Comparison of nonlinear models for the description of carbon mineralization in soils treated with pig slurry

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Abstract

One of the strategies to reduce environmental impacts caused by pig slurry is its application to soils for agricultural productions. Carbon mineralization curves can be used to determine the best periods for the use of organic matter for an adequate management of soils and growing plants. The objective of this study was to evaluate the fit of nonlinear models for soil carbon mineralization. The experiment was conducted using a randomized block design with four replications and four treatments. The treatments consisted of monthly applications of pig slurry at rates of 0, 7.5, 15.0, and 30.0 m³ ha⁻¹ of pig slurry. Soil samples were collected and incubated for 26 days; then, seven observations of mineralized carbon volume were made over time. The description of the carbon mineralization followed the Stanford and Smith, Cabrera, and Juma models, considering the structure of autoregressive errors AR (1), when necessary; the fits were compared using the Akaike Information Criterion (AIC). The description of carbon mineralization in the treatments by nonlinear models was, in general, adequate. Juma was the most adequate model to describe the treatment with rate of 0. Stanford and Smith was the most adequate model to describe the treatments with rates of 7.5 and 15.0 m³ ha⁻¹. **Keywords:** Organic waste. Stanford and Smith model. Cabrera model. Juma model.

Introduction

Pig production is relevant in the Brazilian agrobusiness due to the high number of people employed in this production chain and the expressive generation of income for producers and exports to the country. Brazil is the fourth largest pig meat producer and exporter country (CONAB, 2017; GUIMARÃES et al., 2017). Its high pig production generates a large amount of liquid wastes, which can cause several environmental problems when not appropriately used or disposed, such as contamination of water bodies and public health problems due to the release of substances, such as nitrate in water courses (CADONÁ, 2017).

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However, an alternative for the use of pig slurry to decrease its environmental impacts is its use as a source of nutrients to agricultural crops. The chemical composition of pig slurry includes a large amount of nitrogen, which is required in large amounts by plants (BISON PINTO et al., 2014). Moreover, the input of organic compounds to the soil stimulates the growth of microorganism populations, resulting in carbon immobilization or mineralization as carbon dioxide; and the amount and quality of the substrate and its interaction with the soil microbiota can result in mineralization of the native soil organic matter (FERNANDES et al., 2011).

Several factors affect the decomposition process of organic compounds in the soil, such as the relation between the compound pH and soil pH, the compound chemical composition, the amount of carbon, the C to N ratio, and the form of application to the soil (e.g. incorporation). Most of the carbon mineralization occurs, in general, at the beginning of the decomposition of organic compounds in the soil because of a greater soluble fraction with labile compounds in this period; when this fraction decreases, the mineralization is slower because of the more resistant compounds to microorganisms (GIACOMINI et al., 2008). This dynamic of the mineralization curve can be described by mathematical functions that constitute nonlinear regression models (FERNANDES et al., 2011; SILVA et al., 2019a).

Thus, studying carbon mineralization curves over time is important and necessary to understand the decomposition dynamics of organic compounds that can assist in more favorable soil management practices for agricultural production. Nonlinear models are used to describe carbon mineralization curves; they provide a good fit and gather the information contained in the data into few parameters, providing estimates with biological and practical interpretations, which are useful to rural producers (SILVEIRA et al., 2018).

One of the most used nonlinear models to describe soil carbon mineralization over time is the Stanford and Smith (1972). This model was used in several studies on dynamics of carbon, presenting good results in researches on eucalyptus plantations (BARRETO et al., 2010), tannery sludge (MARTINES et al., 2006), septic tank sludge, anaerobic digestor sludge, reactor sludge (SILVA, 2017), carcass and residue of small ruminants (PEREIRA, 2014), pig slurry and oat plant residues (SILVA et al., 2019a), and sewage sludge and oat plant residues (SILVA et al., 2019b).

In studies on nonlinear models with measures in the same experimental unities over time, observations normally present correlations, which also occurs in studies of decompositions in soils (SILVA et al., 2019a), presenting structures of dependence in the experimental errors. According to Silveira et al. (2018), considering the modeling of this correlation is necessary to obtain an appropriate fit.

The objective of the present work was to evaluate the fit of nonlinear regression Models Cabrera (1993), Juma et al. (1984), and Stanford and Smith (1972) for the description of carbon mineralization in soils from the 2nd to the 26th day after pig slurry application, and to identify the most adequate model to describe the dynamics of decomposition of organic compounds in the soil.

