

Comparison of nonlinear models in the description of carbon mineralization in litter soil

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Abstract

Litter is an important source of nutrients for trees and can improve the quality of degraded soils. The objective of this study was to describe the dynamics of carbon mineralization in litter soils using nonlinear models, estimating half-life times. Soil carbon mineralization under three types of forest cover was evaluated: Atlantic forest fragment (capoeira), *Acacia auriculiformis* trees (acacia), and *Mimosa caesalpiniifolia* (sabiá) from a reforested area with a history of degradation. Twelve measurements of the mineralized carbon were made up to 222 days after the beginning of the incubation of litter soils. Stanford and Smith, Juma, and Cabrera models were fitted by the least squares method using the Gauss-Newton algorithm in the R software. The Stanford and Smith model was more appropriate in describing all treatments, based on the Akaike Information Criterion, with estimates of half-life for Acácia, Capoeira, and Sabiá soils at 25, 44, and 51 days, respectively. The Stanford and Smith and Juma nonlinear models satisfactorily described the carbon mineralization of soils of all treatments.

Keywords: Nutrient cycling. Carbon dioxide. Forest soil.

Introduction

Forest sustainability is related to nutrient cycling in order to enhance their return to the trees, with the accumulated litter being an important source of nutrients for the trees in the forest ecosystem, because as the leaves, branches and roots are incorporated into the litter and undergo the decomposition process, they release nutrients to the soil and, consequently, are available to trees (BARRETO *et al.*, 2010; GODINHO *et al.*, 2014). In addition, planting tree species is an alternative for recovering degraded areas (NUNES *et al.*, 2016), however, 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).

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The greater amount of organic matter and the presence of easily decomposing substances favor carbon mineralization at the beginning of the process, that is, the decomposition dynamics occur at decreasing rates, as the organic material is mineralized (PULROLNIK, 2009; MOREIRA; SIQUEIRA, 2006), consequently, the release of other nutrients to the soil occurs. These processes can be described by nonlinear models (PAULA *et al.*, 2019; PEREIRA; MUNIZ; SILVA, 2005; SILVA *et al.*, 2019a; SILVA *et al.*, 2019b; ZEVIANI *et al.*, 2012; OLIVEIRA *et al.*, 2013). The knowledge of the carbon (C) mineralization dynamics in the soil is essential for the development of appropriate practices in the soil use, being indicative of the organic residues contributing to the demand of trees throughout the crop cycle (BARRETO *et al.*, 2010; GODINHO *et al.*, 2014).

The nonlinear model most used to describe the dynamics of carbon in the soil is Stanford and Smith (ANDRADE; ANDREAZZA; CAMARGO, 2016; ANDRADE *et al.*, 2015), including litter decomposition data (BARRETO *et al.*, 2010; NUNES *et al.*, 2016). It is a model with two parameters that represent the potentially mineralizable carbon and the mineralization constant. Another model used is the nonlinear Juma (PAULA *et al.*, 2019; PEREIRA; MUNIZ; SILVA, 2005) with two parameters that present direct practical interpretation, potentially mineralizable carbon, and half-life, respectively. In litter soils, it may be that the mineralization process has two phases of mineralization, one phase due to easily mineralizable substances and another phase due to the more resistant substances. In processes with two phases, the use of the Cabrera model has shown a good fit (PAULA *et al.*, 2019; SILVA *et al.*, 2019a; SILVA *et al.*, 2019b; ZEVIANI *et al.*, 2012; PEREIRA *et al.*, 2009).

The objective of the study was to describe the dynamics of carbon mineralization in litter soils using the nonlinear models Stanford and Smith (1972), Juma, Paul and Mary (1984) and Cabrera (1993), indicating the most appropriate model and, also, estimating potentially mineralizable carbon and half-life times.

