# Comparison of nonlinear models for the description of carbon mineralization in degraded pasture soil and in soils with plant cover

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## Abstract

Tree planting is an important way to restore degraded areas, however, the quality of the plant residue added to the soil influences the organic matter decomposition rate and, consequently, carbon availability. Carbon mineralization curves over time make it possible to understand the decomposition of organic residues and improve soil management. Nonlinear regression models have been used to describe the dynamics of carbon mineralization over time, as they summarize the information contained in the data in just a few parameters with practical interpretations. Thus, this study aimed at evaluating the nonlinear models Cabrera, Juma and Stanford & Smith to describe the soil carbon mineralization in the following plantations: Secondary forest, *Acacia auriculiformis*, *Mimosa caesalpiniifolia* and Pasture, obtained from the first to the twentieth week. All the computational part involved in the adjustments and analyses was performed using the R statistical software. The most suitable regression model was selected for the description of soil carbon mineralization for each vegetation cover based on the following criteria: adjusted coefficient of determination ($R^2_{adj}$), residual standard deviation (RSD) and Akaike information criterion (AIC). For Acacia, the Cabrera model was indicated as the best to describe this treatment. For Forest and Pasture, the Juma model had the best fit, and the Stanford & Smith model best described the Mimosa treatment.

**Key words:** Nutrient cycling. Carbon dioxide. Forest soil. Regression models.

## Introduction

As leaves, branches and roots are incorporated into the soil and undergo decomposition, nutrients are released into the soil, improving its fertility and, consequently, making them available for trees (BARRETO *et al.,* 2010; GODINHO *et al.,* 2014). In addition, tree planting is an alternative for restoration of degraded areas (NUNES *et al*., 2016), but little is known about natural ecosystems and nutrient cycling in native forests and forest plantations in Brazil (GODINHO *et al.,* 2014; MORAIS *et al.,* 2017).

According to Pulrolnik (2009), the amount of mineralized carbon is proportional to the amount of organic carbon in the soil, therefore, in the first days, the amount of $CO_2$ released is greater, since it has the largest amount of organic carbon. In addition, the carbon of easily degradable substances is mineralized. Over time, the amount of $CO_2$ released reduces, due to the lower amount of organic carbon and the presence of more resistant substances. This behavior can be described by mathematical functions that constitute nonlinear regression models (PAULA *et al*., 2020).

The knowledge of carbon mineralization curves over time is fundamental for understanding the dynamics of organic residues decomposition and to assist in the most favorable soil management practices. Nonlinear models have been widely used to describe carbon mineralization curves, as they provide a good fit and, in addition, summarize the information contained in the data in just a

few parameters, providing estimated values with biological interpretations and useful practices for researchers. and producers (FERNANDES *et al.,* 2015; FERNANDES *et al.,* 2017; FRUHAUF *et al.,* 2020; JANE *et al.,* 2019; JANE et al, 2020a; SILVA *et al.,* 2020b).

Among nonlinear models, the most used to describe soil carbon dynamics is Stanford & Smith (ANDRADE *et al.,* 2016; ANDRADE *et al.,* 2015), including litter decomposition data (BARRETO *et al.,* 2010; NUNES *et al.,* 2016). It is a model with two parameters representing the potentially mineralizable carbon and the mineralization constant. The Cabrera model has shown good fits in processes with two phases of mineralization, one easily mineralizable with exponential behavior and the other resistant with constant behavior (PAULA *et al.,* 2020; PEREIRA *et al.,* 2009; SILVA *et al.,* 2020a; SILVA *et al.,* 2019a; SILVA *et al.,* 2019b; ZEVIANI *et al.,* 2012). Another model used is the nonlinear Juma (PAULA *et al.,* 2019; PEREIRA *et al.,* 2005), with two parameters presenting a direct practical interpretation, potentially mineralizable carbon and half-life, respectively.

The goal of the present study was to evaluate the fit of nonlinear regression models Cabrera (1993), Juma *et al.* (1984) and Stanford & Smith (1972) to describe soil carbon mineralization with the following plantations: Secondary forest, *Acacia auriculiformis*, *Mimosa caesalpiniifolia* and pasture; as well as to identify the most suitable model to describe the decomposition dynamics of each plantation.