Material and methods

The data used to fit the models were extracted from Fernandes et al. (2011) and correspond to mean results of an experiment that evaluated carbon mineralization in soils using different rates of pig slurry. The experiment was conducted in São Gabriel do Oeste, MS, Brazil. The soil of the area was classified as a Typic Hapludox (Latossolo Vermelho Distrófico - SiBCS); it was covered with pastures

for bovine milk production. Soil samples were collected from the 0-10 cm layer. The pig slurry used consisted of feces and urine, feed leftovers, and water from the drinkers and cleaning processes.

The experiment was conducted in a randomized block experimental design, with four treatments and four replications. The treatments consisted of monthly applications of pig slurry at rates of 0, 7.5, 15.0, and 30.0 m³ ha⁻¹ of pig slurry. The carbon mineralization (C) data was obtained in laboratory conditions by measuring the C released by the soil microbial activity as carbon dioxide (CO_2). The soil samples were air dried and sieved (2.0 mm mesh). Aliquots of 50.0 g of soil were placed in 100.0-ml flasks. The soil moisture was corrected to 60.0% of maximum water retention capacity. The amount of mineralized carbon was evaluated after 2, 6, 9, 13, 16, 22, and 26 days of incubation.

The nonlinear models evaluated were: Cabrera (1), Juma (2), and Stanford and Smith (3), according to the following equations:

$$C_{i} = C_{1}(1 - \exp(-k_{1}t_{i})) + k_{0}t_{i} + u_{i}$$
(1)

$$C_{i} = C_{0}t_{i}/(v + t_{i}) + u_{i}$$
 (2)

$$C_i = CO(1 - exp(-kt_i)) + u_i$$
 (3)

at which

 $u_i = \phi_1 u_{i-1} + ... + \phi_p u_{i-p} + \varepsilon_i$, with i = 1, 2, ..., n (n = number of evaluation times); u_i is the residue of the fit in the *i*th time;

 ϕ_1 is the autoregressive parameter of order 1;

 $u_{i,1}$ is the residue of the fit of the preceding time to the *i*th measure;

 ϕ_{n} is the autoregressive parameter of order p;

 u_{i-p} is the residue of the fit in the p times before the *i*th measure;

 ϵ_i is the experimental error, with normal distribution with mean zero and variance σ^2 , e. g., $\epsilon_i \gtrsim N(0, \sigma^2)$.

When the residues in the models were independent, the parameters ϕ_i were null and, consequently, $u_i = \varepsilon_i$ (MAZZINI et al., 2003; GUEDES et al., 2004, SAVIAN et al., 2007; MENDES et al., 2008; PRADO et al., 2013; SOUZA et al., 2014).

The C_i in the equations (1), (2), and (3) defines the mean value of the amount of mineralized carbon in the times t_i in days; C₀ indicates the value of the amount of potentially mineralizable carbon; C₁ is the amount of easily mineralizable carbon; k, k₁, k₀ are mineralization rates; v is the half-life time; t_i is the time of the *i*th evaluation, expressed in days (PEREIRA et al., 2005; PEREIRA et al., 2009). The half-life time (v) of potentially mineralizable carbon for the Stanford and Smith model, and of easily mineralizable carbon for the Cabrera model was estimated by v = ln(2)/k, and v = ln(2)/k₁, respectively. When the parameter k₀ of the Cabrera model was zero, the model became the Stanford and Smith model. Moreover, the Cabrera model considers two carbon fractions: an easily mineralizable (C₁) and a resistant (k₀) fraction. The Juma model and the Stanford and Smith model consider only one carbon fraction: potentially mineralizable fraction (C₀).

The estimation of the parameters C_0 , C_1 , k, k_1 , k_0 , and v of the models was done using the minimum square method, obtaining the nonlinear normal equation system. In the case of nonlinear models, the system presents no direct solution, and use of iterative algorithms of numerical search is necessary to obtain the estimates of the parameters (CARNEIRO et al., 2014; MUIANGA et al.,

2016). Several iterative processes are described in the literature; the one used in the present work was the Gauss-Newton algorithm (MUNIZ et al., 2017; RIBEIRO et al., 2018a; RIBEIRO et al., 2018b). This algorithm considers the expansion in series of Taylor to approach the nonlinear regression model with linear terms, then, applying the ordinary minimum square method to estimate the parameters. The calculations of estimates for the sampled data, their fit to graphics, and all computational processes involved with the elaboration of this work were developed using the R program (R DEVELOPMENT CORE TEAM, 2016).

