Ciência Rural, Santa Maria, v.54:05, e20230230, 2024
http://doi.org/10.1590/0103-8478cr20230230
ISSNe 1678-4596
ANIMAL PRODUCTION

Mathematical models for adjustments in the quantification of ammonia volatilization from urea fertilizer applied on tropical pastures

Vanessa Zirondi Longhini[1] **Luís Carlos Vinhas Ítavo**[1] **Antonio Leandro Chaves Gurgel**[2*] **Abmael da Silva Cardoso**[3] **Robert Michael Boddey**[4] **Gelson dos Santos Difante**[1] **Alexandre Menezes Dias**[1] **Camila Celeste Brandão Ferreira Ítavo**[1] **Gabriel de Souza Lombardi da Silva**[1] **Ana Claudia Ruggieri**[5]

[1]Universidade Federal do Mato Grosso do Sul (UFMS), Campo Grande, MS, Brasil.
[2]Universidade Federal do Piauí (UFPI), Campus Professora Cinobelina Elvas, 64900-000, Bom Jesus, PI, Brasil. E-mail: antonio.gurgel@ufpi.edu.br.
[*]Corresponding author.
[3]Range Cattle Research and Education Center, University of Florida, Ona, USA.
[4]Embrapa Agrobiologia, Seropédica, RJ, Brasil.
[5]Departamento de Zootecnia, Universidade Estadual de São Paulo (Unesp), Jaboticabal, SP, Brasil.

ABSTRACT: In Brazil, urea is the most used nitrogen (N) fertilizer to improve forage production. However, their excessive use can cause environmental impacts through N losses, such as ammonia (NH_3) volatilization. Therefore, the current study adjusted and estimated the NH_3 volatilization from urea applied on tropical pastures in three rainfall conditions using mathematical models. Data were collected from Marandu grass (*Brachiaria brizantha*) fertilized with 50 kg N ha^{-1} during wet, intermediate, and dry conditions. Ammonia volatilization was measured in five semi-open chambers for 21 days. The linear, quadratic, exponential, Gompertz, Groot, and Richards models were tested for fitting and estimating the NH_3 volatilization. The Gompertz, Groot, and Richards models generated predictions similar to the observed data, with a high determination coefficient, indicating a better fit of these equations to data, with precision and accuracy. However, the Groot model was selected due to the lowest root mean square error of prediction (0.29 % total N lost as NH_3). The greatest N loss as NH_3 volatilization occurred in the wet, followed by intermediate and dry conditions (20.2, 17.0, and 11.3 % total N lost as NH_3, respectively). Therefore, nitrogen losses as NH_3 volatilization after application of 50 kg N ha^{-1}, as urea source, are altered according to the weather conditions, reaching 20% of N added in the wet rainfall period. The Groot model is recommended for fitting and estimating the NH_3 volatilization from urea applied on Marandu grass pastures in the wet and dry rainfall conditions.
Key words: ammonia volatilization, marandu grass, mathematical model, synthetic fertilizer, tropical pasture, urea.

Modelos matemáticos para ajustes na quantificação da volatilização de amônia do fertilizante ureia aplicado em pastagens tropicais

RESUMO: No Brasil, a ureia é o fertilizante nitrogenado mais utilizado para melhorar a produção de forragem. No entanto, seu uso excessivo pode causar impactos ambientais por meio de perdas de nitrogênio (N), como a volatilização da amônia (NH_3). Portanto, o objetivo do presente estudo foi ajustar a volatilização de NH_3 da ureia aplicada em pastos tropicais em três condições de chuva utilizando modelos matemáticos. Dados foram coletados de pastos de capim-marandu (*Brachiaria brizantha*) adubado com 50 kg N ha^{-1} em condições úmidas, intermediárias e secas. A volatilização da NH_3 foi medida em cinco câmaras semiabertas durante 21 dias. Os modelos, linear, quadrático, exponencial, Gompertz, Groot e Richards foram testados para ajuste e estimativa da volatilização do NH_3. Os modelos de Gompertz, Groot e Richards geraram predições semelhantes aos dados observados, com alto coeficiente de determinação, indicando um melhor ajuste dessas equações aos dados, com acurácia e precisão. No entanto, o modelo Groot foi selecionado devido ao menor erro quadrático médio das predições (0,29% de N total perdido como NH_3). A maior volatilização de NH_3 ocorreu em condições climáticas úmida, seguido por intermediária e seca (20,2; 17,0 e 11,3% de N total perdido como NH_3, respectivamente). Portanto, as perdas de N como volatilização de NH_3 após a aplicação de 50 kg N ha^{-1}, como fonte de ureia, são alteradas de acordo com as condições climáticas, atingindo a 20% do N adicionado nas condições úmidas. O modelo Groot é recomendado para ajuste e estimativa da volatilização de NH_3 da ureia aplicada em pastos de capim Marandu em condições úmidas e secas.
Palavras-chave: adubação sintética, capim-marandu, modelo matemático, pastagem tropical, ureia, volatilização de amônia.

INTRODUCTION

In Brazil, around 163.1 million ha are used for grassland, supporting about 196.5 million cattle (ABIEC, 2022). Approximately 90 million ha of this area belongs to the genus *Brachiaria*, where the cultivar Marandu occupies more than 50% (JANK et al., 2014). In grassland systems, nitrogen (N) fertilizer plays a vital role in increasing forage productivity (DELEVATTI et al., 2019). In Brazil, urea is the most used fertilizer because its cost per kilogram is lower than other N fertilizers (GURGEL

Received 04.27.23 Approved 08.30.23 Returned by the author 10.30.23
CR-2023-0230.R1
Editors: Leandro Souza da Silva Alberto Cargnelutti Filho

et al., 2020). SALES et al. (2019) reported that N fertilization doses between 50 to 75 kg N ha^{-1} $cycle^{-1}$ in marandu grass pastures result in greater production and forage accumulation than doses of 25 and 100 kg N ha^{-1} $cycle^{-1}$.

