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Modeling nitrogen loss due to ammonia volatilization in fertilizers applied to coffee plants

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ABSTRACT. The coffee tree has a strong dependence on nitrogen (N), which influences the nutritional aspect and plant productivity. The knowledge of the nutritional behavior of coffee crops, as well as the pattern of nutrient release and loss, contribute to the appropriate crop management, influencing quality, productivity and minimizing economic losses. Therefore, the objective of this article is to select the non-linear model that best describes nitrogen losses due to ammonia (NH_3) volatilization, in seven conventional and increased efficiency fertilizers, applied in three installments to coffee plants and indicate the fertilizers that presented the highest and lowest nitrogen losses due to NH_3 volatilization. The data come from an experiment carried out during the 2015/2016 harvest at the Coffee Innovation Agency (INOVACAFÉ) of the Federal University of Lavras, in a randomized block design with 3 replications of 7 treatments (nitrogen fertilizers). The estimation method used was the least squares method (MMQ), with the Gauss-Newton convergence algorithm as the iterative method. As diagnostic measures to determine the best model, the adjusted coefficient of determination (R2aj), residual standard deviation (RSD), Akaike information criterion (AIC) and mean absolute deviation (MAD) were used. It was verified that all models exhibited good adjustments, however, the Brody and Logistic models stood out in describing the accumulated nitrogen losses, due to ammonia volatilization, in relation to the seven treatments applied and evaluated. It was found that ammonium nitrate and ammonium sulfate fertilizers presented the lowest N losses, while Prilled Urea and Urea + anionic polymer contribute the greatest losses due to the volatilization of NH_3, in the three fertilizations on coffee plants.

Keywords: nutrient; coffee; nitrogen fertilizer; productivity; non-linear regression.

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Introduction

Coffee culture has a great contribution to the economy of several countries, and not only with traditional coffee, but also with specialty coffees. According to Souza et al. (2023), Brazil is the largest coffee exporter on the market and accounts for a third of world coffee production, and, to achieve these numbers, many investments in technology have been directed to fertilizing coffee crops. The performance of a coffee crop depends on some factors, mainly the management used, cultural treatments, soil fertility, irrigation, climate of the region, productive potential of the cultivar and fertilization (Souza et al., 2018; Lima et al., 2016).

Among these factors, one of the aspects that deserves attention is the supply of nutrients to the soil, through fertilization, for the development of the coffee tree, as the plant is extremely demanding in nutrients, which are not fully supplied by the soil. Studies carried out on the use of fertilizers admit that appropriate fertilization of coffee crops, associated with other management practices, can help supplement the plant's nutrition, contributing to its development and productivity (Lima et al., 2016; Parecido et al., 2021).

Among the essential nutrients for plants are nitrogen (N), phosphorus (P) and potassium (K), however, for coffee crops, nitrogen is involved with productivity, as it provides an increase in leaf area, increased number of flowering buds, development of branching of plagiotropic branches, increased production of starch and other carbohydrates essential for fruit formation and growth (Parecido et al., 2022). Due to its enormous importance in productivity, nitrogen is the nutrient needed in the greatest quantity, in addition to being the second most exported one by grains (Chagas et al., 2016).

The nitrogen fertilizer most used in Brazil is urea, which, due to its high concentration of N, allows for a lower cost per unit of the nutrient. However, the loss of nitrogen to the atmosphere, in its gaseous form, predominantly ammonia (NH_3), through the volatilization process is one of the main causes of reduced efficiency in the use of nitrogen fertilizers in coffee crops (Souza et al., 2023). According to Dominghetti et al. (2016), the ammonia volatilization process has its losses influenced by several factors and, among the main ones are: soil pH; soil moisture at the fertilization time and rainfall volume after fertilization; soil cover and cation exchange capacity (CEC); activity of urease, the enzyme responsible for the hydrolysis of the urea molecule.

The behavior of these losses accumulation over the evaluation time presents a sigmoidal aspect, which can be described by non-linear regression models, considering the effects of several key factors (for example, release and loss of nitrogen) that influence the volatilization of NH_3. These models present a good quality of fit even using few parameters, in addition to the possibility of practical interpretation of the parameters (Minato et al., 2020; Fernandes et al., 2015).

Therefore, nonlinear regression models are capable of modeling multiple phenomena and in different areas of knowledge (Jane et al., 2020; Frühauf et al., 2020), of which, the most used in growth curve studies, according to Fernandes et al. (2015), are Logistic, Gompertz, Brody, and von Bertalanffy. Given this context, this work aimed to select the most appropriate non-linear regression model to describe the accumulated nitrogen losses, due to ammonia (NH_3) volatilization, in seven conventional and increased efficiency fertilizers applied in three installments to coffee plants and indicate the fertilizers that presented the highest and lowest nitrogen losses due to NH_3 volatilization.

Material and methods

The database used is part of the experiment carried out by Chagas et al. (2019), during the 2015/2016 harvest, at the Coffee Innovation Agency (INOVACAFÉ) of the Federal University of Lavras (UFLA), located in Lavras, Minas Gerais Strate, Brazil. The municipality is located at an altitude of 910 m, at latitude 21°14'06" South and longitude 45°00'00" West. The region's climate is type Cwa, mesothermal with mild summers, and a dry period in winter, according to the Köppen classification. The average annual temperature is 19.4ºC, with potential evapotranspiration (ETP) of around 899 to 873 mm per year, and with average annual precipitation of approximately 1,472 mm. The soil was classified as Distroferric Red Yellow Latosol (LVdf). The coffee crop belongs to the Catuaí Vermelho cultivar, lineage 144, 6 years old, spaced 3.7 m between rows and 0.7 m between plants, totaling 3,861 plants ha^{-1}.

