuric acid digestion and were determined according to the micro-Kjeldahl method (Malavolta, Vitti, & De Oliveira, 1997). Conversely, the N uptake in the grain was determined by multiplying the grain N content by the corn grain yield.

### Capture and determination of ammonia volatilization

Immediately after N application, the detection of N losses via ammonia volatilization began. The methodology employed required the use of a semi-static chamber constructed in a plastic bottle (Polyethylene terephthalate - PET) with an area of  $0.007854 \text{ m}^2$  to capture the  $\text{NH}_3\text{-N}$  volatilization (Araújo et al., 2009; Jantalia et al., 2012). The chamber bottles contained a 2.5 cm wide and 25 cm long filter paper strip with a base immersed in a  $50 \text{ cm}^3$  flask with 20 mL of a solution of  $0.05 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  and 2% (v/v) glycerin. The used bottles were replaced with new ones until the ammonia loss stabilized. After each collection, the chambers were rotated between the three sites within each plot to minimize the effects of environmental factors, such as rainfall. Subsequently, the samples were refrigerated, and the amount of volatilized  $\text{NH}_3\text{-N}$  was determined by UV/VIS spectrophotometry using the salicylate–hypochlorite method (Bower & Holm-Hansen, 1980). The  $\text{NH}_3\text{-N}$  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 rainfall, air relative humidity, and maximum and minimum air temperatures were recorded.

### Soil sampling and chemical analysis

Soil sub-samples were obtained after corn harvesting in 2015 and 2017. To obtain a composite sample, two soil samples were collected at a depth of 0 - 0.05 m in each subplot using a shovel. Prior to the chemical analysis, the soils were air-dried, ground and passed through a 2 mm sieve. Soil pH was determined in a  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$  suspension (1:2.5 soil/solution, v/v) (Pavan, Bloch, Zempulski, Miyazawa, & Zocoler, 1992).

### Statistical analyses

All statistical analyses were performed in SAS (version 9.3; SAS, Cary, NC) using the PROC MIXED (restricted maximum likelihood) procedure. Lime and gypsum were considered random factors in the model, and blocks were considered to be fixed factors. When lime or gypsum was significant at  $p < 0.05$ , the rate was subjected to a polynomial regression. Time was included as a repeated measure in the model to evaluate N losses via  $\text{NH}_3\text{-N}$  over time (Littell, Milliken, Stroup, Wolfinger, & Schabenberger, 2006). The Akaike information criterion value was used as the model selection criterion to determine the best covariance model for the repeated variables. The corrected denominator degrees of freedom were obtained using the Kenward–Roger adjustment. When interactions with time was observed, the data were subjected to nonlinear regression using the logistic model represented by Equation 1, as described by Seber and Wild (2003). Note that this

model is traditionally used to estimate cumulative ammonia volatilization (Silva, Sequeira, Sermarini, & Otto, 2017; Cantarella, Otto, Soares, & Silva, 2018; Minato et al., 2019; Minato et al., 2020).

$$\hat{Y} = \frac{\alpha}{1 + \exp[-(time - \beta)/\gamma]} \quad (1)$$

where  $\hat{Y}$  is the amount of volatilized N accumulated in the form of  $\text{NH}_3\text{-N}$  in  $\text{kg ha}^{-1}$  at a given time;  $\alpha$  is the asymptotic value, indicating the stabilization value of the cumulative volatilization relative to time (maximum volatilization);  $\beta$  is the time when  $\alpha$  reaches half of its maximum value and the curve inflection point (the day when the maximum daily loss of  $\text{NH}_3\text{-N}$  occurs); and  $\gamma$  is a parameter used to calculate the maximum daily loss (MDL) of  $\text{NH}_3\text{-N}$ , as given by Equation 2.