## Material and methods

Data used to adjust the models were extracted from Nunes *et al.* (2016) and correspond to the average results of an experiment evaluating carbon mineralization in degraded soil with different plant covers. The experiment was carried out in the north of the state of Rio de Janeiro.

Soils are Reddish-Yellow Latosols with a clayey texture. The experimental area consisted of four study sites, at the same elevation above sea level and next to each other, with the following plantations: Secondary forest, *Acacia auriculiformis*, *Mimosa caesalpiniifolia* and pasture. Two sites supported pure stands of the tree species *Acacia auriculiformis* and *Mimosa caesalpiniifolia*. Trees from both sites were 14 years old, planted at 3 m x 2 m spacing. The third site was a degraded pasture that supports *Melinis minutiflora* P. Beauv. (molasses grass), *Paspalum maritimum* Trin. (coastal sand paspalum) and *Imperata brasiliensis* Trin. (Brazilian satintail). The fourth site was a secondary forest under anthropogenic (harvest) disturbance, with dense stands of trees that included species at different successional stages and the native legume *Anadenanthera colubrine*. Litter accumulation at the fourth site was about 6.7 Mg $ha^{-1}$.

Soil samples were collected from 0 to 10 cm depth in four uniform plots of each plantation (in terms of soil homogeneity, density, slope and tree age) in the middle of each site. Soil samples were separated to remove clods, sieved through a 2 mm mesh and homogenized; roots and visible plant and animal residues were removed from the samples. Moisture was standardized to 40% maximum soil saturation capacity.

An aerobic incubation experiment was conducted in the laboratory using a completely randomized design with four replications and the four cover crops were the treatments. Released $CO_2$ was measured after 1, 2, 3, 4, 6, 8, 12, 16 and 20 weeks of incubation.

The $CO_2$ released during the incubation period was used to measure the soil carbon mineralization rate. At the top of each percolation tube, a glass container was fixed to the lid by means of a plastic rod; 10 mL 1 M NaOH was then added to the vessel to absorb the $CO_2$ released during incubation. After the addition of NaOH to the glass vessel, the ends of the percolator

were immediately closed to avoid environmental absorption of $CO_2$. Thus, after each incubation period, the 1 M NaOH solution in the containers was changed and the percolators were then sealed again. C- $CO_2$ levels in the NaOH solution were determined by potentiometric titration with 0.5 M HCl.

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

$$C_i = C_1(1 - \exp(-k_1 t_i)) + k_0 t_i + u_i \; ; \quad (1)$$

$$C_i = C_0 t_i/(v + t_i) + u_i \; ; \quad (2)$$

$$C_i = C_0(1 - \exp(-k t_i)) + u_i \; ; \quad (3)$$

where $u_i = \phi_1 u_{i-1} + \ldots + \phi_p u_{i-p} + \varepsilon_i$, with i= 1, 2, ..., n and n is the number of times the measurements were taken; $u_i$ is the residue of the adjustment at the i-th time; $\phi_1$ is the order 1 autoregressive parameter; $u_{i-1}$ is the residual of the time fit immediately preceding the i-th measurement; $\phi_p$ is the autoregressive parameter of order p; $u_{i-p}$ is the residual of the fit in p times before the i-th measurement; $\varepsilon_i$ is the white residual, with a normal distribution with zero mean and constant variance $\sigma^2$, that is, $\varepsilon_i \sim N(0,\sigma^2)$. In the models, when the residuals are independent, the parameters $\phi_i$ will be null and, consequently, $u_i = \varepsilon_i$ (MAZZINI *et al.,* 2005)

In equations 1, 2 and 3, $C_i$ defines the average value of the amount of mineralized carbon in time $t_i$ in weeks; $C_0$ indicates the value of the amount of potentially mineralizable carbon; $C_1$ represents the amount of easily mineralizable carbon; k, $k_1$, $k_0$ are mineralization rates; v is the half-life; $t_i$ refers to the time of the i-th measurement, expressed in weeks (PEREIRA *et al.,* 2005). To adjust the models, we used the R software (R DEVELOPMENT CORE TEAM, 2020).