The design used was randomized blocks (DBC) with 7 treatments (Table 1) and 3 replications. Each experimental unit was 10 meters long and had a total of 14 plants, using the 10 central plants to carry out the evaluations. The plots were delineated along the planting line, with a double border system being adopted between the useful lines of the experiment (Chagas et al., 2019).

Table 1. Nitrogen fertilizers evaluated in the experiment and their respective N content.

Treatments	% N
1 – Prilled urea	45
2 - Urea dissolved in water	45
3 - Ammonium sulfate	19
4 - Ammonium nitrate	31
5 - Urea + Cu + B	44
6 - Urea + anionic polymer	41
7 - Urea + NBPT	45

Note: for all fertilizers, 300 kg of N ha^{-1} were applied.

To meet the demand for K and P, potassium chloride (KCl) and triple super phosphate (SFT) were applied. The treatment doses were applied in three installments, 100 kg per hectare, starting in November and ending in March, respecting an interval of 60 days between applications.

Nitrogen losses, due to ammonia volatilization, resulting from the soil application of the different treatments, were quantified using the semi-open PVC collector method, adapted by Cabezas et al. (1999). The collection chambers were prepared with PVC tubes with 20 cm in diameter and 50 cm high coupled to a 10 cm PVC base, 5 cm of them were fixed to the ground, under the projection of the plants canopy.

In each experimental plot, three collectors were arranged and for the application of fertilizers, within these bases, the total area was calculated and, proportionally, for the area of the PVC base. To collect volatilized NH_3, two laminated foam discs with 0.02 g cm^{-3} density and 2 cm thickness were placed inside each PVC tube, cut to the same diameter as the tube. The discs were positioned inside the chambers at a height of 30 and 40 cm from the ground. The lower sponge was previously soaked with 80 ml of a solution of phosphoric acid (H_3PO_4; 60 mL L^{-1}) and glycerin (50 mL L^{-1}), to retain the volatilized ammonia. The upper sponge had the function of protecting the lower sponge against possible environmental contamination.

Nitrogen losses were quantified through the lower sponges, responsible for retaining volatilized ammonia, collected on the 1^{st}, 2^{nd}, 3^{rd}, 4^{th}, 5^{th}, 7^{th}, 9^{th}, 12^{th}, 15^{th}, 19^{th}, 24^{th}, and 31^{st} day after nitrogenated fertilizer application. The solution from the sponges collected in the field was extracted through filtration in a Büchner funnel with the aid of a vacuum pump, after washing five times in sequential extractions with 80 mL of deionized water each one. An aliquot was removed from the extract and stored in a cold room at 50°C to determine the N content by distillation using the Kjedahl method. Precipitation in the region is concentrated between October and March, and is followed by a dry period for the remaining six months.

The non-linear regression models adjusted to the data were: Logistic $\left(y_i = \frac{\alpha}{1+e^{k(\beta-x_i)}} + \varepsilon_i\right)$; Gompertz $\left(y_i = \alpha e^{-e^{k(\beta-x_i)}} + \varepsilon_i\right)$; von Bertalanffy $\left(y_i = \alpha\,(1-[e^{k(\beta-x_i)}/3])^3 + \varepsilon_i\right)$; and Brody $\left(y_i = \alpha(1-\beta e^{(-kx_i)}) + \varepsilon_i\right)$. Where, y_i represents the accumulated nitrogen loss, due to ammonia volatilization, in kg ha^{-1}, observed in the i^{th} installment of nitrogen fertilizers applied to the crop; x_i denotes the i^{th} day on which nitrogen loss was measured.

Regarding the practical interpretation of the parameters of each one of the respective models, we have: α representing the estimated maximum accumulated loss of nitrogen by volatilization of NH_3 for all models; for the Logistic, Gompertz and von Bertalanffy models, the parameter β represents the abscissa of the inflection point, indicating the day on which nitrogen loss, through volatilization, presented a maximum rate, whereas for the Brody model, this parameter has no practical interpretation; k represents the index associated with the speed of nitrogen loss for all models and, ε_i is the random error associated with the i^{th} observation, which assumes that, $\varepsilon_i \overset{i.i.d.}{\sim} N(0, \sigma^2)$.

To estimate the model parameters, the least squares method (MMQ) was used; the iterative method adopted was the Gauss-Newton convergence algorithm.

In the analysis of residuals, the Shapiro-Wilk, Breusch-Pagan and Durbin-Watson tests were used to verify the assumptions of normality, homoscedasticity and residual independence, respectively. All tests were performed at a significance level of 1%. The models that met all assumptions were considered for comparison and selection of the model that best describes the data, through the results found for the adjusted coefficient of determination (R^2aj), residual standard deviation (RSD), Akaike information criterion (AIC) and mean absolute deviation (MAD).

The entire computational part was carried out using the open access R software (R Core Team, 2021), using the *car, gridBase, lattice, lattice-Extra, lmtest, qpcR,* and *rpanel* packages.