$$\text{MDL} = \frac{\alpha}{4\gamma} \quad (2)$$

## Results

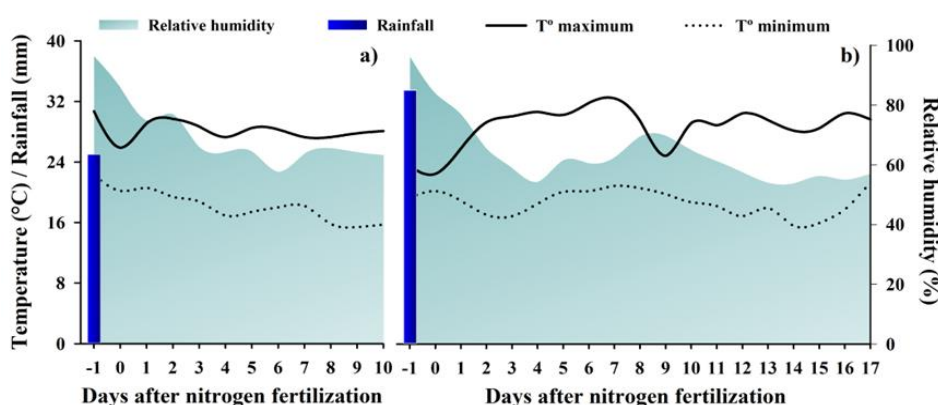
### N losses through $\text{NH}_3\text{-N}$ volatilization

Cumulative volatilization was significantly influenced by the interaction of the rates of surface-applied lime and time over the two-year study (Table 2). In both years, N fertilizers were applied 24h after rainfall events of 25 and 34 mm for the seasons of 2015 and 2017, respectively. During the first 24h after N fertilizer application, the maximum and minimum temperatures ranged from 25.9 to 22.8°C and from 20.2 to 20.8°C, respectively (Figure 1), and the relative humidity was above the critical relative humidity of urea (80% at 20°C) (Adams & Merz, 1929).

**Table 2.** Statistical analysis summary of cumulative volatilization (Cumul. Volat.), total volatilization (Total Volat.), soil pH, N contained in leaf (N Leaf), and N stored in grain (N Uptake) as a function of lime and gypsum over time.

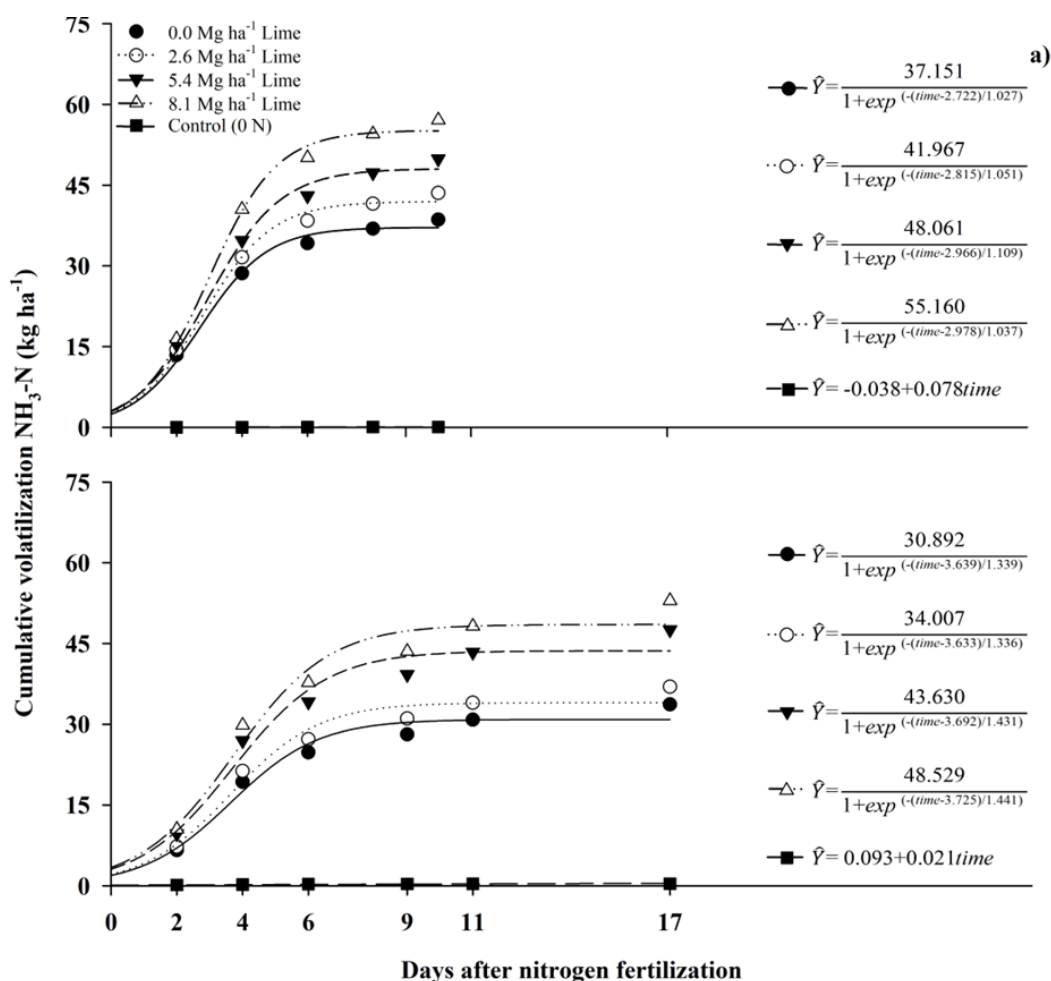
Variation Source	Cumul. Volat.		Total Volat.		P value†		N Leaf		N Uptake	
	2015	2017	2015	2017	Soil pH	Soil pH	2015	2017	2015	2017
Lime	0.001	0.001	0.001	0.001	0.001	0.001	0.971	0.717	0.586	0.357
Gypsum	0.758	0.279	0.808	0.327	0.078	0.691	0.080	0.849	0.097	0.958
Lime*Gypsum	0.959	0.783	0.933	0.578	0.308	0.897	0.702	0.819	0.237	0.551
Time	0.001	0.001	-	-	-	-	-	-	-	-
Time*Lime	0.001	0.001	-	-	-	-	-	-	-	-
Time*Gypsum	0.274	0.548	-	-	-	-	-	-	-	-
Time*Lime*Gypsum	0.906	0.780	-	-	-	-	-	-	-	-