Material and methods

Data used to fit the models were extracted from Nunes, Rodrigues and Rodrigues (2009) and correspond to the average results of an experiment with a Red Yellow Latosol in the municipality of Conceição de Macabu, state of Rio de Janeiro, which evaluated the soil carbon mineralization under three types of forest cover: Atlantic forest fragment (capoeira), *Acacia auriculiformis* trees (acacia) and *Mimosa caesalpiniifolia* (sabiá) from a reforested area with a history of degradation.

The evaluated soil was collected in the interrow at a layer 0-10cm deep, samples were duplicated, using 50g each soil. Samples were incubated in percolation columns constructed with PVC tubes (29.4 cm in height and 4.7 cm in diameter). Carbon mineralization was assessed by CO₂ emission during incubation. The released CO₂ was captured in 10mL of a 1 mol L⁻¹ NaOH solution, the excess of which was titrated with a 0.5 mol L⁻¹ HCl solution. In litter soil samples, mineralized carbon was always measured in the same experimental units at 6, 12, 18, 25, 38, 53, 84, 112, 138, 168, 194, and 222 days from the beginning of the incubation.

Stanford and Smith models were evaluated:

$$C_i = C_0 (1 - \exp(-kt_i)) + \varepsilon_i \quad (1)$$

Juma:

$$C_i = \frac{C_0 t_i}{t_{1/2} + t_i} + \varepsilon_i \quad (2)$$

Cabrera:

$$C_i = C_1 (1 - \exp(-k_1 t_i)) + k_0 t_i + \varepsilon_i \quad (3)$$

In the models, C_i is the mineralized carbon, in mg CO₂ kg⁻¹, until time t_i (in days); C_0 is the fraction of organic carbon susceptible to mineralization; k , k_1 , and k_0 are mineralization constants; $t_{1/2}$ is the half-life of the potentially mineralizable carbon; C_1 is the fraction of easily mineralizable organic carbon and ε is the experimental error with normal distribution with mean 0 and variance σ^2 . The half-life ($t_{1/2}$) of the Stanford and Smith and Cabrera models were estimated by $t_{1/2} = \ln(2)/k$ and $t_{1/2} = \ln(2)/k_1$, respectively (ZEVIANI *et al.*, 2012).

Tests applied to check the assumptions of the regression models: Shapiro-Wilk, to check the assumption of error normality; Breusch-Pagan, to test the hypothesis that the errors are homoscedastic and the Durbin-Watson test, to check the independence of the errors. When the Durbin-Watson test rejected the null hypothesis that the experimental errors were independent, the model errors were considered as follows: $\varepsilon_t = \varphi \varepsilon_{t-1} + \lambda_t$, at which φ is the first-order autocorrelation parameter AR(1) and λ_t is white noise (MORETTIN; TOLOI, 2006; SAVIAN; MUNIZ, 2007; PRADO; SAVIAN; MUNIZ, 2013; SOUSA *et al.*, 2014; MUANGA *et al.*, 2016; MUNIZ; NASCIMENTO; FERNANDES, 2017; RIBEIRO *et al.*, 2018a; JANE, *et al.*, 2020; PRADO *et al.*, 2020). In cases in which the assumption of normality was met, the confidence interval was estimated with a 95% probability for the model parameters based on the expression:

$$\text{IC}(\theta) \Rightarrow \hat{\theta}_i \pm t_{(q; 0.025)} S(\hat{\theta}_i) \quad (4)$$

at which: $\hat{\theta}_i$ is the estimate of the model parameter; $t_{(q; 0.025)}$ is the value in the t-Student distribution with $q = n - p$ degrees of freedom and area of 0.025 to the right; $S(\hat{\theta}_i)$ is the standard error of the estimate of the parameter $\hat{\theta}_i$, obtained by the square root of the corresponding term on the diagonal of the estimated variance and covariance matrix (DRAPER; SMITH, 2014).