Confidence intervals of the estimated parameters were obtained under the supposition of normality of residues. According to Draper and Smith (2014), an interval of 95% of confidence for the parameter β i of the model is defined as:

$$IC(\beta_{i}): b_{i} \pm t(vv;0;025).S(b_{i})$$
(4)

at which:

b_i is the estimate for the parameter (β_i);

S(b_i) is the standard error of the estimate;

t(v;0;025) is the upper quantile of the Student t distribution, considering $\alpha = 5\%$ and the degrees of freedom v=n - d, at which d is the number of parameters of the model.

The Durbin Watson test was applied to verify the presence of residual dependence between the measures, evaluating if the residue of an observation is associated with the residue of the adjacent observations (FURTADO et al., 2019). The Breusch-Pagam test was used to verify the homogeneity of residues, and the Shapiro-Wilk test was used to verify their normality.

The models were compared for quality of fit, and the most adequate model to describe the C mineralization curve over time was indicated. The following criteria was used:

i . Adjusted coefficient of determination, ${\sf R}^2_{\ _{ai}},$ defined by:

$$R_{aj}^{2} = 1 - \frac{(1 - R^{2})(n - 1)}{n - d};$$
(5)

at which

R² the coefficient of determination;

n is the number of observations and *d* is the number of parameters of the model.

A model should be preferred than the other when presenting a higher value of AIC.

ii. Akaike information criterion (AIC) given by the expression:

$$AIC = -2\log L(\tilde{\theta}) + 2p \tag{6}$$

at which

L (θ) is the maximum of the likelihood function;

p is the number of parameters in the model;

log is the natural logarithm operator. Between two models, the lower the value of AIC, the better the model fits the data.

Results and discussion

The results obtained by analysis of experimental errors (TABLE 1) were expressed by the Shapiro-Wilk, Breusch-Pagan, and Durbin-Watson tests. According to the results, the Shapiro-Wilk test indicated residual normality for all models and all treatments evaluated, except for the treatment with pig slurry rate of 0 of the Stanford and Smith model (p<0.05); thus, this model was disregarded, and the estimates of the parameters were not presented, as well as the evaluators of quality of fit of this model for the rate of 0. The Breusch-Pagan test indicated residual homogeneity for all models and treatments (p>0.05). The Durbin-Watson test showed correlations for all treatments of the Juma model, and for the treatment with rate of 30.0 m³ ha⁻¹ of the Cabrera model; thus, the correlation was considered in the study and the fits with autoregressive errors of order 1 AR(1) was presented to explain the dependence of residues of these treatments. This correlation of the errors was expected, since the measures were made in the same plot over time. Silva et al. (2019a) also found correlation for the fit of nonlinear models to data of carbon mineralization from pig slurry; and Silveira et al. (2018) found correlation of errors when fitting nonlinear models to accumulated production of biogas from pig waste. The treatments evaluated by the Stanford and Smith model and Cabrera model presented independence of errors in the pig slurry rates of 0, 7.5, and 15.0 m³ ha⁻¹.

Treatments (Rate of slurry)	Model	SW p-value	BP p-value	DW p-value
0	Stanford and Smith	0.0172	0.7773	0.6880
0	Cabrera	0.3564	0.2199	0.9240
0	Juma	0.4946	0.1730	0.0220
7.5	Stanford and Smith	0.4235	0.0824	0.0620
7.5	Cabrera	0.6256	0.1797	0.1280
7.5	Juma	0.3216	0.1876	0.0120
15	Stanford and Smith	0.7274	0.1939	0.7220
15	Cabrera	0.6247	0.2079	0.7020
15	Juma	0.3421	0.2237	0.0100
30	Stanford and Smith	0.5128	0.8778	0.6260
30	Cabrera	0.2637	0.1472	0.0200
30	Juma	0.3857	0.1469	0.0200

Table 1 – P-values of Shapiro-Wilk (SW), Durbin-Watson (DW), and Breusch-Pagan (BP) tests applied to errors
of models for mineralized carbon (mg CO_2 kg ⁻¹) of the evaluated treatments.

Source: Elaborated by the authors (2019).