† The source of variation was assumed to be significant at  $p < 0.05$ .



**Figure 1.** Rainfall, air relative humidity, and maximum and minimum air temperatures during the N losses observed in the ammonia volatilization experiment in (a) 2015 and (b) 2017.

For all the lime application rates in both years, the cumulative volatilization exhibited sigmoidal behavior, starting with a small rate, increasing to a high rate when the volatilization rate gradually decreased, and then stabilizing at a maximum (Figure 2). According to the logistic model, which was adjusted for each lime rate over time, the parameter  $\alpha$  in both years increased with increasing lime rate, with losses of 37.2, 42.0, 48.0, and 55.2  $\text{kg ha}^{-1}$   $\text{NH}_3\text{-N}$  in relation to lime rates of 0, 2.6, 5.4, and 8.1  $\text{Mg}^{-1}$ , respectively, in 2015 (Table 3) and 30.9, 34.0, 43.7, and 48.6  $\text{kg ha}^{-1}$   $\text{NH}_3\text{-N}$  in 2017, respectively (Table 3).



**Figure 2.** Cumulative volatilization  $\text{NH}_3\text{-N}$  ( $\text{kg ha}^{-1}$ ) during (a) 2015 and (b) 2017 for second-season corn after urea application by broadcast ( $100 \text{ kg ha}^{-1} \text{ N}$ ) and after lime application to the surface in an experiment under continuous no-till. The lime $\times$ gypsum $\times$ time interactions were not significant at  $p < 0.05$ . Further, a regression analysis was conducted using the mean of the four gypsum rates and the four replications.

**Table 3.** Parameters of the sigmoid regression adjusted for the cumulative losses of  $\text{NH}_3\text{-N}$  during 2015 and 2017 for second-season corn after urea broadcast application ( $100 \text{ kg ha}^{-1} \text{ N}$ ) and after lime application to the surface in an experiment under continuous no-till.

Treatments ( $\text{Mg ha}^{-1}$ )	Parameter			$R^2$	MDL $\text{kg ha}^{-1} \text{ day}^{-1}$ $\text{NH}_3\text{-N}$	
	$\alpha$ $\text{kg ha}^{-1}$ $\text{NH}_3\text{-N}$	$\gamma$	$\beta$ day			
Lime 2015	0.0	37.15	1.02	2.72	0.99	9.11
	2.6	41.96	1.05	2.81	0.99	9.99
	5.4	48.06	1.11	2.96	0.99	10.82
	8.1	55.16	1.04	2.98	0.99	13.26
Lime 2017	0.0	30.89	1.34	3.64	0.99	5.76
	2.6	34.00	1.33	3.63	0.99	6.39
	5.4	43.63	1.43	3.69	0.99	7.63
	8.1	58.53	1.44	3.72	0.99	10.16