Results and discussion

Daily nitrogen losses due to NH_3 volatilization in the 2015/2016 harvest, for the three installments (a, b and c) over 31 days after each fertilization and the climate data (d) are presented in Figure 1. Chagas et al. (2019) assesses that ammonia volatilization is directly related to precipitation.

In the tables presented below, of model fit quality evaluators, those ones that did not meet all the assumptions of the residual analysis were not considered in the selection (indicated with "-").

First fertilization

It was found that ammonium Nitrate, ammonium Sulfate and Urea + Cu + B contribute to the lowest accumulated losses of ammonia from nitrogen fertilizers, in the first fertilization, while Prilled Urea and Urea + anionic polymer promote the greatest losses of nitrogen, by ammonia volatilization (Figure 1a).

Dominghetti et al. (2016) evaluated nitrogen losses through volatilization, in fertilizers used in coffee cultivation, and using the Skott-Knott test, they found that the application of ammonium Nitrate and Sulfate contributed to the lowest losses, in the same way that occurred between the treatments applied and evaluated in this work.

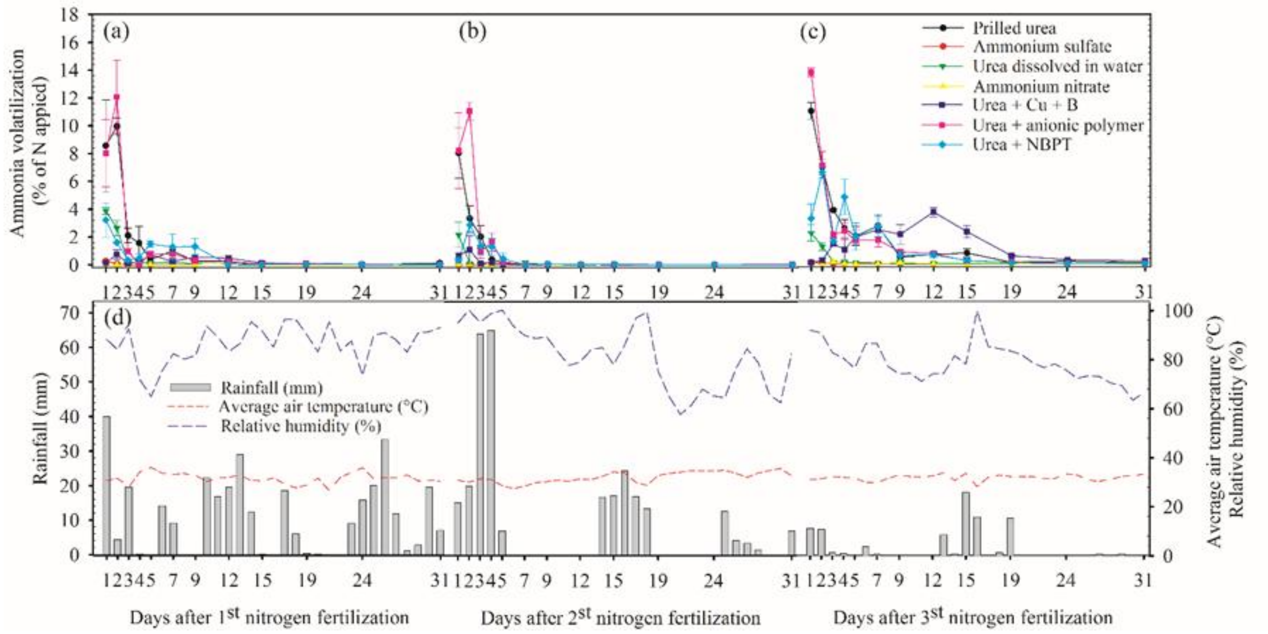

Figure 1. Daily losses of N-NH_3 in the first (a), second (b) and third (c) installments of nitrogen fertilizers and climatic conditions (d) of the 2015/2016 harvest.

Based on the quality of fit evaluators (Table 2), it can be observed that all adjusted models proved to be adequate to describe nitrogen loss, due to NH_3 volatilization. Comparatively, the Brody model presented, slightly, the highest value for R^2aj and, basically, the lowest values for AIC, RSD, and MAD.

Table 2. Quality of fit evaluators, adjusted coefficient of determination (R^2aj), Akaike information criterion (AIC), residual standard deviation (RSD), and mean absolute deviation (MAD) of the Logistic, Gompertz, von Bertalanffy, and Brody models.

Treatment	Model	R^2aj	AIC	RSD	MAD
Prilled urea	Logistic	-	-	-	-
	Gompertz	0.967	30.848	0.708	0.523
	von Bertalanffy	0.972	29.120	0.658	0.482
	Brody	0.980	25.015	0.553	0.395
Ammonium sulfate	Logistic	0.960	-56.773	0.016	0.010
	Gompertz	0.961	-57.014	0.016	0.010
	von Bertalanffy	0.961	-57.070	0.016	0.010
	Brody	0.961	-57.131	0.016	0.010
Urea + water	Logistic	-	-	-	-
	Gompertz	0.792	-0.556	0.322	0.179
	von Bertalanffy	0.802	-0.998	0.304	0.173
	Brody	0.823	-1.984	0.270	0.162
Ammonium nitrate	Logistic	0.906	-52.253	0.025	0.019
	Gompertz	0.914	-53.089	0.023	0.017
	von Bertalanffy	0.917	-53.357	0.023	0.016
	Brody	0.919	-53.593	0.022	0.016
Urea + Cu + B	Logistic	0.979	-2.209	0.209	0.113
	Gompertz	0.980	-2.637	0.168	0.106
	von Bertalanffy	0.979	-1.924	0.156	0.106
	Brody	0.971	1.588	0.163	0.115
Urea + Polymer Anionic	Logistic	0.849	37.204	0.897	0.658
	Gompertz	-	-	-	-
	von Bertalanffy	0.868	35.885	0.852	0.640
	Brody	0.881	34.873	0.817	0.614
Urea + NBPT	Logistic	0.977	17.516	0.340	0.226
	Gompertz	0.974	19.289	0.400	0.275
	von Bertalanffy	0.972	20.168	0.426	0.293
	Brody	0.966	22.364	0.489	0.334