Parameters $C_0$, $C_1$, k, $k_1$, $k_0$ and v of the models were estimated using the least squares method, through which the nonlinear System of Normal Equations is obtained. In the case of nonlinear models, the system does not present a direct solution, requiring the use of iterative numerical search algorithms to obtain the parameter estimates (DRAPER; SMITH, 2014; OLIVEIRA *et al.,* 2013; RIBEIRO *et al.,* 2018a; PRADO *et al.,* 2020). Several iterative processes are described in the literature, and the Gauss-Newton algorithm was used in this study. This algorithm considers the Taylor series expansion to approximate the nonlinear regression model with linear terms and then apply the ordinary least squares method to estimate the parameters (RIBEIRO *et al.,* 2018b; SILVA *et al.,* 2019c; SILVA *et al.,* 2021; SILVEIRA *et al.,* 2018).

The assumptions of regression models were tested by the following tests: Shapiro-Wilk, to check the assumption of normality of errors; Breusch-Pagan, to test the hypothesis that errors are homoscedastic and the Durbin-Watson test, to check the independence of errors. When the Durbin-Watson test rejected the null hypothesis that the experimental errors were independent, the model errors were considered as follows: $u_i = \phi_1 u_{i-1} + \varepsilon_i$, where $\phi_1$ is the first-order autocorrelation parameter AR(1) and $\varepsilon_i$ is white noise (FRUHAUF, *et al.,* 2022; JANE, *et al.,* 2020b; MORETTIN; TOLOI, 2006). In cases where the assumption of normality was met, the confidence interval with 95% probability was estimated for the model parameters based on the expression:

$$\mathrm{CI}(\beta i) : \mathrm{bi} \pm \mathrm{t}(v;0;025).\mathrm{S}(\mathrm{bi})$$

where: $b_i$ is the estimate for the parameter ($\beta_i$); $S(b_i)$ is the standard error of the estimate and $t(v;0;025)$ is the upper quantile of the Student's t-distribution, considering $\alpha$= 5 % and the degree of freedom $v=n-d$, where $d$ is the number of parameters of the model.

The models are compared regarding the quality of the fit and it is indicated which model is most suitable to describe the mineralization curve as a function of time. The following criteria were used:

**i.** Adjusted coefficient of determination, $R^2_{aj}$:

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

where: $R^2$ is the coefficient of determination; n is the number of observations and $d$ is the number of model parameters. One model should be preferred over the other if it has a higher value of $R^2_{aj}$.

**ii.** Residual standard deviation, $RSD$:

$$DPR = \sqrt{QME}$$

where: $QME$ is an estimate of the residual variance. The lower the $RSD$ value, the better the model fit.

**iii.** Akaike Information Criterion, AIC

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

where: $L\left(\tilde{\theta}\right)$ is the maximum of the likelihood function, p is the number of parameters in the model, and log is the natural logarithm operator.

## Results and discussion

The results obtained by the 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 ($p$>0.05). The Breusch-Pagan test indicated residual homoscedasticity for all models and treatments ($p$>0.05). In the Durbin-Watson test, there was a correlation between Forest and Acacia treatments, for the Stanford & Smith model and the Juma model, and an adjustment with AR(1) first-order autoregressive errors was presented to model the dependence of residuals of these treatments. Error correlation was expected because measurements were made over time for the same observation. Silva *et al.* (2019a) observed a correlation in the fit of nonlinear models to carbon mineralization data for pig manure. The treatments evaluated by the Cabrera model showed independence of errors ($p$>0.05); the Mimosa and Pasture treatments in the Stanford & Smith and Juma models also showed independence of residual errors ($p$>0.05).

Model parameter estimates and their respective 95% confidence intervals are presented in Tables 2, 3 and 4. For the Stanford & Smith and Juma models (TABLES 2; 3), the confidence intervals did not include the value zero in any treatment, indicating that all parameters were significant, thus, the models fitted these treatments (ZEVIANI *et al.*, 2012).