The goodness of fit was assessed by the adjusted coefficient of determination:

$$R_{aj}^2 = 1 - \frac{(n - i)(1 - R^2)}{n - p} \quad (5)$$

And by residual standard deviation:

$$DPR = \sqrt{QME} \quad (6)$$

The selection of the best model was made based on Akaike's information criterion:

$$AIC = -2 \ln L(\hat{\theta}) + 2p. \quad (7)$$

In the expressions, n is the number of observations used to fit the model; i is related to the intercept of the model, which is equal to 1 if there is an intercept and 0 if not, p is the number of parameters; $R^2 = 1 - \frac{SSE}{SST}$ is the coefficient of determination, with SSE being the sum of squares of errors, SST being the sum of squares of the total, $MSE = \frac{SSE}{n-p}$, the mean square of the error; $\ln L(\hat{\theta})$ is the value of the natural logarithm of the likelihood function, considering parameter estimates.

Estimation of parameters of nonlinear regression models was done approximately way by iterative numerical methods, as there is no closed way to solve the system of normal equations. Among the iterative methods, the Gauss-Newton method is the most used (PEREIRA; MUNIZ; SILVA, 2005; FERNANDES et al., 2015; FERNANDES; PEREIRA; MUNIZ, 2017; SILVEIRA et al., 2018; RIBEIRO et al., 2018b; JANE, et al., 2019; SILVA et al., 2019c; SILVA et al., 2019d). Parameters were estimated using the generalized least squares method, implemented in the gnls function, from the nlme package (PINHEIRO et al., 2015), in R software (R DEVELOPMENT CORE TEAM, 2015).

Results and discussion

The Cabrera model did not fit any treatment, since the confidence intervals for at least one parameter included a value of zero, indicating that the treatments did not have two mineralizable carbon compartments. Thus, the results for this model were not presented in the following tables. In fitting the Molina model (double exponential) to C mineralization data from soil under eucalyptus plantation, Barreto et al. (2010) obtained non-significant parameters for the model, thus indicating that the process did not have two carbon compartments. On the other hand, Silva et al. (2019a) reported two phases of carbon mineralization of the treatments soil + oat straw, soil + pig slurry, and soil + pig slurry + oat straw, in addition, Silva et al. (2019b) observed the same behavior for soil + sewage sludge + oat straw.

Table 1 lists the results of the analysis of errors estimated by the Stanford and Smith and Juma models, based on carbon mineralization data in litter soil for the Shapiro-Wilk (SW), Breusch-Pagan (BP), and Durbin-Watson (DW) tests. For all treatments and both models, the SW test was not significant (p -value > 0.05), thus the assumption of error normality was corroborated by the test. The BP test evidenced that the hypothesis of homogeneity of variances was not rejected (p -value > 0.05) for all treatments and both models, indicating that the residual variance was homogeneous. The DW test indicated that for all treatments and both models the errors were independent (p -value > 0.05), except for the Juma model fit to the Acacia soil treatment (p -value < 0.05). The independence of errors was rejected for this treatment because the measurements were made in the same experimental unit, so the parameter ϕ was added to explain this correlation (TABLE 3), that is, for this treatment an adjustment with first-order auto-regressive error AR (1). Silva et al. (2019a), Silva et al. (2019b), and Hess and Schmidt (1995) also observed a correlation in errors when fitting nonlinear models to cumulative data of CO_2 mineralization of various organic residues in the soil.

Table 1 – P-values of the Shapiro-Wilk (SW), Durbin-Watson (DW), and Breusch-Pagan (BP) tests applied to errors of the models and goodness of fit evaluators, adjusted coefficient of determination (R_{aj}^2), residual standard deviation (RSD), and Akaike's information criterion (AIC) for mineralized carbon, for treatments.

Treatments	Model	SW p-value	DW p-value	BP p-value	Raj2	RSD	AIC
Acácia	Stanford and Smith	0.5489	0.3620	0.2516	0.9887	21.53	120.52
	Juma	0.7665	0.0060	0.1790	0.9690	33.61	130.28
Capoeira	Stanford and Smith	0.4174	0.9540	0.1371	0.9947	19.86	118.42
	Juma	0.9507	0.3700	0.7260	0.9921	23.58	122.89
Sabiá	Stanford and Smith	0.7716	0.7100	0.7228	0.9827	35.17	133.28
	Juma	0.9561	0.2400	0.4232	0.9744	42.48	138.19

Source: Elaborated by the authors (2020).