The Brody model is characterized by the absence of an inflection point, meaning that nitrogen loss presents its maximum rate at the beginning of measurements and decreases over time.

The estimated values of the maximum asymptotic accumulated loss (α) were close to the maximum observed values, regarding N losses, which were 24.24; 0.58; 7.34; 0.28; 3.65; 23.38; and 10.89 kg ha^{-1}, respectively, for each of these fertilizers: Prilled urea, Ammonium sulfate, Urea + water, Ammonium nitrate, Urea + Cu + B, Urea + anionic polymer, and Urea + NBPT (Table 3).

Table 3. Estimates obtained for the Brody model parameters adjusted to the data on accumulated nitrogen losses, due to NH_3 volatilization, in the seven treatments applied.

Treatment	Estimates		
	A	β	κ
Prilled urea	23,837	1,466	0,853
Ammonium sulfate	0,583	0,535	0,146
Urea + water	7,252	0,970	0,946
Ammonium nitrate	0,276	1,026	0,119
Urea + Cu + B	3,651	1,143	0,161
Urea + anionic polymer	22,787	2,607	1,423
Urea + NBPT	10,246	0,837	0,197

The Prilled urea and Urea + anionic polymer treatments lost approximately 1/4 of applied N (estimated α values), which was also observed by Guelfi et al. (2017) in corn crops, in which accumulated nitrogen losses due to ammonia volatilization were 31 and 20%, respectively, reinforcing that the use of these two treatments, even in different crops, led to a significant loss of nitrogen.

According to Ruark et al. (2018), urea has some advantages, such as higher N concentration (45%) and solubility (1.0 to 1.2 kg L^{-1}), lower corrosivity and greater ease of handling and application than other N fertilizers. When applied to the soil, urea has a hydrolysis reaction, which causes an increase in pH in the region where the fertilizer granules are applied (Dominghetti et al., 2016). This alkalinization results from the formation of bicarbonate (HCO_3^-) and hydroxyl (OH^-) ions and the absence of protons (H^+ ions), favoring the transformation of ammonium ($N\text{-}NH_4^+$) into ammonia (NH_3), which is a gas that is easily lost in the atmosphere (Chagas et al., 2016). Thus, the lower losses of N due to volatilization of NH_3 from Ammonium sulfate and Ammonium nitrate fertilizers estimated by α are not related to the %N in Table 1.

For the parameter β, which represents the abscissa value of the inflection point, at which the concavity of the curve changes its upward growth trajectory to a less accentuated growth trajectory and it is also, at this point, that the curve presents its highest rate of growth, it was observed that, in all treatments, the abscissa's estimates of the inflection point were low for all models. In other words, the dizzying loss of nitrogen fertilizer occurred shortly after the first or second day of fertilization, as also observed by Chagas et al. (2019) and Dominghetti et al. (2016).

Meanwhile, the applied fertilizers that had the longest absorption time until the greatest losses, identified by the inflection point, were observed in the treatments: Ammonium nitrate and Urea + Cu + B, adjusted by the Logistic model. Souza et al. (2017) assessed that daily NH_3 losses are significantly influenced by conventional, stabilized and controlled-release nitrogen fertilizers applied to corn plantations, and found that all controlled-release and stabilized-release fertilizers, (in this experiment, ammonium nitrate and sulfate and ammonium Urea + Cu + B, reduce the speed peaks of daily ammonia losses, in the first 3 days, compared to treatments based on granulated urea.

Given the estimates of the volatilization speed (κ), it was found that the higher these values are, the shorter the time will be to reach the maximum loss of nitrogen and, the lower these values will be, the longer the time will be to reach the maximum loss of nitrogen, emphasizing the characteristics of each fertilizer, which collaborates with Minato et al. (2020). In other words, the lower the estimated volatilization speed, the better, as it helps plants conserve the applied nitrogen for longer, without its loss occurring in a drastic and sudden way. Or, the lower this value makes it possible to reach the upper asymptote slowly, which favors greater absorption of the nutrient.

The Brody model proved to be more suitable for estimating nitrogen losses after application of the fertilizers Prilled urea, Urea + water, and Urea + anionic polymer, since the loss starts accelerated from the first days, that is, the model does not present inflection point. This model was also used by Frühauf et al. (2020) to describe the diametric growth of cedar over time and in the study conducted by Azevedo et al. (2018) who evaluated discrimination of accessions with greater and lesser root dehydration among sweet potato accessions. Both cases are characterized by accelerated growth of the study object, right at the beginning of the cycle.