The estimates of parameters of models and their respective confidence intervals at 95% probability are presented in Table 2. The estimate of confidence interval of parameter k_0 of the Cabrera model for the rates of 0, 7.5, and 15 m³ ha⁻¹ included the value zero. According to Zeviani et al. (2012), this result indicates that the parameter value is zero, therefore, the model did not fit for these treatments; when the parameter $k_{0,}$ is not considered, the model reduces itself to the Stanford and Smith model, with only one fraction of carbon (potentially mineralizable fraction). For the rate of 30 of the Cabrera model, the estimates of confidence intervals showed that all parameters of the model did not include the value zero, showing that the model describes the treatment, and the half-life time (v) of easily mineralizable carbon was estimated in 2.5 days (table 2). Only this treatment presented two mineralization phases, an easily mineralizable (C_1) and a resistant phase (k_0). Silva et al. (2019a) found that the Cabrera model was more adequate for the use of pig slurry at rates of 20 m³ ha⁻¹, incorporated to the soil; thus, the treatment presented two phases of carbon mineralization.

Table 2 – Estimates of the parameters of the models, and their respective asymptotic confidence intervals of 95% (LL = lower limit, and UL = upper limit) in the fit of mineralized C (mg of CO_2 kg⁻¹) of the evaluated treatments.

Stanford and Smith Model									
		Rate 0					Rate 7	.5	
C _o k v	LL 	Estimates 	 		C _o k v	LL 93.6419 0.249 2 .477	9 0.2		UL 96.1986 0.2798 2.7736
		Rate 15			Rate 30				
C _o k v	LL 97.3797 0.2627 2.5159	Estimates 97.9326 0.2690 2.5767	5 UL 98.4894 0.2755 2.6385		C _o k v	LL 100.822 0.258 2.558	6 0.2		UL 101.9444 0.2709 2.6803
Cabrera Model									
Rate 0				Rate 7.5					
$egin{array}{c} {\sf C}_1 \\ {\sf k}_0 \\ {\sf k}_1 \end{array}$	LL 87.0386 -0.2614 0.2443	Estimates 91.5985 0.0285 0.2694	UL 96.8376 0.1813 0.2964	C ₁ k ₀ k ₁	-	LL 38.1567 0.0177 0.2598	Estimates 91.5890 0.1539 0.2800	UL 95.39 0.31 0.30	29
V	2.3386	2.5729	2.8372	v		2.3005	2.4755	2.66	80
	Rate 15 Rate 30								
$egin{array}{c} {C_1} \\ {k_0} \\ {k_1} \end{array}$	LL 95.2927 -0.1682 0.2518	Estimates 98.3546 -0.0195 0.2672	UL 101.6897 0.1199 0.2832	C ₁ k ₀ k ₁		LL 98.8410 0.0548 0.2692	Estimates 100.0313 0.0638 0.2702	0.	_ 2218 .0726 .2711
V	2.4476	2.5941	2.7528	v ф		2.5568	2.5653 -0.9544	2.	5748

	Juma Model						
		Rate 0				Rate 7.5	
С _о v ф	LL 95.1644 1.7842	Estimates 105.4848 3.0315 0.3152	UL 115.8052 4.2789	С _о v ф	LL 101.679 2.1089	Estimates 110.0563 3.0908 0.3056	UL 118.4334 4.0727
Rate 15					Rate 30		
C _o v ¢	LL 102.9182 1.8619	Estimates 113.4426 3.0481 0.3190	UL 123.9671 4.2344	С _о v ф	LL 107.5219 1.9906	Estimates 117.7371 3.1155 0.2985	UL 127.9524 4.2403

Source: Elaborated by the authors (2019).

The Stanford and Smith model fitted to the rates of 7.5, 15.0, and 30.0 m³ ha⁻¹, and the Juma model fitted to the data of the four treatments, since the estimates of confidence intervals showed that all parameters of the model did not include the value zero.

Considering the confidence intervals to estimate the parameter C_0 in the Stanford and Smith model, there was no superposition between confidence intervals in the treatments with rates of 7.5, 15.0, and 30.0 m³ ha⁻¹. Thus, the rate of 30.0 m³ ha⁻¹ presented higher potentially mineralizable carbon than the rates of 15.0 and 7.5 m³ ha⁻¹; and the rate of 15.0 m³ ha⁻¹ had higher potentially mineralizable carbon than the rate of 7.5 m³ ha⁻¹. These results were expected, since a higher rate can stimulate the microbial activity, increasing the mineralization of the carbon added to the soil and the degradation of the native soil organic matter (FERNANDES et al., 2011). Despite the differences in amount of potentially mineralizable carbon (C_0), the parameter half-life time (v) of all treatments in the Stanford and Smith model had superposition of confidence intervals, showing that all treatments needed approximately 2.6 days to mineralize half of the potentially mineralizable carbon.