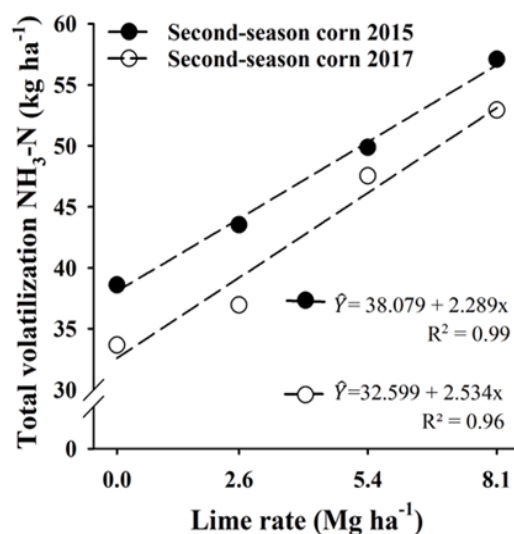
$\alpha$ : maximum cumulative volatilization;  $\beta$ : time at which 50% of the losses occur, corresponding to the curve inflection point;  $\gamma$ : parameter of the equation used to calculate the MDL; and MDL: maximum daily loss of  $\text{NH}_3\text{-N}$ .

Peak  $\text{NH}_3\text{-N}$  volatilization ( $\beta$ ), which was considered at 50% of the maximum cumulative volatilization of  $\text{NH}_3\text{-N}$  ( $\text{kg ha}^{-1}$ ), occurred between 2.72 and 2.98 days after N fertilization in 2015 (Table 3) and between 3.64 and 3.72 days after N fertilization in 2017 (Table 3). The maximum daily loss of  $\text{NH}_3\text{-N}$  parameter MDL, were adjusted for each lime rate over time, for each year increased according with increasing lime rate, with losses of 9.1, 10.0, 10.8, and 13.2  $\text{kg ha}^{-1} \text{ NH}_3\text{-N}$  in relation to lime rates of 0, 2.6, 5.4, and 8.1  $\text{Mg}^{-1}$ , respectively, in 2015 (Table 3) and 5.7, 6.4, 7.6, and 10.1  $\text{kg ha}^{-1} \text{ NH}_3\text{-N}$  and 8.1  $\text{Mg}^{-1}$  in 2017, respectively (Table 3).

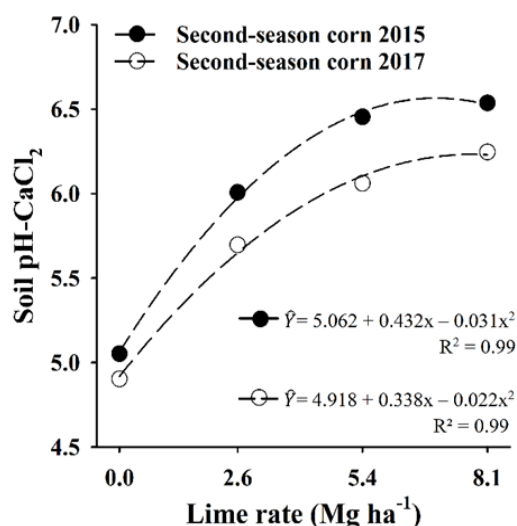
The total volatilization was influenced only by lime application (Table 2). Specifically, the lime rates increased the  $\text{NH}_3\text{-N}$  volatilization linearly, wherein for each  $\text{Mg ha}^{-1}$  of lime applied, the  $\text{NH}_3\text{-N}$  volatilization of the applied N increased by 2.3 and 2.5% during 2015 and 2017 in the second-season corn, respectively (Figure 3).

### Soil chemical attributes

The soil pH at a depth of 0 – 0.05 m in 2015 and 2017 was significantly influenced by the surface lime application rate (Table 2). In particular, the application of surface lime changed the soil pH in a quadratic manner for both study years (Figure 4). However, the magnitude of the soil pH change varied according to the lime application rate and the time after lime application. For example, the soil pH after the second season corn in 2017 was higher than that in 2015. Further, after lime application, the soil pH ranged from 4.9 to 6.2 in 2015 from 5.0 to 6.5 in 2017 at rates of 0 and 8.1  $\text{Mg ha}^{-1}$ , respectively.



**Figure 3.** Total volatilization  $\text{NH}_3\text{-N}$  ( $\text{kg ha}^{-1}$ ) during 2015 and 2017 for the second-season corn after urea application by broadcast ( $100 \text{ kg ha}^{-1} \text{ N}$ ) and after lime application to the surface under a continuous no-till. The lime $\times$ gypsum interaction was not significant at  $p < 0.05$ . A regression analysis was conducted using the means of the four gypsum rates and the four replications.