Estimates of parameters of the Stanford and Smith model and the half-life ($t_{1/2}$) with their respective 95% confidence intervals are listed in Table 2. It can be seen from the confidence intervals that all model parameters did not include the zero value, indicating that they are significant for all treatments.

Table 2 – Estimates for the parameters of the Stanford and Smith model fitted to the mineralized carbon of the treatments, half-life ($t_{1/2}$), and their respective 95% asymptotic confidence intervals (LL - lower limit and UL - upper limit).

Parameters	LL	Estimates		UL
		Acácia	Capoeira	
C_0	546.1478	569.0000		592.9476
	0.0238	0.0273		0.0313
	22.1198	25.3714		29.1238
$t_{1/2}$	737.3757	770.00000		806.7935
	0.0137	0.0156		0.0176
	39.3609	44.3472		50.2644
C_0	722.6286	785.7000		867.2678
	0.0106	0.0135		0.0167
	41.4066	51.2682		64.9622

Source: Elaborated by the authors (2020).

Considering the confidence intervals of C_0 of litter soils, there was no overlap between the Acácia soil and the Capoeira, and Sabiá soils, thus indicating that the potentially mineralizable carbon of this treatment was lower than that of the two treatments (TABLE 2). A similar result was obtained for $t_{1/2}$. The half-lives of the Acácia, Capoeira and Sabiá soils considering the Stanford and Smith

model were approximately 25, 44, and 51 days, and the potential mineralizable carbon estimated at 569, 770 and 785 mg CO₂ kg⁻¹, respectively.

Table 3 lists the estimates of parameters of the Juma model with their respective 95% confidence intervals.

Table 3 – Estimates for the parameters of the Juma model fitted to the mineralized carbon of treatments and their respective 95% asymptotic confidence intervals (LL - lower limit and UL - upper limit).

Parameters	LL	Estimates	UL
		Acácia	
C_0	585.2125	669.3164	753.4202
$t_{1/2}$	18.8531	33.3629	47.8727
φ		0.5225	
		Capoeira	
C_0	943.9254	1019.3420	1109.4929
$t_{1/2}$	59.5298	72.7270	89.5100
		Sabiá	
C_0	932.3150	1084.1800	1305.0996
$t_{1/2}$	63.4984	91.6100	136.6673

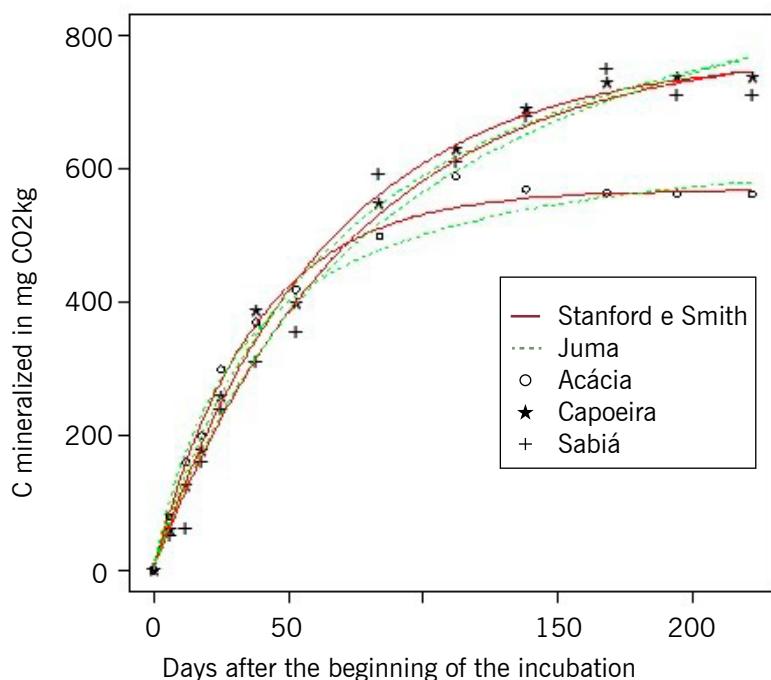
Source: Elaborated by the authors (2020).