Superposition was found in the Juma model when considering the confidence intervals for the estimate of the parameter C_0 in all treatments; thus, all treatments presented the same amount of potentially mineralizable carbon. Although the amount of carbon added was different, this factor alone does not totally explain the complexity in the soil ecosystem, where several other factors, such as C to N ratio and the type of N ions, can affect the carbon mineralization by microorganisms (FERNANDES et al., 2011). Superposition was found between the confidence intervals of the parameter half-life time (v) in all treatments of the model; as well as the Stanford and Smith model, this indicates that all treatments needed approximately 3 days to decompose half of the potentially mineralizable carbon.

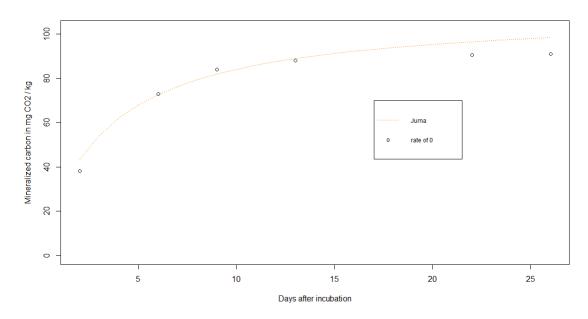
All models presented, in general, good fit in all treatments, since the values of the adjusted coefficient of determination (R^2_{aj}) were above 94% (TABLE 3). The fits are shown in Figures 1 to 4. Silva et al. (2019a) studied the fit of the nonlinear models (Stanford and Smith, and Cabrera) for carbon mineralization from pig slurry and oat plant residues in soils and found R^2_{aj} values higher than 0.97, indicating that the models describe adequately the data. For the rate of 0, Juma was the only model that described the carbon mineralization. For the rates of 7.5 and 15.0 m³ ha⁻¹, Stanford and Smith was the model that best described the carbon mineralization, which presented lower AIC values and higher R^2_{aj} values than the Juma model. For the rate of 30.0 m³ ha⁻¹, Cabrera was the model that best described the carbon mineralization, presenting the lowest AIC and the highest R^2_{aj} , followed by the Stanford and Smith model and Juma model.

Treatments	Model	Selec	tion criteria
		R^2_{aj}	AIC
	Stanford and Smith	0.9993	12.4458
Rate 0	Cabrera	0.9992	14.1103
	Juma	0.9482	39.5166
	Stanford and Smith	0.9988	16.9311
Rate 7.5	Cabrera	0.9995	11.0225
	Juma	0.9701	36.9607
	Stanford and Smith	0.9997	7.1026
Rate 15.0	Cabrera	0.9997	8.7364
	Juma	0.9544	39.6909
	Stanford and Smith	0.9998	7.1097
Rate 30.0	Cabrera	0.9999	1.5950
	Juma	0.9610	37.3420

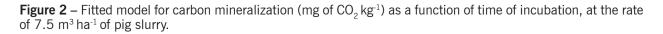
Table 3 – Estimates of selection criteria: adjusted coefficient of determination (R_{ai}^2) and Akaike information criterion (AIC) for the fitted models for the description of mineralized carbon (mg CO_2 kg⁻¹) of the evaluated treatments.

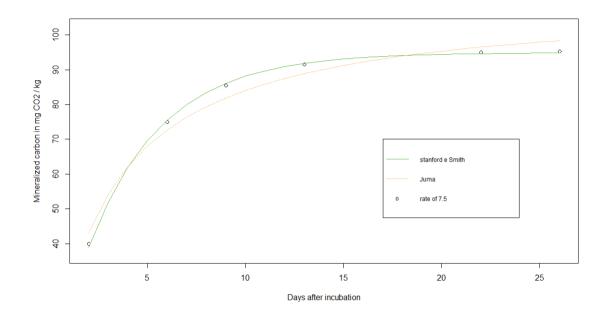
Source: Elaborated by the authors (2019).

