

Sigmoid models in the description of CO₂ evolved from legumes in the soil

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Received in: 08/01/2023

Accepted in: 10/04/2023

Abstract

The decomposition of legumes in the soil over time can be described by nonlinear sigmoid models. Thus, this study aimed to describe and to compare the fit of the nonlinear sigmoid models, Logistic and Gompertz, to the CO₂ mineralization of four legume species over time in the soil, and indicate the most suitable model. Furthermore, it is also proposed to evaluate the CO₂ mineralization of legumes from two different edaphoclimatic conditions when added to the soil under controlled temperature and humidity conditions. The following legume species used in green manure were evaluated: *Arachis pintoi* (forage peanut), *Calopogonium mucunoides* (calopo), *Stylosanthes guianensis* (Caribbean stylo), and *Stizolobium aterrimum* (*mucuna*). A randomized block design with four replications was used. The soils from both areas are classified as Red-Yellow Latosol and have a clayey texture. The mineralized carbon was measured at 48, 96, 144, 192, 240, 312, 384, and 480 hours from the beginning of incubation. Legumes in different locations had the same amount of potentially mineralizable carbon, and microorganisms had the same adaptation time to reach the maximum decomposition rate. The maximum decomposition rate occurs at the beginning of mineralization, and therefore the Gompertz model was more suitable than the Logistic model in describing the decomposition of the four legumes in the soil.

Keywords: Decomposition. Mineralization. Gompertz Model. Logistic Model.

Introduction

The inappropriate and intensive use of soils has increased their degradation process, requiring interventions based on proper practices to maintain their productive capacity (TEODORO et al., 2011). In this context, green manure on the soil surface is an important intervention that promotes controlled temperature and moisture conditions, increases organic matter, and protects against various forms of soil erosion. Furthermore, soil cover is greatly important for agriculture as it promotes nutrient cycling, benefiting the crops (RODRIGUES et al., 2012).

The use of legumes as cover crops has been highlighted since, in addition to providing similar benefits to other species, they are capable of accumulating nitrogen via biological fixation (RODRIGUES et al., 2012). The use

of legumes as green manure has also been a viable alternative for agriculture since their residue decomposition process can incorporate and release nutrients from their biomass into the soil for the next crop (PEREIRA et al., 2016). Therefore, understanding the decomposition dynamics over time is essential to establish more efficient green manure management strategies that meet the needs of the target crop and enhance the process of nutrient cycling and availability (MATOS et al., 2008). Additionally, other factors affect nutrient cycling, such as management system, geographic location, and cultivation season, as these factors influence the quality of green manure by altering its chemical and biochemical composition (THÖNNISSEN et al., 2000; MATOS et al., 2008).

According to Giacomini et al. (2008) and Pulrolnik (2009), for residues maintained on the

soil surface, the microbial colonization of the substrate is initially slower due to the adaptation phase of the microbial population to the substrate. Subsequently, decomposition becomes more intense due to higher amounts of easily decomposable materials, and, as the process continues, the predominance of more recalcitrant materials may reduce microbial action. Among the various applications of nonlinear regression models (MARTINS FILHO et al., 2008; PEREIRA et al., 2009; SOUZA et al., 2010; SILVEIRA et al., 2018; JANE et al., 2020b; SILVA et al., 2020b; SILVA et al., 2022), the decomposition processes of legumes in the soil over time can be described by a nonlinear sigmoidal model. Generally, the Logistic model has been used to describe this process (MATOS et al., 2008; MONTEIRO et al., 2002).

The Logistic model is symmetrical to the inflection point, and in the decomposition process, it is expected that the maximum CO₂ release rate occurs in the first days (GIACOMINI et al., 2008). Thus, to better understand decomposition dynamics and employ appropriate soil management, other models must be evaluated in this process. Gompertz model is an alternative for describing decomposition as it considers the abscissa of the inflection point at the beginning of the process (SILVA et al., 2021a; JANE et al., 2020a; FRÜHAUF et al., 2020; PRADO et al., 2020; JANE et al., 2019; SARI et al., 2018; RIBEIRO et al., 2018; MICHAN and PINHO, 2014).

Thus, this study aimed to describe and compare the fit of the nonlinear sigmoid models, Logistic and Gompertz, to the CO₂ mineralization of four legume species over time in the soil, and indicate the most suitable model. In addition, it is also proposed to evaluate the CO₂ mineralization of legumes based on two different edaphoclimatic conditions when added to the soil under controlled temperature and moisture conditions.