Nitrogen fertilizer over the recommended dose can lead to ammonia (NH_3) losses (ZAMAN et al., 2009). The NH_3 is an important atmospheric pollutant responsible for cause negative environmental impacts (BEUSEN et al., 2008). Furthermore, N applied from urea fertilizer may be lost more than 50% as NH_3 volatilized to the environment (MORAIS et al., 2013; ROCHETTE et al., 2009). It is estimated that N global annual losses from synthetic N fertilizers are around 17 million tons (XU et al., 2019).

The Intergovernmental Panel on Climate Change (IPCC) suggests a default NH_3 emission factor of 15% of applied N (uncertainty range, 3–43%) for urea fertilizer for national greenhouse gas inventory methodology (IPCC, 2019). However, these large variations in the rate of NH_3 volatilization from urea are explained by several factors, like changes in weather conditions, such as air temperature and rainfall amount (BURCHILL et al., 2017; ENGEL et al., 2011; SANZ-COBENA et al., 2011; SIMAN et al., 2020), strong wind and moisture (NUNES et al., 2023), soil pH, application rate and placement depth (ROCHETTE et al., 2013). CORRÊA et al. (2021) using urea fertilization at a rate of 270 kg N ha^{-1} in Marandu grass, reported 44.5% of N applied lost as NH_3 in a single dose; however, when it was divided into three applications, there was a reduction to 24.1% of N applied lost as NH_3. For this reason, the NH_3 volatilization assessment from different weather conditions plays an important role in providing country-specific emissions data for agriculture inventory calculation.

Mathematical models have been used in several research areas. In the Agricultural Science, they have been used, for example, to adjust the kinetics of *in vitro* cumulative gas production (GURGEL et al., 2021a; ZORNITTA et al., 2021), in animal growth curve (GURGEL et al., 2021b; SOUZA et al., 2022), and in bacterial growth curve (ZWIETERING et al., 1990). According to HAN et al. (2022) there were several empirical models to estimate NH_3 volatilization. However, these models need to be able to describe this process with sufficient precision and accuracy. Therefore, this study compared mathematical models to adjust and estimate the NH_3 volatilization from urea fertilizer applied on tropical pastures in wet, intermediate, and dry rainfall conditions.

MATERIALS AND METHODS

This study used a dataset from LONGHINI et al. (2020), ninety data were collected from pastures of *Brachiaria brizantha* cv. Marandu fertilized with 50 kg N ha^{-1} during wet (3 May 2017), intermediate (4 April 2018), and dry (8 June 2018) rainfall conditions, using urea as a fertilizer. The study was carried out at Sao Paulo State University, Jaboticabal, Sao Paulo, Brazil (21°14′20″ S, 48°17′27″ W; 583 m a.s.l.). The total annual rainfall in this area is 1,424 mm and mean annual air temperature is 22.3°C. Daily rainfall, air temperature (maximum, average, and minimum), and relative humidity were obtained from the Agrometeorological Station, Department of Exact Sciences, UNESP, Jaboticabal Campus, located at 700 m from the experimental site (Figure 1 and 2). Soil samples (0–20-cm depth) were as follows: pH ($CaCl_2$) 5.3; organic matter 32.4 g kg^{-1}; cation exchange capacity 74.8 $mmol_c$ dm^{-3}; P (ion-exchange resin extraction method) 10.9 mg dm^{-3}; Mehlich-1 extractable Ca 28.3 $mmol_c$ dm^{-3}; Mehlich-1 extractable Mg 9.7 $mmol_c$ dm^{-3}; Mehlich-1 extractable K 4.2 $mmol_c$ dm^{-3}; base saturation 561 g kg^{-1}, respectively (LONGHINI et al., 2020). Soil texture was 340 g kg^{-1} sand, 140 g kg^{-1} silt, and 520 g kg^{-1} clay (LONGHINI et al., 2020).

The field NH_3 volatilization was measured in Marandu grass pasture (1,200 m^2), seeded in 2014. The area had not been grazed or treated with N (urea fertilizer or animal excreta) during the previous 2 yr. The experiment was a randomized complete block design, with five replicates. Treatments were urea fertilizer (50 kg N ha^{-1}) and control without fertilizer (0 kg N ha^{-1}). The evaluations were replicated three times during different natural rainfall conditions, which were classified as wet, intermediate, and dry (Table 1).

A semi-open chamber (0.008 m²) was used to quantify NH_3 volatilization from urea (ARAUJO et al., 2009). The methodological description and validation of these chambers using the ^{15}N technique were reported in the studies of ARAUJO et al. (2009), in Brazil and JANTALIA et al. (2012) in the United States. Urea fertilizer was applied by hand at a rate of 50 kg N ha^{-1} (2.67 g of urea $plot^{-1}$). Each plot measured 0.4 m × 0.6 m (0.24 m^2), totaling 10 plots per replication (rainfall conditions). Before of the experimental period, Marandu grass was cut at a height of 10 cm. Ammonia volatilization was monitored for 21 d after urea application on the Marandu grass. After urea application, the foam strips were changed for new strips 1, 3, 5, 9, 14, and 21 d. Ammonia volatilization for treatment in each sampling interval was calculated following Equation described by LONGHINI et al. (2020):