Considering the confidence intervals for the estimation of parameter $C_0$ of the Stanford & Smith model (TABLE 2), there was an overlap between the confidence intervals in the Forest, Pasture and Acacia treatments, indicating that

**Table 1** – P-values of the tests applied to the model errors for mineralized carbon in mg $CO_2 kg^{-1}$ of the analyzed treatments.

| Treatments | Model | SW p-value | BP p-value | DW p-value |
|---|---|---|---|---|
| Mimosa | Stanford & Smith | 0.7601 | 0.3436 | 0.7080 |
| Mimosa | Cabrera | 0.9990 | 0.5313 | 0.6440 |
| Mimosa | Juma | 0.7149 | 0.8218 | 0.2720 |
| Floresta | Stanford & Smith | 0.2850 | 0.0783 | 0.0320 |
| Floresta | Cabrera | 0.2825 | 0.1540 | 0.0620 |
| Floresta | Juma | 0.6234 | 0.1764 | 0.0180 |
| Acácia | Stanford & Smith | 0.3795 | 0.6055 | 0.0240 |
| Acácia | Cabrera | 0.1015 | 0.4546 | 0.7640 |
| Acácia | Juma | 0.4692 | 0.5121 | 0.0420 |
| Pastagem | Stanford & Smith | 0.3795 | 0.2928 | 0.1300 |
| Pastagem | Cabrera | 0.4713 | 0.5870 | 0.1340 |
| Pastagem | Juma | 0.7661 | 0.3217 | 0.1680 |

Shapiro-Wilk (SW), Durbin-Watson (DW) and Breusch-Pagan (BP)

**Source:** Prepared by the authors (2022).

the amount of mineralizable carbon is the same for these treatments. For the Forest and Mimosa treatments, there was a difference in potentially mineralizable carbon, as there was no overlap of confidence intervals, with the Forest treatment having the highest amount of potentially mineralizable carbon (TABLE 2).

For the half-life time parameter (v), in the Stanford & Smith model, there was an overlap of the confidence intervals for the Acacia, Mimosa and Pasture treatments (TABLE 2), showing that the time to mineralize half of the potentially mineralizable carbon is the same in these treatments. For the Forest and Mimosa treatments, there was no overlap in the confidence interval, thus, the time to mineralize half of the potentially mineralizable carbon is different. Floresta had a longer half-life than mimosa.

For the confidence intervals for estimating the $C_0$ parameter of the Juma model (TABLE 3), there was no overlap between the confidence intervals in the Forest and Mimosa and Forest and Acacia treatments, so there was a difference in potentially mineralizable carbon. Although plantations are different, this factor alone does not explain all the complexity existing in the soil ecosystem. Several other factors, such as the C:N ratio, the form of the N ion, among others, can influence the acceleration of carbon mineralization (FERNANDES *et al*., 2011).

The half-life time parameter (v) in the Juma model had overlapping confidence intervals for the Acacia, Mimosa and Pasture treatments, showing that the time to mineralize half of the potentially mineralizable carbon is the same. For the Forest and Mimosa treatments, there was no overlap in the confidence interval, thus, the time to mineralize half of the potentially mineralizable carbon is different. In this model, Forest had a longer half-life than Mimosa.

The Cabrera model presents two phases of mineralization, one that is easily mineralizable ($C_1$) and the other, resistant ($k_0$). The confidence interval of the parameter $k_0$ included zero for the Forest, Mimosa and Pasture treatments, so this model is reduced to Stanford & Smith, not being adequate in the description of these treatments (ZEVIANI *et al.*, 2012). Thus, in Table 4, only the parameter estimates of the Acacia treatment were presented. In fitting the Molina model (double exponential) to soil C mineralization data under eucalyptus plantations, Barreto *et al.*