Material and methods

The analyzed data were obtained from an experiment conducted by Matos et al. (2008) in partnership with UFV/EPAMIG/CTA, from December 2003 to April 2004, green manures were obtained from areas of family farmers in the municipalities of Araçuaia and Pedra Dourada, both located in the Zona da Mata region of the state of Minas Gerais. The property, located in Araçuaia, is situated at 20° 38'S and 42° 31'W, at an average altitude of 950 m, with the experimental unit facing west for sun exposure. The municipality of Pedra Dourada is located at 20° 50'S and 42° 08'W, with an average altitude of 690 m, and the experimental unit faces south for sun exposure.

The soils from both areas are classified as Red-Yellow Latosol and have a clayey texture. Coffee is cultivated in the area with a spacing of 2.8–3.0 × 0.5–0.8 m, under organic management since the planting of seedlings. At the time of the experiments' introduction, coffee was in the establishment phase, three years after planting. At the time of experiment installation, the following soil attributes were recorded for the Araçuaia property: pH (H₂O) of 5.2; Al³⁺ of 0.60, Ca²⁺ of 1.77, and Mg²⁺ of 0.70 cmol_c dm⁻³; available P and K (Mehlich-1) of 1.8 and 74 mg dm⁻³, respectively; and organic carbon content of 28 g kg⁻¹ (Walkey-Black method). For the Pedra Dourada area, the following were recorded: pH (H₂O) of 5.0; Al³⁺ of 1.0, Ca²⁺ of 0.48, and Mg²⁺ of 0.14 cmol_c dm⁻³; available P and K (Mehlich-1) of 2.4 and 56 mg dm⁻³, respectively; and organic carbon content of 36 g kg⁻¹ (Walkey-Black method).

Before sowing the legumes, soil correction was performed. In Araçuaia, 0.26 t ha⁻¹ of limestone, 64 kg ha⁻¹ gypsum, 125 kg ha⁻¹ potassium sulfate, and 800 kg ha⁻¹ thermophosphate were applied. In Pedra Dourada, 1.20 t ha⁻¹ of limestone, 300 kg ha⁻¹ gypsum, 125 kg ha⁻¹ potassium sulfate, and

800 kg ha⁻¹ thermophosphate were applied. The soil amendments and fertilizers were applied in the spaces between rows and were incorporated into the soil during the planting process. All commercially obtained legume seeds were sown in furrows and incorporated to an average depth of 1 cm. Seed inoculation was not performed before sowing.

The treatments consisted of combinations between two coffee cultivation locations (Araponga and Pedra Dourada) and four legume species used for green manure: *Arachis pintoi* (forage peanuts), *Calopogonium mucunoides* (calopogon), *Stylosanthes guianensis* (Caribbean stylo) and *Stizolobium aterrimum* (*mucuna*). The legumes were cultivated in the coffee tree interrows in 2 × 2 m plots. Approximately 120 days after planting (flowering stage), the aerial parts of the legumes were collected, and a sample of each material was used for moisture determination and subsequent chemical analyses. The randomized block design was used in a 2 × 4 factorial arrangement (two locations and four legume species) with four blocks (replications), totaling 32 experimental units.

The green manure, after being dried in an oven, ground and sieved through a 2 mm sieve, were chemically and biochemically characterized, with carbon (C) content determined by dry combustion using a Perkin Elmer CHNS/O 2400 analyzer. To assess the residue mineralization, the plant materials were incubated in samples of a very clayey Red-Yellow Latosol.

The mineralizable C was evaluated via respirometry assays, measuring the evolution of C-CO₂ using a continuous flow respirometer. The mass of each plant material equivalent to 2 g of carbon was mixed with 100 cm³ of soil and placed in the incubation chambers of the respirometer (hermetically sealed containers of 377 mL) at 70% of field capacity under controlled temperature conditions (25 ± 1°C). The CO₂ resulting from microbial activity was

quantified by capturing it in a 0.5 mol L⁻¹ NaOH solution and subsequently titrating it with a 0.25 mol L⁻¹ HCl solution. Eight measurements of evolved C-CO₂ were taken, with the first five measurements at 48-hour intervals, followed by two measurements at 72-hour intervals, and the final measurement at 96 hours, totaling 480 hours. The Logistic model (Equation 1) and the Gompertz model (Equation 2) were fitted to the C-CO₂ evolutions, expressed as a function of time (hours) using the following statistical model:

$$y_i = \frac{C_0}{1 + e^{k(\beta - t_i)}} + \varepsilon_i \quad (1)$$

$$y_i = C_0 e^{-e^{-k(\beta - t_i)}} + \varepsilon_i \quad (2)$$

The parameter “C₀” indicates the potentially mineralizable carbon, while “β” indicates the abscissa of the inflection point. The parameter “k” indicates the evolution constant of C-CO₂. The magnitude of the parameters “C₀” and “β” reflects the degradability of the legume and the microbial activity, respectively. In turn, “ε_i” is the random error, which is assumed to have a normal distribution with mean 0 and constant variance σ², that is, ε_i ~ N(0, σ²). According to Fernandes et al. (2015), in this parameterization of the Logistic model, the inflection point occurs at the coordinate $(\beta, \frac{C_0}{2})$, whereas in the Gompertz model it occurs at the coordinate $(\beta, \frac{C_0}{e})$. In other words, the Logistic model is symmetric with respect to the inflection point, and the Gompertz model is earlier.

The parameters estimation was performed using the least squares method, which involves minimizing the sum of squared residuals and leads to a system of normal equations. For the nonlinear model, there is no explicit solution, so it is necessary to use iterative methods to obtain the estimates (FRÜHAUF et al., 2022a; VILELA et al., 2022; SILVA et al., 2020a; OLIVEIRA et al., 2013; ZEVIANI et al., 2012; PEREIRA

et al., 2005). Among the various iterative methods proposed in the literature, the Gauss-Newton algorithm was used, and the initial values for the process were chosen based on an initial exploratory analysis of the data.

After fitting the models, it was necessary to verify the assumptions of normality, independence, and homoscedasticity of the residual vector, which ensure correct inference about the parameters (FRÜHAUF et al., 2022b; MIRANDA et al., 2021; ARCHONTOULIS; MIGUEZ, 2015; FERNANDES et al., 2014). The Shapiro-Wilk test was used to check the assumption of normality, the Durbin-Watson test for independence, and the Breusch-Pagan test for homoscedasticity. When the residuals showed autocorrelation, the model was adjusted using the method of generalized least squares, incorporating the autoregressive parameter of first order AR (1) (SILVA et al., 2021b; PAULA et al., 2020; SILVA et al., 2019a; SILVA et al., 2019b). When the assumption of normality was met, a 95% confidence interval was constructed for the model parameters (DRAPER and SMITH, 2014).

The comparison of the models regarding the quality of the fit was based on the results found for the coefficient of determination (R^2), adjusted coefficient of determination (R_{aj}^2), Akaike information criterion (AIC), and residual standard deviation (DPR). The model that achieves the highest value for R^2 and R_{aj}^2 and the lowest values for AIC and DPR is the one with the best fit to the data. All the computational aspects involved in this work were performed using the freely accessible statistical software R (R CORE TEAM, 2022).

Results and discussion

After fitting the models, an analysis of the residuals was performed to check if any of the assumptions of the regression models were not met. If this occurs, the deviation should

be incorporated into the fitting process, as the model may generate imprecise estimates, rendering it inadequate for representing the dataset (ARCHONTOULIS; MIGUEZ, 2015; FERNANDES et al., 2014). Therefore, Table 1 presents the results obtained for the Shapiro-Wilk, Breusch-Pagan, and Durbin-Watson tests. It can be observed that the p-values of the Shapiro-Wilk and Breusch-Pagan tests were greater than 0.05 for all treatments and in both models, indicating no evidence to reject the hypotheses of normality and homoscedasticity of the residuals. On the other hand, except for the soil treatment in Araponga and Pedra Dourada, in both models, and the Gompertz model in Araponga for the *S. guianensis* treatment, the p-value of the Durbin-Watson test was less than 0.05, indicating evidence to reject the hypothesis that the residuals of the models were independent. In these cases, to correct for residual dependence, the autoregressive parameter of first order AR(1) was added to the parameter estimation of the models.

For the soil treatment in Araponga, according to Table 1, higher values of R_{aj}^2 and R^2 were obtained for the Logistic model, along with lower values of RSD and AIC. Therefore, the Logistic model was more suitable for describing the decomposition dynamics in this treatment. For the remaining treatments, higher values of R_{aj}^2 and R^2 and lower values of RSD and AIC were obtained for the Gompertz model, indicating that it is more suitable for modeling the decomposition dynamics in those treatments. Except for the soil treatment in Araponga, all the treatments were better described by the Gompertz model, which is earlier in terms of the inflection point compared to the Logistic model (FERNANDES et al., 2015). This indicates that the maximum rate of mineralization occurs in the early hours (GIACOMINI et al., 2008).