**Figure 4.** Soil pH ( $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ ) at a depth of 0 – 0.05 m in the 2015 and 2017 second-season corn after surface application of lime under a continuous no-till. The lime $\times$ gypsum interaction was not significant at  $p < 0.05$ . A regression analysis conducted using the mean of four gypsum rates and four replications.

### Leaf N content and N uptake

The leaf N content and N uptake in the grain were not significantly influenced by lime or gypsum application (Table 2). Specifically, the leaf N content in the corn presented averages of 32.4 and 30.7  $\text{g kg}^{-1}$  in

2015 and 2017, respectively (Table 4). Meanwhile, in 2017, the corn N uptake was 63% higher than in 2015, increasing, on average, from 60.62 to 98.77 kg ha<sup>-1</sup> (Table 4).

**Table 4.** Leaf N content (Leaf N) and N uptake in grain (N uptake) for the 2015 and 2017 second-season corn after lime and gypsum application to the soil surface under continuous no-till conditions.

Treatment		Leaf N g kg <sup>-1</sup>		N Uptake kg ha <sup>-1</sup>	
		2015	2017	2015	2017
Lime (Mg ha <sup>-1</sup> )	0.0	32.4 ns	30.5 ns	60.5 ns	96.5 ns
	2.6	32.4	30.7	60.5	101.4
	5.4	32.3	30.9	62.6	99.6
	8.1	32.5	30.6	58.9	97.6
Gypsum (Mg ha <sup>-1</sup> )	0.0	31.9	30.6	57.6	99.2
	4.0	32.4	30.6	60.8	98.0
	8.0	32.6	30.9	62.0	99.2
	12	32.7	30.6	62.1	98.7
Means	-	32.4	30.7	60.6	98.8

ns: Lime and gypsum not significant at  $p < 0.05$ .

## Discussion

### Lime enhances N losses via ammonia volatilization in NT

The relative humidity in the first 24h after fertilizer application exceeded the critical relative humidity of urea, which triggers the process of fertilizer dissolution (Skujinš & McLaren, 1971). Fertilizer dissolution provides the conditions necessary for the volatilization process to begin. The sigmoidal behaviour of the increase in cumulative NH<sub>3</sub>-N volatilization (Figure 2) is characterized by an increase in urease enzyme activity (Vale, Sousa, & Scivittaro, 2014), which is influenced by soil moisture. Under dry soil conditions, the hydrolysis rate of urease is low. However, urease activity increases with increasing soil moisture content up to 20% (Sahrawat, 1984). After activating the urease enzyme, it consumes protons by urea hydrolysis and thus increases the soil pH around fertilizer granules up to 8.7, thereby changing the balance between NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> (Rochette et al., 2009).

After reaching the maximum loss point, the NH<sub>3</sub>-N gas flow decreased over time owing to a gradual reduction in pH and N stabilization in the form of N-NH<sub>4</sub><sup>+</sup> (Otto, Zavaschi, Netto, Machado, & De Mira, 2017). Similarly, the linear increase in the NH<sub>3</sub>-N losses of the  $\alpha$  and MDL parameters is the result of the increase in lime dosage (Figure 3 and Table 3), which contributes to the increase in hydroxyls generated by the dissolution of lime, thereby increasing the pH of the soil surface (Figure 4), as corroborated by Caires et al. (2015), and contributing to the formation of NH<sub>3</sub> (Rochette et al., 2009). Therefore, the balance between NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> is controlled by the pH of the medium, favoring the generation of NH<sub>3</sub> gas, which is susceptible to atmospheric loss with increasing pH (Sunderlage & Cook, 2018) (Figures 2 and 3).

Different anthropogenic, edaphic, and climatic characteristics, including application rate (Silva et al., 2017), environmental temperature (Tasca et al., 2011; Watson, Akhonzada, Hamilton, & Matthews, 2008), soil moisture (Holcomb, Sullivan, Horneck, & Clough, 2011), soil pH (Sommer & Ersbøll, 1996; Sunderlage & Cook, 2018; Sha, Li, Lv, Misselbrook, & Liu, 2019), cation exchange capacity, and organic matter content (Rochette et al., 2009; Sunderlage & Cook, 2018), may interfere with N losses via NH<sub>3</sub>-N volatilization. In addition, Ferguson, Kissel, Koelliker, and Basel (1984) and Sunderlage and Cook (2018) showed that the initial soil pH is not a good indicator for predicting NH<sub>3</sub>-N losses, and that, in NT, the pH of the topsoil has a great impact on NH<sub>3</sub>-N loss. This is especially important in NT because the correctives and N fertilizer are applied in the same layer and manner, increasing the pH and thereby favoring NH<sub>3</sub> formation rather than NH<sub>4</sub><sup>+</sup> formation (Sommer & Ersbøll, 1996; Tasca et al., 2011).