**Table 2** – Stanford & Smith model parameters estimates and their respective asymptotic 95 % confidence intervals in the adjustment of mineralized C in mg $CO_2 kg^{-1}$ of the analyzed treatments

| | **Floresta** | | | | **Acácia** | | |
|---|---|---|---|---|---|---|---|
| | LL | Estimates | UL | | LL | Estimates | UL |
| $C_0$ | 1099.1750 | 1156.2270 | 1213.2790 | $C_0$ | 649.5234 | 892.5438 | 1135.5642 |
| k | 0.0552 | 0.0596 | 0.0630 | k | 0.0355 | 0.0680 | 0.1005 |
| v | 11.0023 | 11.6299 | 12.5570 | v | 6.8970 | 10.1933 | 19.5253 |
| ϕ | -0.8812 | -0.6061 | -0.0246 | ϕ | -0.0749 | 0.6004 | 0.8528 |
| | **Mimosa** | | | | **Pastagem** | | |
| | LL | Estimates | UL | | LL | Estimates | UL |
| $C_0$ | 955.1156 | 993.3 | 1036.145 | $C_0$ | 1024.2 | 1121 | 1248.74 |
| k | 0.0692 | 0.0743 | 0.0794 | k | 0.0599 | 0.0712 | 0.0830 |
| v | 8.7298 | 9.3290 | 10.0166 | v | 8.3512 | 9.7352 | 11.5717 |

LL - lower limit and UL - upper limit.

**Source:** Prepared by the authors (2022).

**Table 3** –Juma model parameters estimates and their respective asymptotic 95 % confidence intervals in the adjustment of mineralized C in mg $CO_2 kg^{-1}$ of the analyzed treatments.

| | Floresta | | | | Acácia | | |
|---|---|---|---|---|---|---|---|
| | LL | Estimates | UL | | LL | Estimates | UL |
| $C_0$ | 1773.4120 | 1886.7117 | 2000.0115 | $C_0$ | 827.4039 | 1303.6937 | 1679.9835 |
| v | 24.2287 | 26.5685 | 28.9083 | v | 9.7238 | 19.4837 | 29.2437 |
| $\phi$ | -0.8994 | -0.6412 | -0.0514 | $\phi$ | -0.0749 | 0.5339 | 0.8528 |
| | **Mimosa** | | | | **Pastagem** | | |
| | LL | Estimates | UL | | LL | Estimates | UL |
| $C_0$ | 1448.0719 | 1551.2460 | 1671.7478 | $C_0$ | 1531.39 | 1755.2322 | 1979.0662 |
| V | 17.9223 | 20.0840 | 22.6399 | v | 16.6806 | 20.9868 | 25.2929 |

LL - lower limit and UL - upper limit.

**Source:** Prepared by the authors (2022).

(2010) obtained non-significant parameters for the model, indicating the process did not present two carbon compartments.

On the other hand, the confidence intervals for the Cabrera model in the Acacia treatment did not include zero (TABLE 4), indicating that this treatment presents two phases of mineralization, one easily mineralizable with exponential behavior and the other, resistant, with constant mineralization (ZEVIANI *et al.*, 2012). Silva *et al*. (2019a) observed two phases of carbon mineralization of the treatments soil + oat straw, soil + pig manure and soil + pig manure + oat straw, in addition, Silva *et al*. (2019b) observed the same behavior for the soil + sewage sludge + oat straw treatment. The half-life (v) of the easily mineralizable carbon was estimated at 2.6 days (TABLE 4).

**Table 4** – Cabrera model parameters estimates and their respective asymptotic 95 % confidence intervals in the adjustment of mineralized C in mg $CO_2 kg^{-1}$ of the Acacia treatment.

| | Acácia | | |
|---|---|---|---|
| | LL | Estimates | UL |
| $C_1$ | 132.4864 | 165.4614 | 218.0105 |
| $k_1$ | 0.2837 | 0.4444 | 0.7099 |
| $k_0$ | 22.1004 | 25.3036 | 27.6135 |
| v | 0.9764 | 1.5597 | 2.4432 |

LL - lower limit and UL - upper limit.