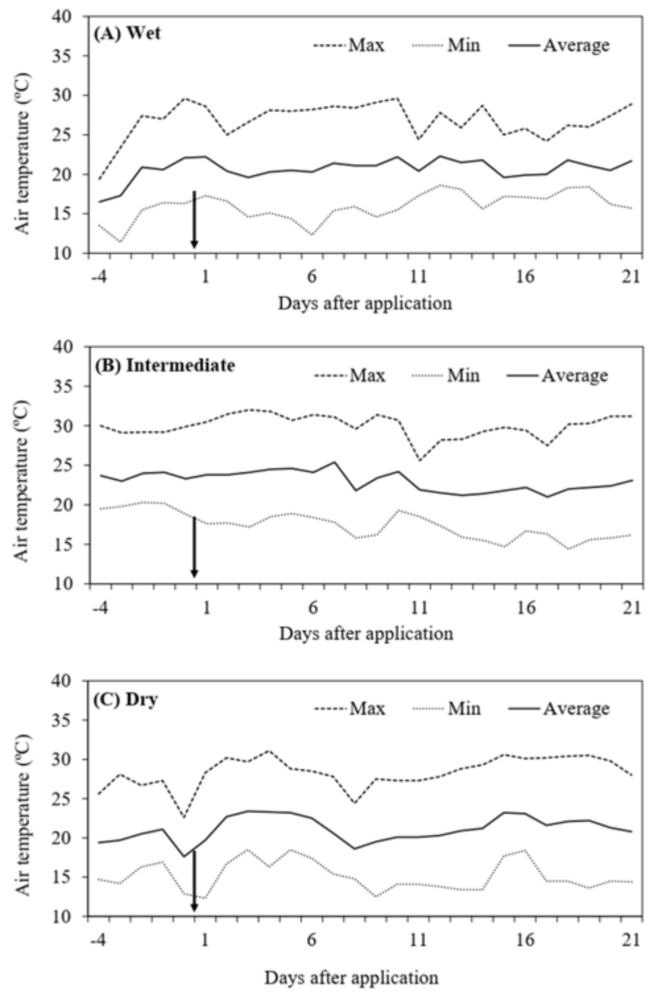

Figure 1 - Daily air temperature (minimum, average, and maximum) for each experimental period. Data from Agrometeorological Station, Department of Exact Sciences, UNESP, Jaboticabal, located 700 m from the experiment site. Arrow indicates the urea application day (day 0).

$$\textit{Ammonia volatilization (\%)} = [NH_{3\,(urea)} - NH_{3\,(control)}]/N_{(applied)}$$

Where: $NH_{3(urea)}$ is the amount of N applied lost as NH_3 for the urea fertilizer treatment; $NH_{3(control)}$ is the amount of N from air + soil + Marandu grass without N addition lost as NH_3 for the control treatment; and $N_{(applied)}$ is the amount of N applied in the area covered by the chamber (kg N ha^{-1}). Cumulative NH_3 volatilization (% total N lost as NH_3) was calculated for the rainfall condition by summing the amounts of NH_3 volatilized in each sampling interval (0–1, 1–3, 3–5, 5–9, 9–14, and 14–21 d). More details are described in LONGHINI et al. (2020).

The linear, quadratic, exponential, Gompertz, Groot, and Richards models were tested to fitting the cumulative NH_3 volatilization in 21 d (Table 2). The sigmoidal model Gompertz was described by SCHOFIELD et al. (1994). GROOT et al. (1996) and RICHARDS (1959) described the sigmoidal model's equations. The parameters of the equations are defined as: $V(t)$ is the cumulative NH_3 volatilization in time t (% total N lost as NH_3); The parameter A is the volume of gases derived from the volatilization of NH_3 when $t \rightarrow \infty$; The parameter t is the time (days), and e is exponential; In the linear, quadratic, exponential, Gompertz, and Richards models, the parameter b represents interaction constant; in the Groot model, it is the time after urea application at which half of the asymptotic level was reached (days); In

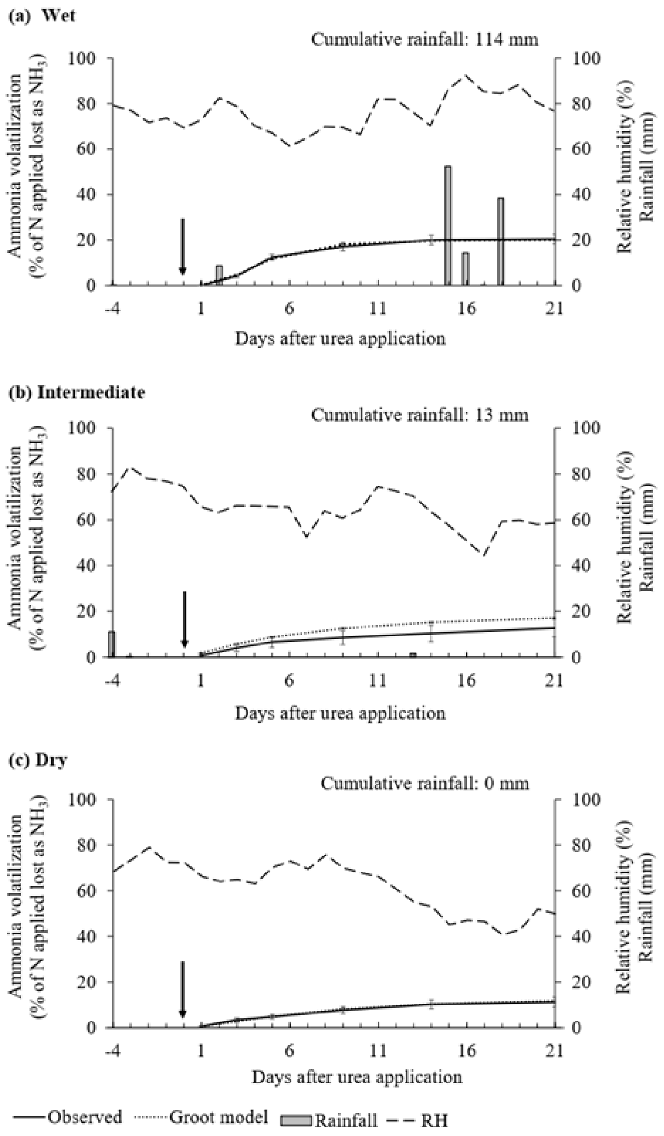

Figure 2 - Daily rainfall, air relative humidity (RH) and curves of cumulative ammonia volatilization from urea fertilizer applied on the Marandu grass pastures in three rainfall conditions fitted in the Groot model. Arrow indicates the urea application day (day 0).

the Gompertz and Richards models, parameter *k* represents the fractional rate of gas production (% h^{-1}); in the Groot model, it is an integration constant that determines the sharpness of the curve. In the Richards model, the parameter *M* is a shape parameter. The variables obtained from the chosen model, time of curve inflection (Ti), time at which volatilization rate is maximum (Trmax), and maximum fractional rate of volatilization in the Trmax (Rmax) were calculated as described in GROOT et al. (1996).