According to the adjusted models (Table 3) and knowing that 100 kg of N were applied per hectare, the maximum average volatilization of ammonia, calculated from the parameter α, decreased as follows: Pearly urea (23.78 kg N ha^{-1}), Urea + anionic polymer (22.73 kg N ha^{-1}), Urea + NBPT (10.12 kg N ha^{-1}), Urea + water (7.25 kg N ha^{-1}), Urea + Cu + B (3.56 kg N ha^{-1}), Ammonium sulfate (0.58 kg N ha^{-1}), and Ammonium nitrate (0.27 kg N ha^{-1}). In this way, Urea + Cu + B, Ammonium sulfate and Ammonium nitrate promoted the lowest losses of nitrogen in the form of ammonia ($N{-}NH_3$), with a percentage reduction in loss of 85.2, 97.8, and 99.1%, respectively, compared to the loss caused by Prilled urea.

Figure 2 refers to the accumulated losses of NH_3 due to volatilization in the first fertilization of conventional and stabilized nitrogen fertilizers of the studied crop.

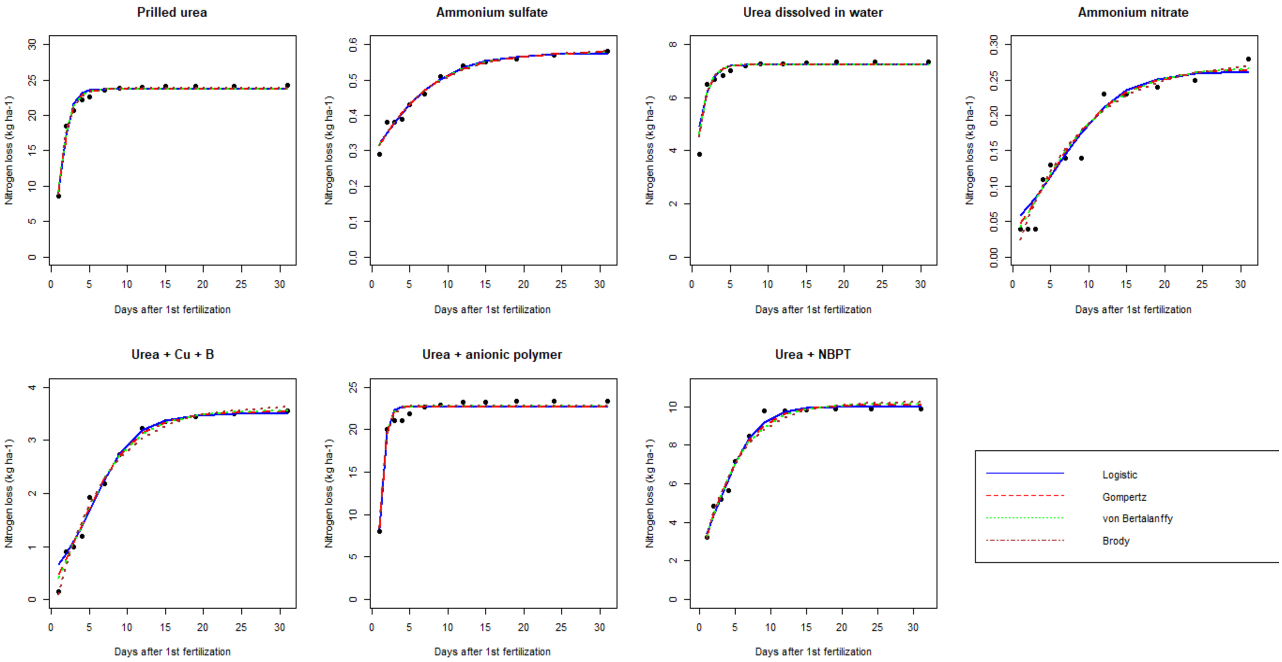

Figure 2. Graphical representation of accumulated nitrogen losses and adjustment of the Logistic, Gompertz, von Bertalanffy, and Brody models, as a function of the days after the first fertilization, for the applied nitrogen fertilizers.

Second fertilization

The second installment was characterized by a large deviation in observations, as there was a violation of assumptions in some treatments, compromising the modeling for these fertilizers. A possible cause was the large amount of rain that fell shortly after the application of the second fertilization (Figure 1d). As observed by Cabezas et al. (1997), precipitation causes great variation in the environment, as water reduces the volatilization of NH_3 if it is in sufficient quantity to dissolve the concentration of hydroxyl ions produced in the hydrolysis reaction, contributing to the incorporation of urea into the soil.

In Table 4, based on the quality of fit evaluators, it can be seen that no deviations from assumptions were observed only for the fertilizers Ammonium sulfate and Urea + water. For all other fertilizers, a deviation in assumptions was observed in at least two models, only allowing the adjustment of the Logistic and Gompertz models for Prilled urea and von Bertalanffy for Urea + NBPT. Comparatively, the Logistic model presented, slightly, the highest value for R^2aj and, basically, the lowest values for AIC, RSD, and MAD.

The result corroborated Vale et al. (2014) who analyzed the accumulated losses of ammonia from nitrogen fertilizer applied superficially to pastures, where it was found that the Logistic model adjusted satisfactorily to the phenomenon.

Table 5 presents the estimates of the Logistic model parameters, except for the Urea + NBPT treatment, which the only adjusted model that met the residual assumptions was the von Bertalanffy model for data on accumulated nitrogen losses, due to NH_3 volatilization. It is worth mentioning that for the treatments Ammonium nitrate, Urea + Cu + B, and Urea + anionic polymer, the adjusted models did not meet any waste assumptions, so they were not presented.