**Source:** Prepared by the authors (2022).

The selection criteria for identifying the most suitable model to describe the decomposition dynamics of each plantation are listed in Table 5. The models obtained good fits in all treatments, since the values of the adjusted coefficient of determination ($R^2$adj) were above 98% (SILVA *et al*., 2019a). In the fit of nonlinear models, Stanford & Smith and Cabrera, in the carbon mineralization of pig manure and oat straw in the soil, Silva *et al*. (2019a) obtained $R^2$adj values greater than 0.97, indicating that the models adequately described the treatments studied.

In general, the models were adequate for the description of the treatments, except for the Cabrera model, which did not fit the Forest, Mimosa and Pasture treatments. The adjustments can be seen in Figures 1, 2, 3 and 4.

For the Forest treatment, the Stanford & Smith and Juma models had a good description of the carbon mineralization dynamics, presenting the same value of adjusted coefficient of determination ($R^2$adj), and the Juma model was indicated as the best to describe the treatment for the lowest Akaike Information Criterion (AIC) (TABLE 5).

The Acacia treatment was better described by the Cabrera model, as it presented lower

**Table 5** – Estimates of selection criteria: adjusted coefficient of determination ($R^2$adj), Akaike information criterion (AIC) and residual standard deviation (RSD) for the adjusted models in the description of mineralized carbon in mg $CO_2 kg^{-1}$ of the analyzed treatments.

| TREATMENTS | MODEL | SELECTION CRITERIA | | |
|---|---|---|---|---|
| | | $R^2_{aj}$ | AIC | DPR |
| Floresta | Stanford Smith | 0.9987 | 74.815 | 8.4009 |
| Floresta | Juma | 0.9987 | 74.7415 | 8.6407 |
| Acácia | Stanford Smith | 0.9882 | 94.6723 | 22.552 |
| Acácia | Juma | 0.9913 | 92.4712 | 19.2143 |
| Acácia | Cabrera | 0.9982 | 76.9349 | 9.081 |
| Mimosa | Stanford Smith | 0.9995 | 66.9897 | 5.709 |
| Mimosa | Juma | 0.9995 | 72.0856 | 7.656 |
| Pastagem | Stanford Smith | 0.9977 | 85.4717 | 14.39 |
| Pastagem | Juma | 0.9977 | 85.1513 | 14.16 |

**Source:** Prepared by the authors (2022).

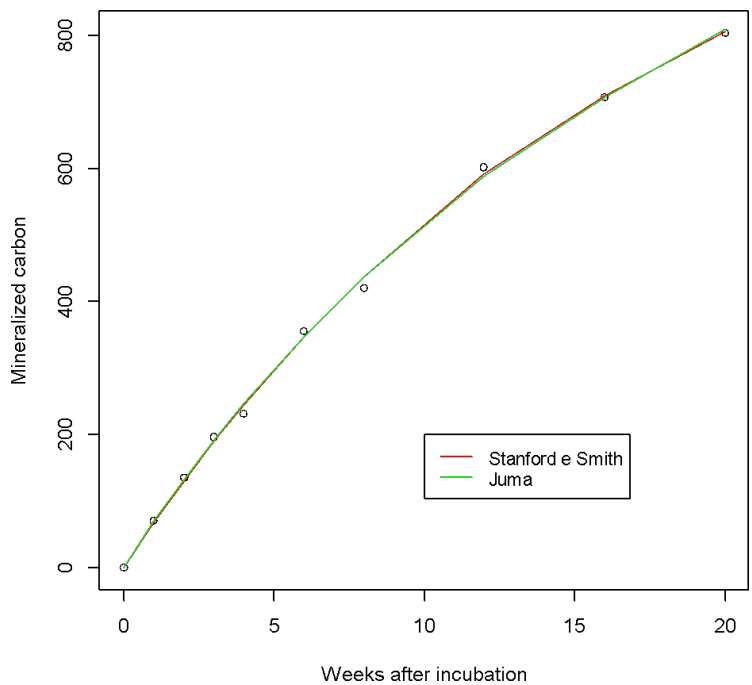
AIC and RSD values and higher $R^2$adj values (TABLE 5).

