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Adjustment of decay rates of organic matter in a *Latossolo Vermelho-Amarelo* in the Araripe National Forest, Brazil

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The use of mathematical models is an alternative way to understand how management practices affect soil organic matter (SOM) dynamics because such models yield results on time scales that would be impossible to observe in field studies. The aim of this study was to parameterise and calibrate the application *Century* 4.0 in terms of the edaphoclimatic conditions of a *Latossolo Vermelho-Amarelo* of the Araripe Plateau and simulate the soil C dynamics in each compartment. The study was conducted in the Araripe National Forest (Floresta Nacional do Araripe — FLONA). The soils are classified as Latossolos Vermelho-Amarelos with a medium clayey texture and a clay fraction consisting of kaolinite with iron and aluminium oxides. The physical and chemical properties of the soils were obtained at a depth of 0.00-0.20 m in 2012 and 2013. The best total organic carbon (TOC) result was an error of only 3% between the measured and simulated values, which was obtained with a PRDX (4) adjustment of 140 g m^{-2} C. After correcting for the C decay rate in the passive (PC), slow (SC) and active compartments (AC), absolute errors lower than 10% were obtained for the C values. The abiotic correction factors specific to each compartment were 0.89 for the active and passive compartments and 1.12 for the slow compartment. The sensitivity analysis indicates that all compartments are sensitive to variations in maximum and minimum temperature and that the clay content affects the TOC and the passive compartment.

Key words: *Century* model calibration, soil carbon compartments.

INTRODUCTION

Stocks of soil organic matter (SOM) are sensitive to cultivation practices, land-use conversions, mineralogy and edaphoclimatic conditions of a region, all of which affect its long-term balance and decomposition (Lin et al., 2014). Thus, one of the possible reasons for reduction of carbon stocks in soil compartments involves changes in the organo-mineral interactions in soils exposed to weathering.

Soils with a high degree of weathering such as the Latosols (predominance of low-activity clays) are very dependent on organic matter to maintain adequate function and sustainability (Silva and Mendonça, 2007).

The use of mathematical models is an alternative approach to understanding how management practices affect the SOM dynamics in that such models yield results on time scales that would be impossible to observe in field studies.

Several mathematical models have been developed to address the SOM distribution in compartments with various soil decay and permanence rates, that is, active (rapid cycling), slow (intermediate) and passive (slow) rates. One example is the *Century* model, which was developed for temperate climate soils (Parton, 1996; Segoli et al., 2013). The proposed model is used to classify the SOM into compartments of decreasing rates that follow first-order kinetics.

Century has been successfully used to simulate SOM dynamics on decadal time scales, which are affected by inputs of organic matter and environmental controls such as temperature and humidity. Therefore, it is necessary to calibrate the model for soils in different climates. This calibration involves, among other actions, the adjustment of abiotic factors that correct the decay constants of the various compartments.

Another aspect to be considered in the SOM dynamics is the effects of the fine-particle fractions (clay and silt) and the mineralogic aspects of the clays (Van Veen and Paul, 1981). However, these mineralogic aspects are not taken into account in *Century*, which can lead to an underestimation of SOM in the passive compartment of soils containing 1:1 clays, such as kaolinites, and abundant iron and aluminium oxides, which are primarily responsible for SOM stability in microaggregates (Sollins et al., 1996). In *Century*, this stabilisation is taken into account by adopting an "aggregation factor" for the passive compartment.

Given the above issues and a lack of data regarding SOM stabilisation in kaolinitic soils in semi-arid regions, the assumptions made in this study are: The reduction of carbon storage in the soil compartments is a result of changes in organo-mineral interactions in the elements exposed soils e the century application allows to evaluate the dynamics of organic matter in soils subjected to cutting shallow type of native vegetation in semiarid region. The assumptions made in this research are: The reduction in the stock of carbon in the soil compartments is a result of changes in organo interactions in the weather exposed soils and Century Application allows evaluation of the dynamics of organic matter in soils subjected to the cut (shallow type) of native vegetation in semi-arid region. The aims of this study were to parameterise and calibrate *Century* 4.0 for the edaphoclimatic conditions of a Latossolo Vermelho-Amarelo of the Araripe Plateau, in northeastern Brazil, and to simulate the C dynamics in each compartment of this soil.

MATERIALS AND METHODS

Location and characterisation of the study area

The study was conducted in the Araripe National Forest (FLONA-Araripe), located in the eastern part of the Araripe Plateau, in the extreme southern part of the state of Ceará. The study area was bounded by latitudes 9183896 and 9199039 N and longitudes 435987 and 460703 S, Zone 24S, SAD-69 datum). FLONA-Araripe has an area of approximately 383 km^2 and is at an elevation of approximately 1,000 m. The topography is generally flat aside from prominent cliffs on the northwest, and the relief is approximately 400 m (Alves et al., 2011).