Table 5 shows the estimated values of the maximum asymptotic accumulated loss (α) for all modeled nitrogen fertilizers. Even in fertilizers that lose more nitrogen through volatilization, in this scenario they lost less, for example, the loss of N in the Prilled urea treatment was only 13.97% of the total applied, corresponding to almost half of the loss in the first installment (23.78 %). This fact can be explained by the rains that occurred immediately after the application of fertilizers. According to Cabezas et al. (1997), moistening the soil, following the application of urea, facilitates the absorption of nitrogen by plants and, thus, the loss through volatilization is minimized.

Table 4. Quality of fit evaluators, adjusted coefficient of determination (R^2aj), Akaike information criterion (AIC), residual standard deviation (RSD) and mean absolute deviation (MAD), of the Logistic, Gompertz, von Bertalanffy, and Brody models.

Treatment	Model	R^2aj	AIC	RSD	MAD
Prilled Urea	Logistic	0.995	-19.764	0.089	0.051
	Gompertz	0.992	-13.550	0.115	0.061
	von Bertalanffy	-	-	-	-
	Brody	-	-	-	-
Ammonium sulfate	Logistic	0.941	-93.885	0.004	0.002
	Gompertz	0.943	-94.178	0.003	0.002
	von Bertalanffy	0.943	-94.181	0.003	0.002
	Brody	0.942	-93.992	0.003	0.002
Urea + water	Logistic	0.929	-46.967	0.028	0.017
	Gompertz	0.928	-46.781	0.028	0.017
	von Bertalanffy	0.927	-46.718	0.028	0.017
	Brody	0.926	-46.589	0.029	0.017
Urea + NBPT	Logistic	-	-	-	-
	Gompertz	-	-	-	-
	von Bertalanffy	0.966	-12.896	0.152	0.077
	Brody	-	-	-	-

Table 5. Estimates obtained for the parameters of the Logistic model adjusted to the data on accumulated nitrogen losses, due to the volatilization of NH_3, except for the Urea + NBPT treatment, in which the only adjusted model was the von Bertalanffy model.

Treatment	Estimates		
	α	β	κ
Prilled urea	13.970	0.785	1.264
Ammonium sulfate	0.058	7.057	0.155
Urea + water	2.450	-6.930	0.243
Urea + NBPT	6.371	1.695	0.999

Minato et al. (2023), states that, 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. Therefore, paying attention to rainfall conditions helps in the use of N in the soil.

For the parameter β, it was observed that, in all treatments, the estimates of the inflection point were low, for all models, that is, the accentuated loss of ammonia occurred soon after the first days of fertilization, whereas, the postponed losses, identified by the inflection point, were observed in the Ammonium sulfate treatment and estimated by the Logistic model. As for the estimates of the volatilization speed (κ), it was found that, in general, the values found are relatively low.

Figure 3 shows the graphical representation of accumulated nitrogen losses and adjustment of the Logistic, Gompertz, von Bertalanffy and Brody models, as a function of the days after the second fertilization, for the applied nitrogen fertilizers.

According to the adjusted models and knowing that 100 kg of N were applied per hectare, the maximum average volatilization of ammonia decreased as follows: Prilled urea (13.97 kg N ha^{-1}), Urea + NBPT (6.37 kg N ha^{-1}), Urea water (2.45 kg N ha^{-1}), and Ammonium sulfate (0.06 kg N ha^{-1}). The application of Urea + water and Ammonium sulfate fertilizers contributed to minimizing nitrogen losses in the form of ammonia ($N{-}NH_3$), with a percentage reduction of 82.7 and 99.5%, respectively, compared to the loss achieved by use of Prilled urea.