For Pasture, the Juma model was also indicated as the best, as it had higher $R^2$adj and lower AIC and RSD (TABLE 5).

The Stanford & Smith model described the Mimosa treatment better than the Juma model, as it had lower AIC and RSD values (TABLE 5).

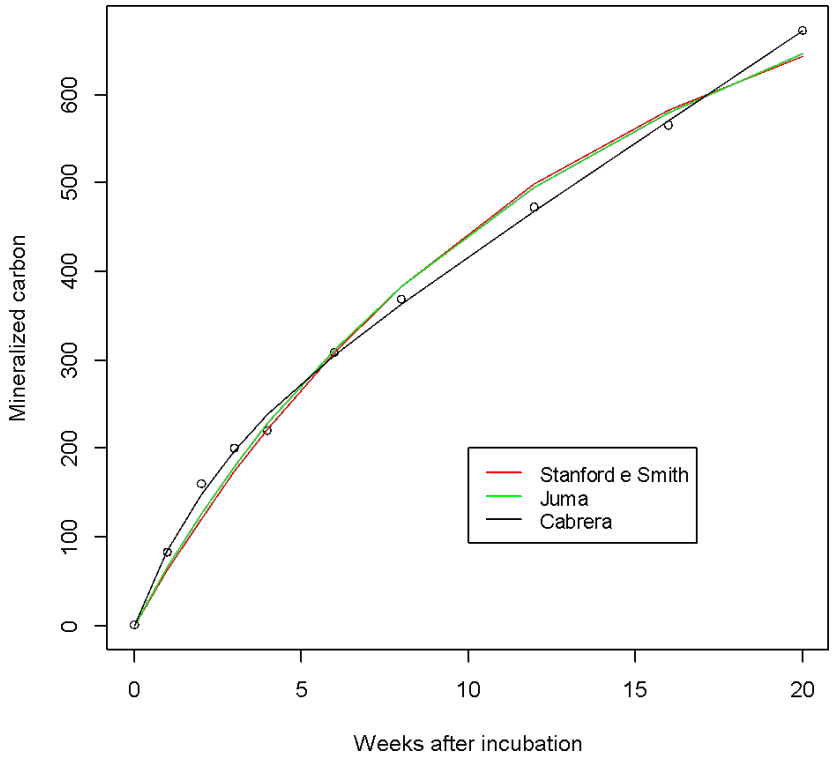
According to the literature, the Stanford & Smith model is the most used to describe soil carbon mineralization (BARRETO *et al*., 2010; FERNANDES *et al*., 2011; MARTINES *et al*.,

**Figure 1** –Stanford & Smith and Juma models to carbon mineralization (mg $CO_2 kg^{-1}$), for the Forest treatment, as a function of incubation time.