A descriptive statistical analysis was performed using the PROC SUMMARY procedure in SAS (SAS University Edition, SAS Institute Inc. Cary, CA, USA). Pearson correlation coefficients between variables were estimated using the PROC CORR procedure in SAS. Model adjustments and variable selection were performed using PROC REG in SAS. The STEPWISE option and Mallow's Cp were used to select the variables included in the equations. Outliers were tested by evaluating the studentized residuals

Table 1 - Summary of weather conditions during each experimental period.

	----------------Rainfall condition--------------		
	Wet	Intermediate	Dry
Mean air temperature (°C)	21	23	21
Mean relative humidity (%)	76	62	60
Cumulative rainfall 4 d before the experimental period	0.2	11.3	0.0
Cumulative rainfall (mm)	113.4	1.7	0.0
Rain days	5	1	0
Initial volumetric soil moisture (%)	30	29	21

in relation to the values predicted by the equations. Residues that fell outside the range of -2.5 to 2.5 were removed. The goodness of fit of the developed equations was evaluated by the coefficients of determination (R^2) and root mean square error (RMSE).

The data estimated by the equations that obtained the best adjustments were compared with the real values, using the regression model: Y = β0 + β1 × X, where Y was the observed value; β0 and β1 represent the intercept and slope of the regression equation, respectively; and X was the value predicted by the equations. The criteria for assessing the adequacy of the equations were: the coefficient of determination (R^2); F test, for the identity of the parameters (β0 = 0 and β1 = 1) of the regression of the predicted data by the observed ones. In addition, the Model Evaluation System version 3.2.2 program was used to estimate the coefficient of correlation and concordance (CCC); the square root of the mean square of the prediction error (RMSPE); and the decomposition of the mean square of the prediction error (MSPE) into mean error, systematic bias, and random error (TEDESCHI, 2006). The significance level was 5% probability in all statistical analyses.

The variables Ti, Trmax, and Rmax were subjected to analysis of variance by the PROC GLM of the SAS statistical package. The means were compared using Tukey's test. Differences were considered significant at $P \leq 0.05$.

RESULTS

The Gompertz, Groot, and Richards models showed average cumulative NH_3 volatilization estimates and standard deviation close to the observed data as well as high determination coefficients (above 98%) of the regression of predicted on observed data (Table 3). The NH_3 volatilization average observed was 8.63% of N applied lost as NH_3. Overall, all models presented predictions similar to the observed data (β0 = 0 and β1 = 1), except for the quadratic model, which was different from the data ($P \leq 0.05$).

The cumulative NH_3 volatilization curves from urea applied on the Marandu grass pasture in

Table 2 - Nonlinear models and equations considered in this study to describe the ammonia volatilization from urea fertilizer applied on the Marandu grass pastures in three rainfall conditions.

Models	Equation[1]		Parameters[2]
Linear	$V(t) = A + b.t$	(2)	2 (A, b)
Quadratic	$V(t) = A + b.t + k.t^2$	(3)	3 (A, b, k)
Exponential	$V(t) = A.e^{(b.t)}$	(4)	2 (A, b)
Gompertz	$V(t) = A.e(-b.e^{(-k.t)})$	(5)	3 (A, b, k)
Groot	$V(t) = A/(1 + (b^k/t^k))$	(6)	3 (A, b, k)
Richards	$V(t) = A.(1-b.e^{(-k.t)})^M$	(7)	4 (A, b, k, M)

[1]*V(t)* is the cumulative NH_3 volatilization in time t (% total N lost as NH_3); [2] The parameter *A* is the volume of gases derived from the NH_3 volatilization when $t \rightarrow \infty$; *t* is the time (days); e is exponential; In the linear, quadratic, exponential, Gompertz, and Richards models, the parameter *b* represents interaction constant; in the Groot model, *b* it is the time after urea application at which half of the asymptotic level was reached (days); In the Gompertz and Richards models, parameter *k* represents the fractional rate of gas production (% h^{-1}); in the Groot model, it is an integration constant that determines the sharpness of the curve. In the Richards model, the parameter *M* is a shape parameter.

Table 3 - Evaluation of the models fitting to estimate the ammonia volatilization from urea fertilizer applied on the Marandu grass pastures in three rainfall conditions.

Model	Mean	SD	R^2	P-value	CCC	RMSEP	-------------Decomposition of MSEP (%)----------		
							ME	SB	RE
Observed data	8.63	5.63	-	-	-	-	-	-	-
Linear	8.60	5.21	0.92	0.99	0.92	2.02	0.02	0.02	99.96
Quadratic	9.76	6.89	0.98	0.05	0.95	1.91	35.11	41.96	22.96
Exponential	8.86	4.43	0.85	0.96	0.82	2.75	0.73	1.21	98.01
Gompertz	8.72	5.47	0.99	0.87	0.99	0.58	2.76	3.84	93.36
Groot	8.66	5.54	0.99	0.86	0.99	0.29	1.48	5.83	92.70
Richards	8.53	5.60	0.99	0.82	0.99	0.31	8.94	0.23	90.82

SD: standard deviation; R^2: coefficient of determination; P-value: probability value associated with the simultaneous F-test for the identity of parameters ($\beta 0 = 0$ and $\beta 1 = 1$) of the regression of observed vs. predicted data; CCC: concordance correlation coefficient; RMSEP: root mean square error of prediction; MSEP: mean square error of prediction. ME: mean error; SB: systematic bias; RE: random error.