By the confidence interval of C_0 (TABLE 3), it was obtained a lower amount of potentially mineralizable carbon for the Acácia treatment in relation to the Capoeira and Sabiá treatments, as there was no overlap of the confidence intervals. The $t_{1/2}$ was estimated at approximately 33, 72, and 91 days for the treatments Acácia, Capoeira, and Sabiá, respectively.

Comparing the ranges (upper limit - lower limit) of the confidence intervals of the parameters C_0 and $t_{1/2}$ of the Juma model (TABLE 3) and the Stanford and Smith model (TABLE 2), it is observed that for all treatments the range of parameters of the Juma model was wider, so the intervals of the estimates were less accurate. In addition, comparing the confidence intervals of C_0 from the Stanford and Smith model (TABLE 2) with those of the Juma model (TABLE 3), it can be seen that the Juma model estimated a higher amount of potentially mineralizable carbon than the Stanford and Smith model, as there was no overlap in the intervals, except for the Acacia treatment. Thus, it is important to emphasize that the variation observed in the estimates of C_0 and $t_{1/2}$ in the different models is due to peculiarities of the statistical models (ZEVIANI et al., 2012).

For both adjusted models, R_{aj}^2 values greater than 96% were obtained (TABLE 1) indicating a good fit of the models to the data, as it can be seen in Figure 1, in addition to the close values of residual standard deviation (RSD) for both models being smaller for the Stanford and Smith model. Thus, the two models were suitable to describe carbon mineralization in soil. As lower AIC values (TABLE 1) were obtained for all treatments with the Stanford and Smith model, this model proved to be more suitable for describing all treatments under study.

Figure 1 – Stanford and Smith and Juma models fitted to the mineralized CO_2 accumulated during soil incubation under Acácia, Sabiá, and Capoeira stand.



Source: Elaborated by the authors (2020).

Conclusion

Stanford and Smith and Juma nonlinear models adequately described the carbon mineralization process of litter soils. The Stanford and Smith model was the most suitable in describing all treatments with estimates of potentially mineralizable carbon at 569, 770 and 785 $\text{mg CO}_2 \text{ kg}^{-1}$ and half-lives of 25, 44 and 51 days of the Acácia, Capoeira and Sabiá, respectively. The Acacia soil obtained a smaller amount of potentially mineralizable carbon than the Capoeira and Sabiá soils.

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Comparação de modelos não lineares na descrição da mineralização de carbono em solo de serapilheira

Resumo

A serapilheira é uma importante fonte de nutrientes para as árvores e pode melhorar a qualidade dos solos degradados. O objetivo deste trabalho foi descrever a dinâmica de mineralização do carbono em solos de serapilheiras por modelos não lineares, estimando os tempos de meia-vida. Foi avaliada a

mineralização de carbono de solo sob três coberturas florestais: fragmento florestal de mata atlântica (capoeira), espécies arbóreas de *Acacia auriculiformis* (acácia) e *Mimosa caesalpiniifolia* (sabiá) de área reflorestada com histórico de degradação. Foram feitas 12 medidas do carbono mineralizado até os 222 dias do início da incubação de solos de serapilheira. Foram ajustados os modelos Stanford e Smith, Juma e Cabrera, pelo método de mínimos quadrados utilizando o algoritmo de Gauss-Newton por meio do software R. O modelo Stanford e Smith foi mais adequado na descrição de todos os tratamentos, com base no Critério de Informação de Akaike com estimativas dos tempos de meia-vida dos solos de Acácia, de Capoeira e de Sabiá de 25, 44 e 51 dias, respectivamente. Os modelos não lineares Stanford e Smith e Juma descreveram de forma satisfatória a mineralização do carbono dos solos de todos os tratamentos.

Palavras-chave: Ciclagem de nutrientes. Dióxido de carbono. Solo florestal.

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