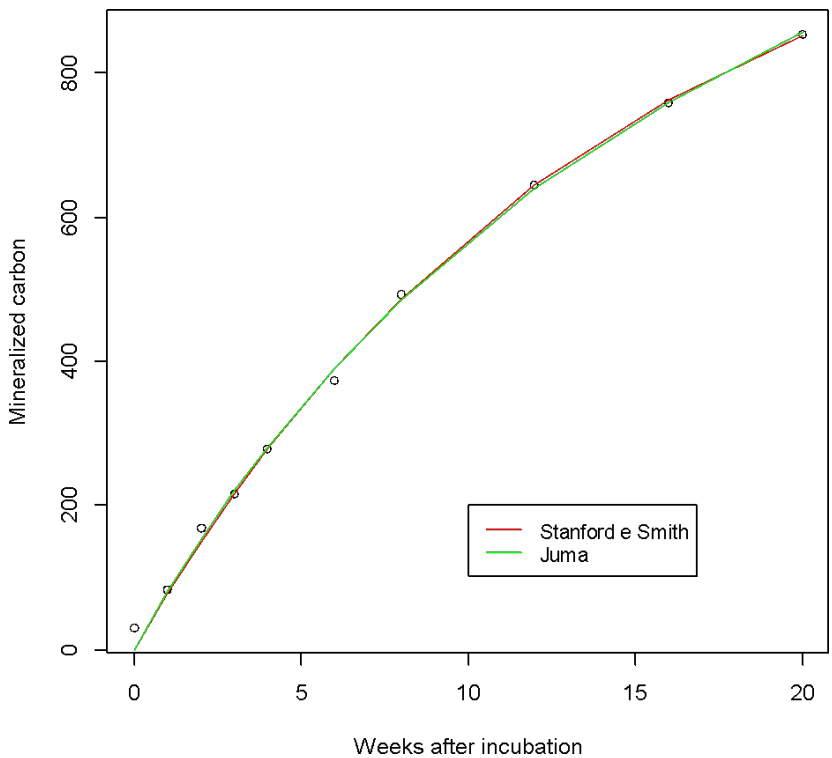

**Source:** Prepared by the authors (2022).

**Figure 2** –Stanford & Smith, Juma and Cabrera models adjusted to carbon mineralization (mg $CO_2 kg^{-1}$), for the Acacia treatment, as a function of incubation time.



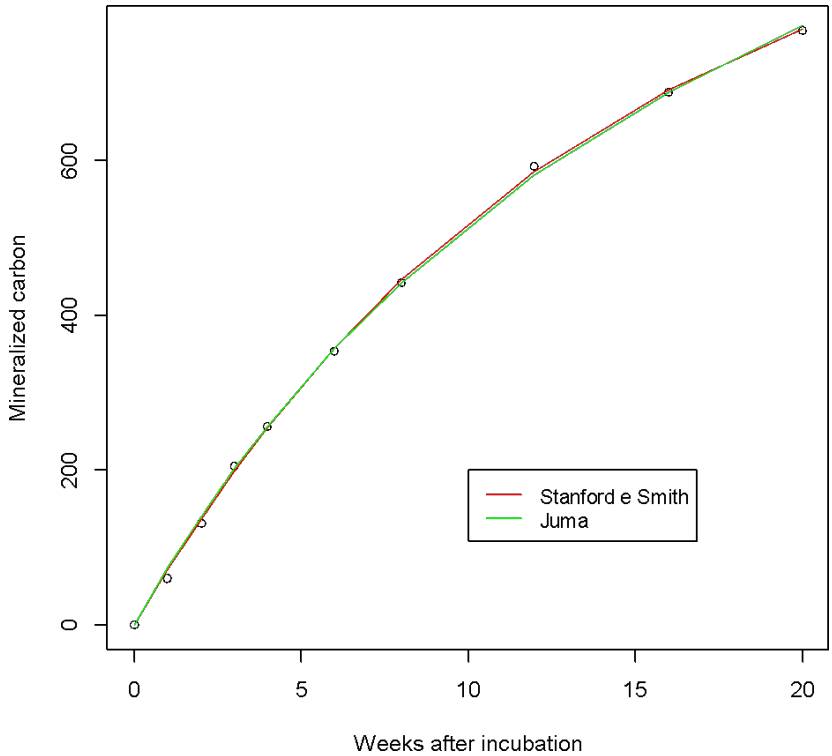

**Source:** Prepared by the authors (2022).

**Figure 3** –Stanford & Smith and Juma models adjusted to carbon mineralization (mg $CO_2 kg^{-1}$), for the Pasture treatment, as a function of incubation time.




**Source:** Prepared by the authors (2022).

**Figure 4.** Stanford & Smith and Juma adjusted to carbon mineralization (mg $CO_2 kg^{-1}$), for the Mimosa treatment, as a function of incubation time.




**Source:** Prepared by the authors (2022).

2006). However, in this study, the most suitable model for Acacia was Cabrera, and for Pasture and Forest, the Juma model.

## Conclusions

The Stanford & Smith and Juma nonlinear models adequately described the carbon mineralization process in pasture soil and soils with plant cover. For the soil with Acacia cover, the Cabrera model was the best. For soil with forest cover and pasture soil, the Juma model obtained the best fit. For the Mimosa-covered soil, the Stanford & Smith model best described carbon mineralization.

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