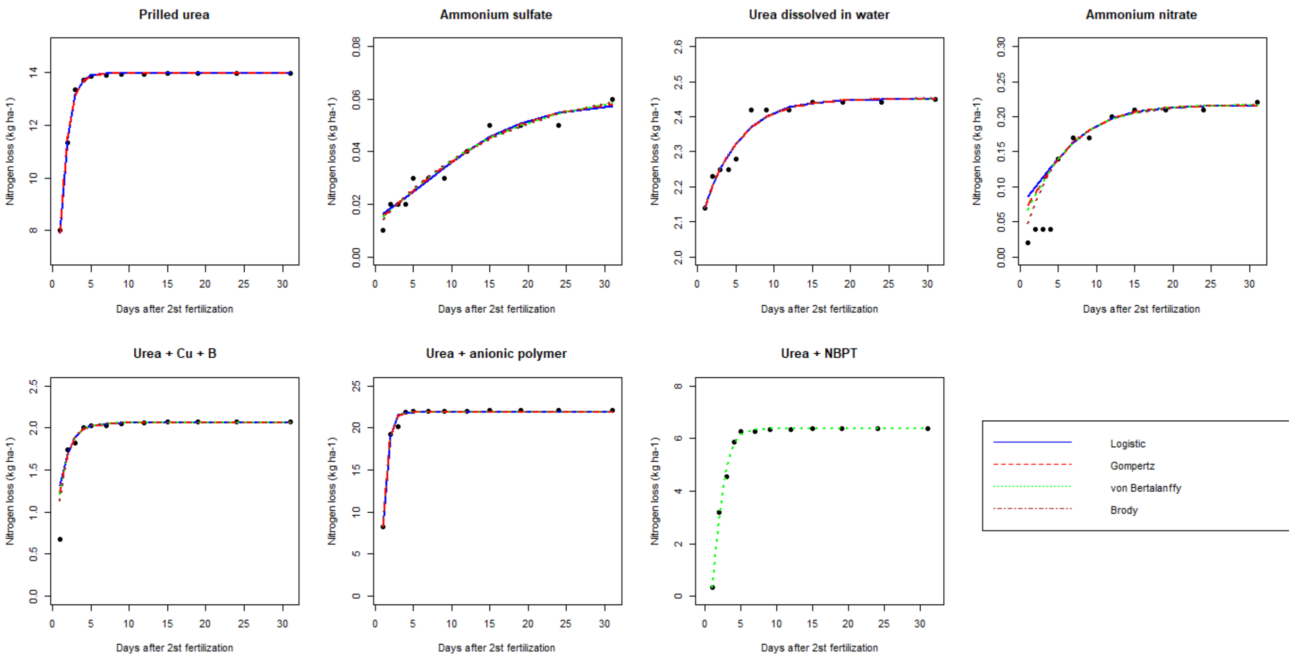

Figure 3. Graphical representation of accumulated nitrogen losses and adjustment of the Logistic, Gompertz, von Bertalanffy, and Brody models, depending on the days after the second fertilization, for the applied nitrogen fertilizers.

Third fertilization

For the third fertilization, it was found that the pattern of accumulated N loss due to NH_3 volatilization remains similar to that one observed in other fertilizations, with Ammonium nitrate and sulfate continuing to contribute to the lowest accumulated ammonia losses, while the other fertilizers promote the greatest losses (Figure 1c).

Table 6 presents the quality of fit evaluators performed for the adjusted models.

Table 6. Quality of fit evaluators, adjusted coefficient of determination (R^2aj), Akaike information criterion (AIC), residual standard deviation (RSD), and mean absolute deviation (MAD) of the Logistic, Gompertz, von Bertalanffy, and Brody models.

Treatment	Model	R^2aj	AIC	RSD	MAD
Prilled Urea	Logistic	-	-	-	-
	Gompertz	-	-	-	-
	von Bertalanffy	-	-	-	-
	Brody	0.994	13.072	0.423	0.286
Ammonium sulfate	Logistic	0.974	-76.981	0.008	0.005
	Gompertz	0.972	-76.197	0.008	0.006
	von Bertalanffy	0.971	-75.876	0.008	0.006
	Brody	0.969	-75.148	0.008	0.006
Urea + water	Logistic	0.926	-19.098	0.094	0.069
	Gompertz	0.938	-20.959	0.087	0.063
	von Bertalanffy	0.942	-21.648	0.084	0.061
	Brody	0.949	-23.139	0.079	0.057
Ammonium nitrate	Logistic	0.886	-41.835	0.030	0.022
	Gompertz	0.883	-41.276	0.033	0.021
	von Bertalanffy	0.882	-40.836	0.034	0.021
	Brody	0.835	-38.473	0.040	0.026
Urea + Cu + B	Logistic	0.997	15.283	0.673	0.424
	Gompertz	0.993	26.327	0.427	0.299
	von Bertalanffy	0,990	31,654	0.444	0.299
	Brody	-	-	-	-
Urea + NBPT	Logistic	0,981	23,931	0.887	0.517
	Gompertz	0,991	14,720	0.714	0.392
	von Bertalanffy	0,993	11,881	0.666	0.350
	Brody	-	-	-	-

Table 7 presents the estimates of the parameters of the Brody model adjusted to the treatments Prilled urea and Urea + water, and of the Logistic model adjusted to the treatments Ammonium sulfate, Ammonium nitrate, Urea + Cu + B, and Urea + NBPT, for the data of accumulated nitrogen losses, through ammonia volatilization. Since the Urea + anionic polymer treatment, the adjusted models did not meet any waste assumptions, so they were not presented.

Table 7. Estimates obtained for the parameters of the Brody model adjusted to the Prilled Urea and Urea + water treatments, and the Logistic model adjusted to the other treatments of data on accumulated nitrogen losses, due to the volatilization of NH_3.

Treatment	Estimates		
	α	β	κ
Prilled urea	31.086	0.873	0.348
Ammonium sulfate	0.307	6.520	0.085
Urea + water	3.819	0.969	0.890
Ammonium nitrate	0.264	6.500	0.460
Urea + Cu + B	16.520	8.178	0.364
Urea + NBPT	22.377	2.879	0.698

The values estimated for α, by the non-linear models (Table 7), represent the greatest losses, in relation to other fertilizations, for the treatments Prilled urea, Ammonium nitrate, Urea + Cu + B, and Urea + NBPT. It can be seen in Figure 1d that in this third fertilization, for the period, the lowest amount of precipitation occurred after application. Therefore, it corroborates the hypothesis that rain reduces nitrogen losses, through ammonia volatilization, according to Dominghetti et al. (2016) and Souza et al. (2017).

It is noted that the Brody model, due to its characteristics, is not suitable for adjusting estimates of the treatments of Ammonium Sulfate, Ammonium Nitrate, Urea + Cu + B, and Urea + NBPT, for the climatic conditions of this fertilization, which was with little precipitation. In this way, the Logistic model is used, just as Cassim et al. (2022), who adjusted the Logistic model to model accumulated losses due to NH3 volatilization for conventional and higher efficiency nitrogen fertilizers and reduced NH3 emissions in relation to urea for clayey and sandy soils in corn cultivation.