Table 2 presents the parameter estimates and their respective 95% confidence intervals of

Table 1. P-values for Shapiro-Wilk (SW), Durbin-Watson (DW), and Breusch-Pagan (BP) tests used in the analysis of the residual vector for fitting the Logistic and Gompertz models, and evaluation criteria for the quality of fit for mineralized carbon as a function of time.

Municipality	Model	Treatment	SW	BP	DW	R ² _{aj}	R ²	RSD	AIC
Pedra D.	Logistic	Soil	0.0837	0.2191	0.1042	0.9839	0.9885	0.5727	18.0257
Pedra D.	Gompertz	Soil	0.6187	0.2476	0.1399	0.9941	0.9957	0.3553	10.3851
Pedra D.	Logistic	<i>S. atterimum</i>	0.8164	0.3059	0.0012	0.9755	0.9825	19.3693	76.2445
Pedra D.	Gompertz	<i>S. atterimum</i>	0.5420	0.2067	0.0024	0.9917	0.9941	11.5384	67.9518
Pedra D.	Logistic	<i>S. mucunoides</i>	0.7120	0.3100	0.0010	0.9771	0.9836	19.5709	76.4039
Pedra D.	Gompertz	<i>S. mucunoides</i>	0.6035	0.2641	0.0021	0.9930	0.9950	11.0708	67.2875
Pedra D.	Logistic	<i>S. guianensis</i>	0.7908	0.3202	0.0007	0.9770	0.9836	21.2581	77.6974
Pedra D.	Gompertz	<i>S. guianensis</i>	0.6776	0.2609	0.0012	0.9929	0.9949	12.1247	68.6793
Pedra D.	Logistic	<i>A. pinto</i>	0.8291	0.3375	0.0007	0.9816	0.9869	20.7784	77.3406
Pedra D.	Gompertz	<i>A. pinto</i>	0.8416	0.1925	0.0020	0.9956	0.9969	10.3425	66.2403
Araponga	Logistic	Soil	0.6068	0.0768	0.1759	0.9870	0.9907	0.5262	16.6703
Araponga	Gompertz	Soil	0.1912	0.1758	0.0747	0.9696	0.9783	0.8180	23.7278
Araponga	Logistic	<i>S. atterimum</i>	0.8858	0.2638	0.0022	0.9776	0.9840	18.2665	75.3922
Araponga	Gompertz	<i>S. atterimum</i>	0.7385	0.1059	0.0078	0.9934	0.9953	10.1372	65.9890
Araponga	Logistic	<i>S. mucunoides</i>	0.8292	0.2390	0.0033	0.9815	0.9868	17.3508	74.5885
Araponga	Gompertz	<i>S. mucunoides</i>	0.5575	0.1181	0.0162	0.9952	0.9966	9.0069	64.0247
Araponga	Logistic	<i>S. guianensis</i>	0.7651	0.2117	0.0066	0.9854	0.9895	16.8184	74.0424
Araponga	Gompertz	<i>S. guianensis</i>	0.7786	0.0897	0.0794	0.9967	0.9976	8.1660	60.5420
Araponga	Logistic	<i>A. pinto</i>	0.9530	0.3016	0.0009	0.9886	0.9918	15.4877	72.6829
Araponga	Gompertz	<i>A. pinto</i>	0.4588	0.0945	0.0187	0.9983	0.9987	6.1296	57.6090

Source: Prepared by the authors (2023).

the best-selected model for describing the Pedra Dourada treatments. It can be seen that there was no overlap in the confidence intervals of the parameter C_0 , which indicates the potentially mineralizable carbon content of the soil and other treatments. The addition of legumes to the soil stimulated microbial activity, leading to increased mineralization of carbon from the legumes in the soil and degradation of native soil organic matter (PAULA et al., 2019; FERNANDES et al., 2011). In addition, there was no overlap in the parameter C_0 of the *S. atterimum*, *S. mucunoides*, and *A. pinto* treatments, indicating that the carbon mineralization in the *A. pinto* treatment was higher than in the other two, as also observed by Matos et al. (2008)