Figure 1 – Fitted model for carbon mineralization (mg of $CO_2 kg^{-1}$) as a function of time of incubation, at the rate of 0 m³ ha⁻¹ of pig slurry.

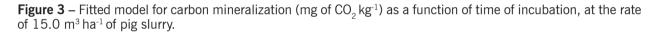


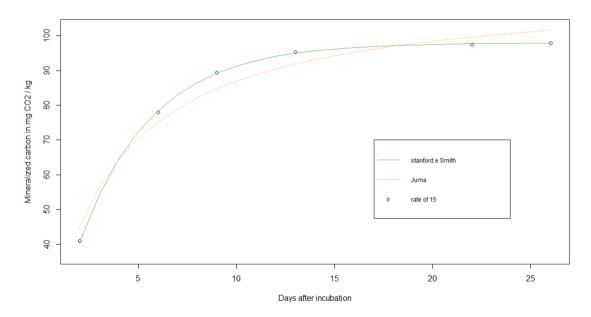
Source: Elaborated by the authors (2019).



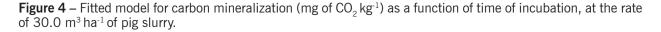


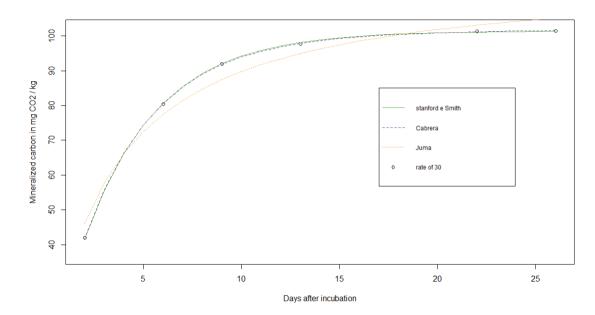
Source: Elaborated by the authors (2019).





Source: Elaborated by the authors (2019).





Source: Elaborated by the authors (2019).

Conclusions

Juma was the most adequate model for the description of carbon mineralization in the treatment with pig slurry at rate of 0 m³ ha⁻¹, thus, this treatment presents only one fraction of carbon that is mineralizable.

Stanford and Smith was the best model for the description of carbon mineralization in the treatments with pig slurry at rates of 7.5 m³ ha⁻¹ and 15 m³ ha⁻¹, i.e., these treatments presented only carbon fractions that are exponentially mineralized.

Cabrera was the most adequate model to describe carbon mineralization in the treatment with pig slurry at rate of 30.0 m³ ha⁻¹, thus, this treatment certainly presents fractions of mineralizable carbon with exponential behavior, and more resistant fractions with constant mineralization.

Comparação de modelos não lineares na descrição da mineralização do carbono no solo tratado com dejetos de suínos

Resumo

Uma estratégia para reduzir os impactos ambientais causados por dejetos de suínos consiste em utilizar esses resíduos em solos para produção de culturas agrícolas. Por meio das curvas de mineralização de carbono é possível determinar os melhores períodos para utilização da matéria orgânica visando ao manejo adequado do solo e das culturas. Objetivou-se com este estudo comparar o ajuste de modelos não lineares que descrevem a mineralização de carbono no solo. O experimento foi realizado usando o delineamento blocos ao acaso com quatro repetições e quatro tratamentos. Foram usados os seguintes tratamentos: sem adição (0), doses mensais de 7,5; 15,0 e 30,0 m³ ha⁻¹ de dejetos de suínos. As amostras de solo coletadas foram incubadas por 26 dias e foram feitas sete observações do volume de carbono mineralizado ao longo do tempo. A descrição da mineralização do carbono foi feita pelos modelos Stanford e Smith, Cabrera e Juma, considerando estrutura de erros autorregressivos AR (1) quando necessário. Para comparar os ajustes foi utilizado o critério de informação Akaike (AIC). Em geral, a descrição da mineralização de carbono nos tratamentos pelos modelos não lineares foi adequada. O modelo Juma foi o mais adequado para descrever o tratamentos de dose 7,5 e 15,0 m³ ha⁻¹. O modelo Cabrera foi o mais adequado para descrever o tratamento de dose 30,0 m³ ha⁻¹. **Palavras-chave:** Resíduo orgânico. Modelo Stanford e Smith. Modelo Cabrera. Modelo Juma.

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