three rainfall conditions (wet, intermediate, and dry), projected from the parameters estimated by each model, are shown in figure 3. The evaluation of models fitting the criteria presented means close to the observed data; although, standard deviations were lower when fitted into models (Table 3). The Gompertz, Groot, and Richards models presented the higher R^2 indicating a better fit of these equations to the NH_3 volatilization data. In addition, the CCC presented the same pattern as R^2, with the Gompertz, Groot, and Richards models closer to the ideal coefficient than other models, reflecting precision and accuracy (Tables 3, 4 and Figure 3). Finally, the Groot model ($V(t) = 15.79/(1 + (5.29^{1.85}/t^{1.85}))$) was considering the best to fitting NH_3 volatilization from urea fertilizer applied on tropical pastures in the wet, intermediate, and dry rainfall conditions, because showed the smaller root mean square error of prediction (RMSEP) (Table 3).

There was an adjustment between predicted and observed curves of cumulative NH_3 volatilization for the Groot model (Figure 2), except for the intermediate rainfall conditions, in which the Groot model overestimated the NH_3 volatilization of the intermediate rainfall conditions (Figure 2B). Across rainfall conditions, the urea fertilizer applied in the wet

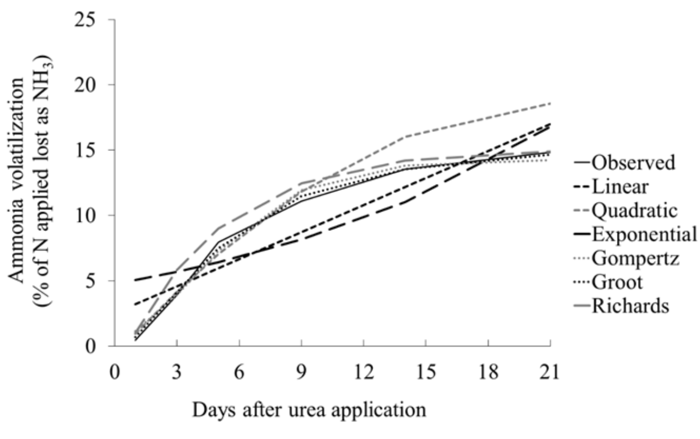

Figure 3 - Cumulative production curves of ammonia volatilization from urea fertilizer applied on the Marandu grass pastures in three rainfall conditions (wet, intermediate, and dry), projected from the parameters estimated by each model.

Table 4 - Models parameters to estimate the ammonia volatilization from urea fertilizer applied on the Marandu grass pastures in three rainfall conditions.

Model	A ± SD	*b* ± SD	k ± SD	M ± SD	N	R^2	RMSE	P-value
Linear	2.50 ± 0.96	0.69 ± 0.08	-	-	90.0	0.42	5.62	<0.0001
Quadratic	- 0.77 ± 1.33	1.76 ± 0.33	- 0.04 ± 0.01	-	90.0	0.49	5.30	<0.0001
Exponential	4.76 ± 0.74	0.06 ± 0.00	-	-	90.0	0.73	5.93	<0.0001
Gompertz	14.29 ± 1.34	3.50 ± 1.40	0.33 ± 0.11	-	90.0	0.79	5.30	<0.0001
Groot	15.79 ± 2.53	5.29 ± 1.40	1.85 ± 0.71	-	90.0	0.79	5.28	<0.0001
Richards	15.12 ± 2.04	1.15 ± 0.20	0.18 ± 0.14	1.16 ± 1.03	90.0	0.78	5.31	<0.0001

A is the volume of gases derived from the NH_3 volatilization when $t\rightarrow\infty$; In the linear, quadratic, exponential, Gompertz, and Richards models, the parameter *b* represents interaction constant; in the Groot model, *b* it is the time after urea application at which half of the asymptotic level was reached (days); In the Gompertz and Richards models, parameter *k* represents the fractional rate of gas production (% h^{-1}); in the Groot model, it is an integration constant that determines the sharpness of the curve. In the Richards model, the parameter *M* is a shape parameter; SD is the standard deviation; N is the number of observations; R^2 is the coefficient of determination; RMSE: root mean squared error.

presented greater NH_3 volatilization (20.2% of N lost as NH_3), followed by intermediate (17.0% of N lost as NH_3) and the smallest in the dry (11.3% of N lost as NH_3) (Table 5; $P \leq 0.05$). In wet rainfall condition, the NH_3 volatilization maximum fractional rate in tropical pastures fertilized with 50 kg of N ha^{-1} using urea was greater, reaching up to 36% of N added in the pasture area, on the day where the loss was maximum. Overall, the NH_3 volatilization maximum peak occurred 4.58 d after the urea application on the Marandu grass.

DISCUSSION

The linear models did not adjust the parameters appropriately for the evaluation periods. Because there were increases in the NH_3 volatilization in the first days after the urea application, which was followed by an inflection curve due to the reduction of the availability of N in the soil until it reached a plateau (Figure 3). For this reason, nonlinear models, which has a sigmoidal function, were the best for fitting NH_3 volatilization from urea fertilizer applied on tropical pastures, and they showed satisfactory precision and accuracy. Previous studies have recommended the Groot model to adjust the pattern of the phenomena biological as a time function (GURGEL et al., 2021a; ZORNITTA et al., 2021). This model does not assume a constant fractional rate, as occurs in the Richards and Gompertz model, simulating a real pattern of the NH_3 volatilization, which provided a more accurate adjustment to the phenomena that exist in the environmental conditions

Table 5 - Parameters and variables obtained by the Groot model to estimate the ammonia volatilization from urea fertilizer applied on the Marandu grass pastures in three rainfall conditions.