Vegetation in FLONA-Araripe consists primarily of semi-evergreen rain forest and savannah ("cerradão"). However, the species *Nectandra cuspidata* Ness, commonly known as *louro urubu,* predominates in the study area.

The regional climate is of the Aw' type, that is, tropical and rainy, with mean annual maximum and minimum temperatures of 34 and 18°C and a mean annual rainfall of 1,033 mm. The monthly mean values are distributed as shown in Figure 1. These data were obtained from the Brazilian National Institute of Meteorology (Instituto Nacional de Meteorologia) (Inmet, 1993).

The soils consist primarily of Latossolo Vermelho-Amarelo (EMBRAPA, 1999) with a clayey texture and containing iron and aluminium oxides; the clay fraction consists of kaolinite. The characterisation was performed by fluorescence and X-ray diffraction with spectral interpretation using the application *X'PERT HighScore Plus* (PW3212).

The physical (texture and density) and chemical (C content and pH) properties of the soils at a depth of 0.00-0.20 m and their respective analytical methods and references are presented in Table 1.

The composite sample for the analyses of the physical and chemical properties of the soils was prepared by homogenising a mixture of five simple samples collected with a Dutch hand auger in 2012 and 2013. The simple samples were collected in a zigzag pattern within a 200-m radius from random georeferenced points. Before the analytical procedures, the composite sample was air dried, crushed and passed through 2-mm mesh sieves.

The climate parameters (Figure 1) and physical and chemical properties of the soils (Table 1) were used in the calibration and sensitivity analysis of the SOM dynamics model in *Century* 4.0 (Parton et al., 1987).

Mathematical model of carbon dynamics

The SOM dynamics are evaluated in various cycling times in *Century*: fast (1 to 5 years), intermediate (20 to 40 years) and slow (200 to 1,500 years), which represent the active, slow and passive compartments, respectively.

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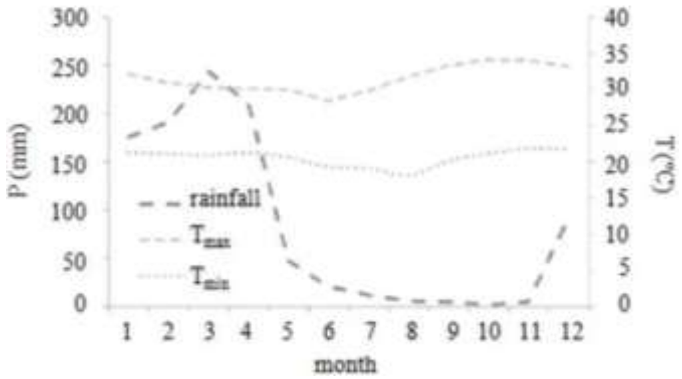


Figure 1. Monthly mean maximum and minimum temperature and rainfall values.

Table 1. Physical and chemical properties of the soils and their respective analytical methods and references.

Property		Method	Reference
		Physical	
Particle size (-)			- Embrapa (1997)
Sand:	0.46	Pipette	
Silt:	0.16		
Clay:	0.38		
Density (g.cm^{-3}):	0.80	Volumetric ring	
		Chemical	
C content (mg.m^{-2})			
TOC:	5,948.8	Oxidation with potassium dichromate	- Adapted from Yeomans and Bremner (1988)*
Passive C:	2,864.0	Differential solubility	- Adapted from Swift (1996)*
Slow C:	2,968.3	Water flotation	- Adapted from Anderson and Ingram (1989)*
Active C:	116.5	Irradiation - extraction	- Adapted from Islam and Weil (1998) and Brookes et al. (1982)*
pH (-):	4.47	Potentiometric	- Embrapa (1997)

*Cited in Mendonça and Matos (2005).

An assessment of the SOM dynamics was conducted based on the C decay rate in the various soil compartments, which is affected by climate factors (humidity and temperature), edaphoclimatic factors (aerobiosis and availability of nutrients) and soil management practices. According to Parton et al. (1987), *Century* incorporates the effects of these factors in the first-order decay kinetics to model the SOM dynamics (Equation 1):

$$dC_i/dt = -K_i C_i, \tag{1}$$

where dC_i/dt is the C decay rate in the *i-th* soil compartment, K_i is the decay constant, and C_i is the C concentration.

There are eight soil compartments: surface and soil structural residues (i = 1 and 2, respectively); the active fraction (i = 3); surface microorganisms (i = 4); surface and soil metabolic residues (i = 5 and 6, respectively) and the slow and passive fractions (i = 7 and 8, respectively).