Although the NT is considered a global strategy for conservation agriculture, adequate N fertilization management that aims to reduce losses of N is essential, especially after liming. Ammonia losses in the system can reduce crop yield and NUE (Abalos et al., 2014), thereby causing negative economic effects for farmers (Good & Beatty, 2011). Further, when transported over long distances, this ammonia loss can contribute indirectly to greenhouse gas emissions, soil acidification, and biodiversity loss (Behera, Sharma, Aneja, & Balasubramanian, 2013; Liu et al., 2013).

According to the adjusted logistic model, lime or gypsum application had little influence on the curve inflection point, demonstrating that they did not accelerate or delay the urease activity. Although the activity of the urease enzyme is strongly dependent on pH, the treatments did not alter the inflection point, possibly because the pH of the soil was within the range of 4.5 to 10.5, which is considered adequate for urease enzyme activity (Krajewska, 2009). Practices that delay the curve inflection point are necessary to keep urea fertilizer in its amidic form  $\text{CO}(\text{NH}_2)_2$  for a longer period before N can be incorporated into the soil in the cropping systems in order to reduce  $\text{NH}_3\text{-N}$  losses, which is important for NUE (Cancellier et al., 2016). For example, the use of urease inhibitors, such as N-(n-butyl) thiophosphoric triamide (NBPT), may delay the curve inflection point by 3.5 days, reducing the  $\text{NH}_3\text{-N}$  losses by approximately 53% (Cantarella et al., 2018).

### Lime and gypsum effects on the status of N in second-season corn

The N losses that occur via  $\text{NH}_3\text{-N}$  volatilization with the use of lime are expected to decrease the N available in the system and, consequently, the N available to the corn, thereby decreasing the leaf N content and grain N uptake. However, in this study, this phenomenon was not observed. The non-alteration of the N status in the second-season corn can be attributed to the N rate applied during sowing fertilization and in the topdressing. Further, although part of the N was lost by  $\text{NH}_3\text{-N}$  volatilization, the remaining N was sufficient to meet the corn N demand. Cantarella et al. (2018) reported that, in many cases, most N uptake by crops comes from the soil, and N from the fertilizer, although important for determining yields, is only complementary. Moreover, Oliveira et al. (2018), who worked with a NT with  $^{15}\text{N}$ , observed that only 33% of the N absorbed by the corn was provided by the N fertilization performed during crop development. In addition, in this study, the previous crop grown in the corn crop field was soybean, which has the capacity to provide  $70 \text{ kg ha}^{-1} \text{ N}$  to the system (Bender, Haegele, & Below, 2015).

In this study, gypsum application did not contribute to increases in leaf N content and N uptake. Improvements in the nutritional status of N caused by gypsum area generally observed in acidic subsoils (Caires et al., 2016; Tiecher et al., 2018), sodic soils (Murtaza et al., 2016), or in soils with a S deficiency (Salvagiotti & Miralles, 2008), which was not verified in the soil in this study.

Further, Tiecher et al. (2018) presented a systematic review of studies representing approximately 73 growing seasons, revealing that gypsum responses in acidic soil were observed when Al saturation was  $>10\%$  or when the exchangeable Ca content was  $<3.0 \text{ cmol}_c \text{ dm}^{-3}$ . Similarly, the soil in this study showed no problems with excess sodium, and its  $\text{S-SO}_4^{2-}$  content was sufficient to meet the corn S demand. The S contents in the soil were sufficient because, according to Pias, Tiecher, Cherubin, Mazurana, and Bayer (2019), who studied 58 crop harvests in NT,  $\text{S-SO}_4^{2-}$  contents above  $7.5 \text{ mg dm}^{-3}$  (0.00 – 0.20 m) and  $8.5$  (0.20 – 0.40 m) are sufficient for supplying crop S demands.

## Conclusion

In this study, lime was applied by broadcasting to the soil surface in NT. The results showed that lime application increased the pH of the topsoil, thereby increasing N losses via  $\text{NH}_3\text{-N}$  volatilization in second-season corn. Further, N losses through ammonia volatilization under NT conditions represent up to 58% of the applied N, increasing by 2.3 to 2.5% for each ton of lime applied to the soil surface. Overall, lime or gypsum application did not improve the status of N in second-season corn in soils with low acidity without a S deficiency.

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