In Table 2, by the confidence intervals of the parameter β , which indicates the abscissa

of the inflection point—that is, how many hours are needed to reach the maximum point of mineralization related to microbial activity—, there was no overlap between the interval of the soil and the legume treatments, indicating that, with the addition of the plant, the maximum rate of mineralization occurred later. Furthermore, the maximum rate of mineralization for the legume treatments in Pedra Dourada occurred between approximately 112 and 119 hours (estimate of β – Table 2). Matos et al. (2008) found estimates between 145 and 152 hours, and this difference is due to the fact that the authors used the Logistic model, which is symmetric with respect to the inflection point, to describe the decomposition process. According to Giacomini et al. (2008), the maximum rate of mineralization occurs at the beginning of the process, which

Table 2. Estimates for the parameters of the Gompertz model fitted to the mineralized carbon data in Pedra Dourada and their respective 95% confidence intervals (LL - lower limit and UL - upper limit).

Treatment	Model	Parameter	LL	Estimate	UL
Soil	Gompertz	C ₀	15.3652	15.8718	16.4081
		β	67.2177	73.6884	79.9413
		k	0.0163	0.0195	0.0235
<i>S. aterrimum</i>	Gompertz	C ₀	377.1442	406.2102	435.2761
		β	98.2786	112.1668	126.0548
		k	0.0083	0.0110	0.0136
		φ	-0.6292	0.1315	0.7635
<i>S. mucunoides</i>	Gompertz	C ₀	390.2938	418.3660	446.4382
		β	103.1348	116.0771	129.0193
		k	0.0085	0.0110	0.0134
		φ	-0.6316	0.1327	0.7663
<i>S. guianensis</i>	Gompertz	C ₀	423.6578	454.7148	485.7719
		β	101.9599	115.2655	128.5711
		k	0.0085	0.0110	0.0135
		φ	-0.6098	0.1625	0.7766
<i>A. pintoii</i>	Gompertz	C ₀	456.0008	481.1145	506.2283
		β	109.8073	119.7426	129.6779
		k	0.0094	0.0115	0.0135
		φ	-0.6675	0.1084	0.7715

Source: Prepared by the authors (2023).

was confirmed by this study in the comparison of the Logistic and Gompertz models, indicating the Gompertz model, which is early to the inflection point, as more appropriate.

Table 3 presents the parameter estimates and their respective 95% confidence intervals of the best-selected model for describing the Araponga treatments. It can be seen that there was no overlap in the confidence intervals of the parameter C₀, of the soil and other treatments. The addition of legumes to the soil stimulated microbial activity, leading to increased mineralization of carbon from the legumes in the soil, as well as degradation of native organic matter (PAULA et al., 2019; FERNANDES et al., 2011). Furthermore, there was no overlap in the parameter C₀ of the *S. aterrimum*, *S. mucunoides*, and *A. pintoii* treatments, indicating that the carbon mineralization in the *S. aterrimum* and *S.*

mucunoides treatments was lower than in the *A. pintoii* treatment, a result similar to that obtained by Matos et al. (2008)

In Table 3, by the confidence intervals of the parameter β , it can be observed that there was overlap between the confidence interval of the soil and the legume treatments, and due to this fact, the Logistic model provided a better fit for the treatment with soil only (Table 1). Furthermore, the maximum rate of mineralization for the legume treatments in Araponga occurred between approximately 117 and 127 hours (estimate of β – Table 3). Matos et al. (2008) found estimates between 150 and 161 hours, and this difference is due to the fact that the authors used the Logistic model, which is symmetric with respect to the inflection point, to describe the decomposition process. According to Giacomini et al. (2008), the maximum rate

Table 3. Estimates for the parameters of the Logistic and Gompertz models fitted to the mineralized carbon data in Araponga and their respective 95% confidence intervals (LL - lower limit and UL - upper limit).