	---------------Rainfall conditions[1]---------------			SEM	P-value
	Wet	Intermediate	Dry		
A	20.4 a	21.2 a	13.7 b	0.240	0.0410
b	4.49	6.64	7.04	0.013	0.0569
k	3.02 a	1.25 b	1.66 b	0.067	0.0003
Cumulative NH_3 volatilization (% total N loss as NH_3)	20.2 a	17.0 ab	11.3 b	0.243	0.0311
Ti (days)	3.57	1.78	2.72	0.175	0.0960
TR max (days)	5.66	3.28	4.79	0.218	0.1666
R max (%)	36 a	13 b	15 b	0.025	0.0001

[1]Means followed by different letters differ statistically by Tukey's test at 5% significance.
A is the volume of gases derived from the NH_3 volatilization when $t\rightarrow\infty$; *b* is the time after urea application at which half of the asymptotic level was reached (days); *k* is an integration constant that determines the sharpness of the curve.
Variables obtained from the parameters: Ti (d): time of curve inflection; TRmax (d): time at which volatilization rate is maximum; Rmax: maximum fractional rate of volatilization in the TRmax (%).

(GURGEL et al., 2021a). The authors also explained that the Groot model uses three parameters in the equation, resulting in greater degrees of freedom.

Changes in weather conditions are the most responsible for the variations in NH_3 volatilization (BURCHILL et al., 2017; SIMAN et al., 2020). Previous studies have shown that the peak of NH_3 volatilization occurs 1-3 d after urea application on wet soils (NUNES et al., 2023; RECH et al., 2017; TURNER et al., 2012). Ideal weather conditions such as strong wind and high soil temperature and moisture are responsible for fast urea hydrolysis (NUNES et al., 2023). Coversely,, in drier soil, TURNER et al. (2012) reported that the NH_3 volatilization peak did not occur until the 6-7 d after urea was applied, while in another experiment, the peak occurred at 4 d affected by a rainfall that occurred at 2 d. On this occasion, there is a lack of moisture or water to dissolve the urea granules, delaying the occurrence of the NH_3 volatilization peak. In our study, the maximum NH_3 volatilization rate was attended at 4.58 d (ranging from 3.28 – 5.66 d) after the urea application, regardless of the rainfall conditions.

Although, the peak of NH_3 volatilization from urea was the same between rainfall conditions, the maximum N fractional rate of NH_3 volatilization in the wet conditions was almost three times that in the intermediate and dry rainfall conditions. This pattern resulted in different intensities in the total N lost as NH_3 volatilization. The greatest cumulative NH_3 volatilization occurred in the wet condition, favored for the rain that fell at 2 d after the urea application (Figure 2A). The amount of rain was low (8.6 mm); however, it was enough to elevate the soil moisture and relative air humidity (above 76%). Urea fertilizer is hygroscopic and absorbs the moisture, resulting in urea hydrolysis and high N losses as NH_3 volatilization (KROL et al., 2020). Conversely,, if the high intensities of rainfall at the end of the evaluation had occurred after urea application, the NH_3 volatilization could reduce due to the incorporation of the urea (LIU et al., 2020). For this reason, to avoid NH_3 volatilization during the rainy season, the urea fertilizer should be applied in dry soil followed by rain or irrigation to allow the N infiltration into the soil. Nonetheless, high rainfall intensity in a short time can increase the NH_3 volatilization due to the soil flood and urea exposition to the environment; this high amount of water can saturate the soil porosity and difficult the urea infiltration (JIANG et al., 2023).

This study showed that the NH_3 volatilization had a different pattern according to the soil moisture and amount of rainfall during the urea application on the Marandu grass. The best Groot model adjustment for evaluating the urea fertilizer means that there was an understanding of how the pattern of NH_3 volatilization occurs. However, despite the good fit, none of the models studied adjusted to data in the intermediate rainfall conditions, which overestimated the NH_3 volatilization. For this reason, other models should be applied better to understand the NH_3 volatilization pattern in these rainfall conditions.

CONCLUSION

Nitrogen losses as NH_3 volatilization can reach 20% using urea at the dose of 50 kg N ha^{-1} in wet rainfall conditions, which was greater than the same rate applied in intermediate and dry rainfall conditions. The Groot model showed satisfactory precision and accuracy to adjust and estimate the NH_3 volatilization from urea fertilizer applied on tropical pastures in wet and dry rainfall conditions.

ACKNOWLEDGMENTS

The authors would like to thank the Universidade Federal do Mato Grosso do Sul (UFMS); Universidade Estadual Paulista (UNESP); This research was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, grant 404169/2013-9), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES under Grant Financing Code 001), the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, grants 2016/11086-1 2017/11274-5), and a grant state scientist from the Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ).

DECLARATION OF CONFLICT OF INTEREST

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

AUTHORS' CONTRIBUTIONS

All authors contributed equally for the conception and writing of the manuscript. All authors critically revised the manuscript and approved of the final version.

REFERENCES

ARAUJO, E. S. et al. Calibration of a semi-opened static chamber for the quantification of volatilized ammonia from soil. **Pesquisa Agropecuária Brasileira**, v.44, n.7, p.769–776, 2009. Available from: <https://doi.org/10.1590/S0100-204X2009000700018>. Accessed: Apr. 27, 2023. doi: 10.1590/S0100-204X2009000700018.

ASSOCIAÇÃO BRASILEIRA DAS INDÚSTRIAS EXPORTADORAS DE CARNES – ABIEC. **Beef Report**: Perfil da Pecuária no Brasil. São Paulo, 2020. Available from: <https://www.abiec.com.br/publicacoes/beef-report-2022/>. Accessed: Aug. 04, 2023.

BEUSEN, A. H. W. et al. Bottom-up uncertainty estimates of global ammonia emissions from global agricultural production systems. **Atmospheric Environment**, v.42, n.24, p.6067–6077, 2008. Available from: <http://dx.doi.org/10.1016/j.atmosenv.2008.03.044>. Accessed: Apr. 27, 2023. doi: 10.1016/j.atmosenv.2008.03.044.