For the parameter β, it was observed that, in almost all treatments, the estimates of the inflection point were low in all four models, that is, the dizzying loss of nitrogen fertilizer occurred within three days after fertilization, as also observed by Chagas et al. (2019) and Souza et al. (2018). Meanwhile, the later losses, identified by the inflection point estimate, which is greater, were observed in the treatments: Ammonium sulfate, Ammonium nitrate, and Urea + Cu + B, adjusted by the Logistic model besides of the treatments Ammonium nitrate and Urea + Cu + B, adjusted by the Gompertz model.

Regarding the estimates of the volatilization speed (κ), it was found that, in general, the values found are low, however, for the Urea + water treatment, the values found help to explain the volatilization of ammonia, in addition to the blend itself.

The treatments Urea + water, Ammonium sulfate, and Ammonium nitrate favored achieving the lowest losses of nitrogen in the form of ammonia at 87.7, 99.0m and 99.3%, respectively, compared to the loss promoted by Prilled urea.

Observing Table 6 of the quality of adjustment evaluators' measurements and Figure 4, which shows the graphic representation of the accumulated nitrogen losses and adjustment of the models, depending on the days after the third fertilization, for the applied nitrogen fertilizers, and knowing that 100 kg of N per hectare were applied, the maximum average volatilization of ammonia decreased as follows: Prilled urea (31.08 kg N ha^{-1}), Urea + NBPT (22.47 kg N ha^{-1}), Urea + Cu + B (16.79 kg N ha^{-1}), Urea + water (3.81 kg N ha^{-1}), Ammonium sulfate (0.35 kg N ha^{-1}), and Nitrate ammonium (0.27 kg N ha^{-1}).

Conclusion

All adjusted models satisfactorily describe the accumulated nitrogen losses due to ammonia volatilization in the coffee plant, however, there is a slight superiority in the adjustments of the Brody and Logistic models in relation to the seven treatments applied and evaluated. Based on the estimates of the parameter α, we found that the ammonium nitrate and sulfate fertilizers presented the lowest nitrogen losses, due to ammonia volatilization, while Prilled urea and Urea + anionic polymer contribute the highest losses, in the three fertilizations in the coffee tree.

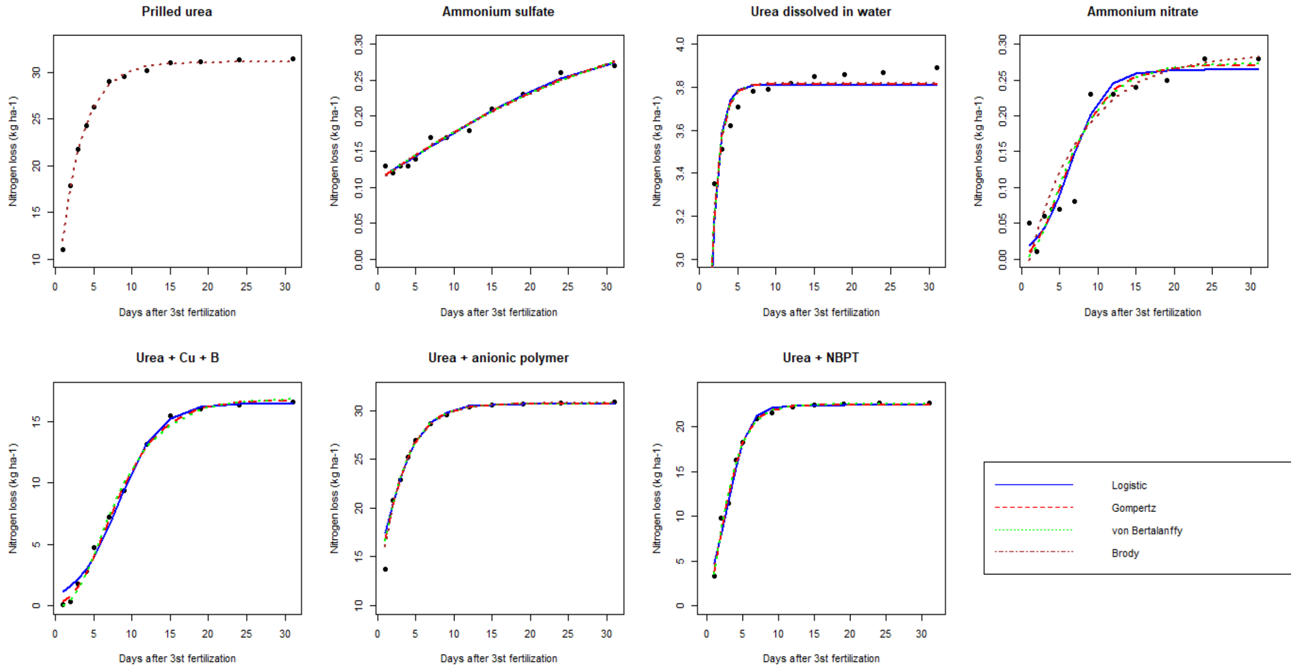

Figure 4. Graphical representation of accumulated nitrogen losses and adjustment of the Logistic, Gompertz, von Bertalanffy, and Brody models, as a function of the days after the third fertilization, for the applied nitrogen fertilizers.

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