Treatment	Model	Parameter	LL	Estimate	UL
Soil	Logistic	C_0	12.4542	13.1800	13.9343
		β	111.7258	124.500	136.9970
		k	0.0193	0.0255	0.0340
<i>S. atterimum</i>	Gompertz	C_0	364.9784	387.8968	410.8152
		β	106.9949	117.8570	128.7192
		k	0.0091	0.0114	0.0137
		φ	-0.7603	-0.0437	0.7208
<i>S. mucunoides</i>	Gompertz	C_0	388.2605	409.3751	430.4896
		β	111.9140	121.1793	130.4446
		k	0.0089	0.0107	0.0125
		φ	-0.7862	-0.1105	0.6854
<i>S. guianensis</i>	Gompertz	C_0	426.4942	447.2000	471.4895
		β	118.2788	127.1000	136.3839
		k	0.0087	0.0102	0.0119
<i>A. pintoii</i>	Gompertz	C_0	439.7498	452.8538	465.9578
		β	118.9809	124.0424	129.1038
		k	0.0100	0.0110	0.0121
		φ	-0.8522	-0.2189	0.6745

Source: Prepared by the authors (2023).

of mineralization occurs at the beginning of the process; therefore, the Logistic model is not the most suitable for describing this dynamics.

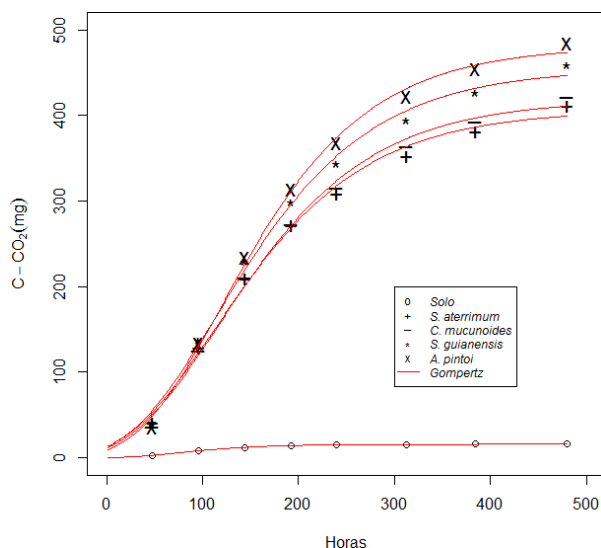
Comparing the confidence intervals of the C_0 parameter, it can be observed that, in the treatments in Pedra Dourada (Table 2) and in Araponga (Table 3), there was always an intersection in the intervals, indicating that the same treatments in different locations did not alter the amount of potentially mineralizable carbon in the legumes. Furthermore, the influence of the different locations no did alter time to adapt these microorganisms until they reached the maximum decomposition rate, as that there was overlap in the confidence intervals of the parameter β .

Both models exhibited excellent fits to the data, as evidenced by the coefficient of determination (R^2) values, all of which were

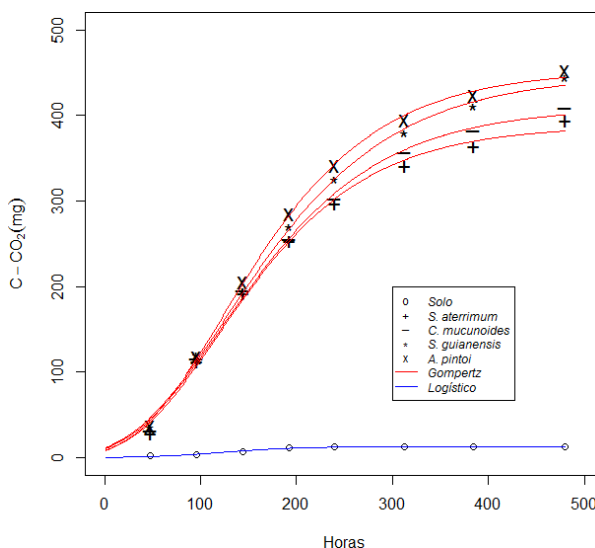
above 97% (Table 1). Furthermore, the best model also exhibited a strong fit to the evolving values of soil CO_2 and legume CO_2 (Figures 1 and 2).

Conclusion

The Gompertz model proved to be more appropriate than the Logistic model in describing the decomposition of legumes in the soil, primarily due to the maximum decomposition rate occurring at the beginning of mineralization. Under controlled temperature and humidity conditions, both the legumes from Pedra Dourada and Araponga exhibited an equal amount of potentially mineralizable carbon. Additionally, the microorganisms in both cases required the same amount of time to adapt and reach the maximum decomposition rate.

Figure 1. Fit of the Gompertz model to the carbon mineralization data from Pedra Dourada.

Source: Prepared by the authors (2023).

Figure 2. Fit of the Logistic model to the carbon mineralization data from Araponga.

Source: Prepared by the authors (2023).

Acknowledgements

We would like to thank the nonlinear regression applied studies group (NLIN) at the Federal University of Lavras (UFLA).

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