BURCHILL, W. et al. Ammonia emissions from urine patches amended with N stabilized fertilizer formulations. **Nutrient Cycling in Agroecosystems**, v.108, n.1, p.163–175, 2017. Available from: <https://doi.org/10.1007/s10705-017-9847-9>. Accessed: Apr. 27, 2023. doi: 10.1007/s10705-017-9847-9.

CORRÊA, D. C. C. et al. Ammonia volatilization, forage accumulation, and nutritive value of marandu palisade grass pastures in different n sources and doses. **Atmosphere**, v.12, p.1179, 2021. Available from: <https://doi.org/10.3390/atmos12091179>. Accessed: Jul. 12, 2023. doi: 10.3390/atmos12091179.

DELEVATTI, L. M. et al. Effect of nitrogen application rate on yield, forage quality, and animal performance in a tropical pasture. **Scientific Reports**, v.9, p.e7596, 2019. Available from: <https://doi.org/10.1038/s41598-019-44138-x>. Accessed: Apr. 27, 2023. doi: 10.1038/s41598-019-44138-x.

ENGEL, R. et al. Ammonia volatilization from urea and mitigation by NBPT following surface application to cold soils. **Soil Science Society of America Journal**, v.75, n.1, p.2348–2357, 2011. Available from: <https://doi.org/10.2136/sssaj2011.0229>. Accessed: Apr. 27, 2023. doi: 10.2136/sssaj2011.0229.

GROOT, J. C. J. et al. Multiphasic analysis of gas production kinetics for in vitro fermentation of ruminant feeds. **Animal Feed Science and Technology**, v.64, n.1, p.77–89, 1996. Available from: <https://doi.org/10.1016/S0377-8401(96)01012-7>. Accessed: Apr. 27, 2023. doi: 10.1016/S0377-8401(96)01012-7.

GURGEL, A. L. C. et al. Evaluation of mathematical models to describe lamb growth during the pre-weaning phase. **Semina: Ciências Agrárias**, v.42, n.3, p.2073-2080, 2021b. Available from: <https://doi.org/10.5433/1679-0359.2021v42n3Supl1p2073>. Accessed: Apr. 27, 2023. doi: 10.1590/0103-8478cr20200993.

GURGEL, A. L. C. et al. Mathematical models to adjust the parameters of *in vitro* cumulative gas production of diets containing preserved Gliricidia. **Ciência Rural**, v.51, n.11, p.e20200993, 2021a. Available from: <https://doi.org/10.1590/0103-8478cr20200993>. Accessed: Apr. 27, 2023. doi: 10.1590/0103-8478cr20200993.

GURGEL, A. L. C. et al. Nitrogen fertilization in tropical pastures: what are the impacts of this practice?. **Australian Journal of Crop Science**, v.14, n.6, p.978-984, 2020. Available from: <https://doi.org/10.21475/ajcs.20.14.06.p2357>. Accessed: Apr. 27, 2023. doi: 10.21475/ajcs.20.14.06.p2357.

HAN, H. et al. A semi-empirical semi-process model of ammonia volatilization from paddy fields under different irrigation modes and urea application regimes. **Agricultural Water Management**, v. 272, p. e107841, 2022. Available from: <https://doi.org/10.1016/j.agwat.2022.107841>. Accessed: Apr. 27, 2023. doi: 10.1016/j.agwat.2022.107841.

INTERGOVERNMENTAL PANEL ON CLIMATE CHANGE – IPCC. **Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories**, 2019. Available from: <https://www.ipcc-nggip.iges.or.jp/public/2019rf/index.html>. Accessed: Feb. 24, 2023.

JANK, L. et al. The value of improved pastures to Brazilian beef production. **Crop and Pasture Science**, v.65, n.11, p.1132-1137, 2014. Available from: <https://doi.org/10.1071/CP13319>. Accessed: Aug. 04, 2023. doi: 10.1071/CP13319.

JANTALIA, C. P. et al. Nitrogen source effects on ammonia volatilization as measured with semi-static chambers. **Agronomy Journal**, v.104, n.6, p.1595–1603, 2012. Available from: <https://doi.org/10.2134/agronj2012.0210>. Accessed: Apr. 27, 2023. doi: 10.2134/agronj2012.0210.

JIANG, R. et al. Modelling the impacts of inhibitors and fertilizer placement on maize yield and ammonia, nitrous oxide and nitrate leaching losses in southwestern Ontario, Canada. **Journal of Cleaner Production**, v.384, p.135511, 2023. Available from: <https://doi.org/10.1016/j.jclepro.2022.135511>. Accessed: Apr. 27, 2023. doi: 10.1016/j.jclepro.2022.135511.

KROL, D. J. et al. Nitrogen fertilisers with urease inhibitors reduce nitrous oxide and ammonia losses, while retaining yield in temperate grassland. **Science of the Total Environment**, v.725, p. e138329, 2020. Available from: <https://doi.org/10.1016/j.scitotenv.2020.138329>. Accessed: Apr. 27, 2023. doi: 10.1016/j.scitotenv.2020.138329.

LIU, X. et al. Comparing ammonia volatilization between conventional and slow-release nitrogen fertilizers in paddy fields in the Taihu Lake region. **Environmental Science and Pollution Research**, v.27, n.1, p.8386–8394, 2020. Available from: <https://doi.org/10.1007/s11356-019-07536-2>. Accessed: Apr. 27, 2023. doi: 10.1007/s11356-019-07536-2.

LONGHINI, V. Z. et al. Nitrogen supply and rainfall affect ammonia emissions from dairy cattle excreta and urea applied on warm-climate pastures. **Journal of Environmental Quality**, v.49, n.1, p.1453–1466, 2020. Available from: <https://doi.org/10.1002/jeq2.20167>. Accessed: Apr. 27, 2023. doi: 10.1007/s11356-019-07536-2.

MORAIS, R. F. et al. Ammonia volatilization and nitrous oxide emissions during soil preparation and N fertilization of elephant grass (*Pennisetum purpureum* Schum.). **Soil Biology and Biochemistry**, v.64, n. 10, p. 80–88, 2013. Available from: <https://doi.org/10.1016/j.soilbio.2013.04.007>. Accessed: Apr. 27, 2023. doi: 10.1007/s11356-019-07536-2.

NUNES, R. S. G. et al. Mitigation of ammonia and greenhouse gases emissions from urea coated with oil shale residues in a silvopastoral system. **Journal of Environmental Management**, v.326, p.e116779, 2023. Available from: <https://doi.org/10.1016/j.jenvman.2022.116779>. Accessed: Apr. 27, 2023. doi: 10.1016/j.jenvman.2022.116779.

RECH, I. et al. Additives incorporated into urea to reduce nitrogen losses after application to the soil. **Pesquisa Agropecuária Brasileira**, v.52, n.3, p.194-204, 2017. Available from: <https://doi.org/10.1590/S0100-204X2017000300007>. Accessed: Apr. 27, 2023. doi: 10.1590/S0100-204X2017000300007.

RICHARDS, F. J. A flexible growth function for empirical use. **Journal of Experimental Botany**, v.10, n.29, p.290–300, 1959. Available from: <https://www.jstor.org/stable/23686557>. Accessed: Apr. 27, 2023.

ROCHETTE, P. et al. Reducing ammonia volatilization in a no-till soil by incorporating urea and pig slurry in shallow bands. **Nutrient Cycling in Agroecosystems**, v.84, n.1, p.71–80, 2009.

Available from: <http://dx.doi.org/10.1007/s10705-008-9227-6>. Accessed: Apr. 27, 2023. doi: 10.1007/s10705-008-9227-6.

ROCHETTE, P. et al. NH_3 volatilization, soil concentration and soil pH following subsurface banding of urea at increasing rates. **Canadian Journal of Soil Science**, v.93, p.261-268, 2013. Available from: <https://doi.org/10.4141/cjss2012-095>. Accessed: Jul. 12, 2023. doi: 10.4141/cjss2012-095.

SALES, K. C. et al. What is the maximum nitrogen in marandu palisadegrass fertilization? **Grassland Science**, v.00, p.1–8, 2019. Available from: <http://dx.doi.org/10.1111/grs.12266>. Accessed: Jul. 19, 2023. doi: 10.1111/grs.12266.

SANZ-COBENA, A. et al. Effect of water addition and the urease inhibitor NBPT on the abatement of ammonia emission from surface applied urea. **Atmospheric Environment**, v.45, n.8, p.1517–1524, 2011. Available from: <https://doi.org/10.1016/j.atmosenv.2010.12.05>. Accessed: Apr. 27, 2023. doi: 10.1016/j.atmosenv.2010.12.05.

SCHOFIELD, P. Kinetics of fiber digestion from in vitro gas production. **Journal of Animal Science**, v.72, n.11, p.2980–2991, 1994. Available from: <https://doi.org/10.2527/1994.72112980x>. Accessed: Apr. 27, 2023. doi: 10.1016/j.atmosenv.2010.12.05.

SIMAN, F. C. et al. Nitrogen fertilizers and NH_3 volatilization: Effect of temperature and soil moisture. **Communications in Soil Science and Plant Analysis**, v.51, p.1283-1292, 2020. Available from: <https://doi.org/10.1080/00103624.2020.1763384>. Accessed: Apr. 27, 2023. doi: 10.1080/00103624.2020.1763384.

SOUZA, J. E. R. et al. Comparison of different models for the estimation of genetic parameters in tropical goats. **Tropical Animal Health and Production**, v.54, n.1, p.1-6, 2022. Available from: <https://doi.org/10.1007/s11250-022-03374-6>. Accessed: Apr. 27, 2023. doi: 10.1007/s11250-022-03374-6.

TEDESCHI, L. O. Assessment of the adequacy of mathematical models. **Agricultural Systems**, v.89, n.2–3, p.225–247, 2006. Available from: <https://doi.org/10.1016/j.agsy.2005.11.004>. Accessed: Apr. 27, 2023. doi: 10.1016/j.agsy.2005.11.004.

TURNER, D. A. et al. Ammonia volatilization from nitrogen fertilizers applied to cereals in two cropping areas of southern Australia. **Nutrient Cycling in Agroecosystems**, v.93, n.1, p.113-126, 2012. Available from: <https://doi.org/10.1007/s10705-012-9504-2>. Accessed: Apr. 27, 2023. doi: 10.1007/s10705-012-9504-2.

XU, R. et al. Global ammonia emissions from synthetic nitrogen fertilizer applications in agricultural systems: Empirical and process-based estimates and uncertainty. **Global Change Biology**, v.25, n.1, p.314–326, 2019. Available from: <http://dx.doi.org/10.1111/gcb.14499>. Accessed: Apr. 27, 2023. doi: 10.1111/gcb.14499.

ZAMAN, M. et al. Effect of urease and nitrification inhibitors on N transformation, gaseous emissions of ammonia and nitrous oxide, pasture yield and N uptake in grazed pasture system. **Soil Biology and Biochemistry**, v.41, n.3, p.1270–1280, 2009. Available from: <https://doi.org/10.1016/j.soilbio.2009.03.011>. Accessed: Apr. 27, 2023. doi: 10.1016/j.soilbio.2009.03.011.

ZORNITTA, C. S. et al. Kinetics of in vitro gas production and fitting mathematical models of corn silage. **Fermentation**, v.7, p.298, 2021. Available from: <https://doi.org/10.3390/fermentation7040298>. Accessed: Apr. 27, 2023. doi: 10.3390/fermentation7040298.

ZWIETERING, M. H. et al. Modeling of the bacterial growth curve. **Applied and Environmental Microbiology**, v.56, n.1, 1875-1881, 1990. Available from: <https://doi.org/10.1128/aem.56.6.1875-1881.1990>. Accessed: Apr. 27, 2023. doi: 10.1128/aem.56.6.1875-1881.1990.