In all compartments, the combined effect of moisture (M_d) (expressed in terms of the monthly total rainfall and potential evapotranspiration) and temperature (T_d) (expressed in terms of mean monthly soil temperature) constitutes an abiotic factor (A) (Equation 2) that corrects Equation 1. The potential evapotranspiration and mean temperature of the soil are calculated from the monthly mean maximum and minimum air temperatures using the Linacre equations (Linacre, 1977).

$$A = M_d\, T_d \tag{2}$$

In the surface and soil structural residue compartments (i = 1 and 2), Equation 1 is also corrected by the L_c factor (Equation 3), which is a function of the lignin content (L_s). In the active compartment (i = 3), it is also corrected by the soil texture factor (T_m) (Equation 4), which is a function of the total fraction of silt and clay (T). In this case, because only the active (i = 3), slow (i = 7) and passive (i = 8) fractions are evaluated, the correction factors of the decay kinetics are not due to the lignin content.

$$L_c = e^{-3L_s} \tag{3}$$

$$T_m = (1 \quad T) \tag{4}$$

In the C dynamics, the total C fraction that leaves the active compartment is subdivided into four different flows: microbial respiration (F_T) (Equation 5), leaching of soluble organic carbon C_{LEA} (Equation 6) and C stabilisation in the passive (C_{AP}) (Equation 7) and slow compartments (C_{AS}) (Equation 8). In this process, the carbon derived from the slow compartment is relocated to the passive (C_{LP}) (Equation 9) and active SOM compartments (C_{LA}) (Equation 10). In relocating to the active compartment, it is believed that 55 % of the C is lost by microbial respiration (Leite et al., 2003).

$$F_T = 0.17 - 0.68T \tag{5}$$

$$C_{LEA} = \frac{(H_2\,O)30}{18\,(0.01+0.04T_S\,)} \tag{6}$$

$$C_{AP} = 0.003 + 0.032T_c \tag{7}$$

$$C_{AS} = \,[1 - (C_{AP} - C_{LEA} - F_T] \tag{8}$$

$$C_{LP} = 0.003 - 0.009T_C \tag{9}$$

$$C_{LA} = 1 - C_{LP} - 0.55 \tag{10}$$

where $(H_2\,O)_{30}$ and 18 are, respectively, the leaching water depth and the critical mineral leaching water depth below a soil depth of 0.30 m, and T_S and T_C are the amounts of sand and clay in the soil, respectively. The leaching water depth is calculated from a simplified water balance.

Calibration of the soil carbon dynamics model, sensitivity analysis and simulation

Century consists of a pre-processor (FILE100, which manages the creation and update of input files, and EVENT100, which creates an event file (.SCH)), a processor (the executable file *Century* (.PLT)) and a post-processor (LIST100, which provides the simulation results).

The model calibration was performed in two steps, considering the equilibrium condition established over 6,000 years in the 0.00-0.20 m layer. In the first step, simulations using the *default* option "Rainforest" were performed by varying the maximum monthly net production of C of the PRDX(4) forest, available in the TREE.100 file of the FILE100 utility, thereby obtaining consecutive TOC and C concentrations in the active, slow and passive compartments. Linear graphs of the "relative error" (E) *versus* PRDX(4) were obtained from the results for each C concentration. The PRDX(4) corresponding to the lowest E of the TOC was estimated from the graphs. In this step, for the same PRDX(4), discrepancies in the C concentrations in each compartment were observed.

In the second step, the PRDX(4) obtained in the first step was fixed, and the decay constants were adjusted in the active (i = 3), slow (i = 7) and passive (i = 8) compartments (DEC3.2, DEC5 and DEC4 of the FIX.100 file of the FILE100 utility, respectively). In this step, linear graphs of the C concentration in each compartment *versus* DEC5, DEC4 and DEC3.2 were obtained. Adjusted decay constants (K_i^*) were obtained from the graphs, corresponding to the lowest E values of the C concentrations in each compartment.

The characteristic correction factor *A** for the study area was obtained based on the adjusted decay constants in each compartment (K_i^*: DEC3.2, for i = 3, DEC5, for i = 7 and DEC4, for i = 8), using Equation 11, and considering the *default* values of the FIX.100 file as a reference (K_i: 7.3 year^{-1}, for i = 3, 0.2 day^{-1}, for i = 7 and 0.0045 year^{-1}, for i = 8).

$$K_i^* = A^*.K_i \tag{11}$$

A sensitivity analysis was performed by evaluating the absolute values of the angular coefficients (a) of the slopes obtained in each step of the calibration (high values of a indicate greater sensitivity of the model to the parameter evaluated in a given compartment). A sensitivity analysis was also performed for the variables $T_{\max}$, $T_{\min}$ and the clay fraction.

Based on the adjusted values of PRDX(4), DEC3.2, DEC5 and DEC4, the C dynamics were simulated in the 0.00-0.20 m layer, considering an equilibrium condition established over 6,000 years.

The data were subjected to an analysis of the correlation coefficient using the Microsoft Excel data analysis tool.

RESULTS AND DISCUSSION

Calibration of *Century*

Figure 2 (A) shows that the best result for the TOC was obtained for a PRDX(4) of 140 g m^{-2} C because the discrepancies between the measured and simulated values generated an error of only 3%. However, for this PRDX, there was an overestimation of C in the slow compartment (16.7%) and an underestimation in the active and passive compartments (9.6 and 10%, respectively).

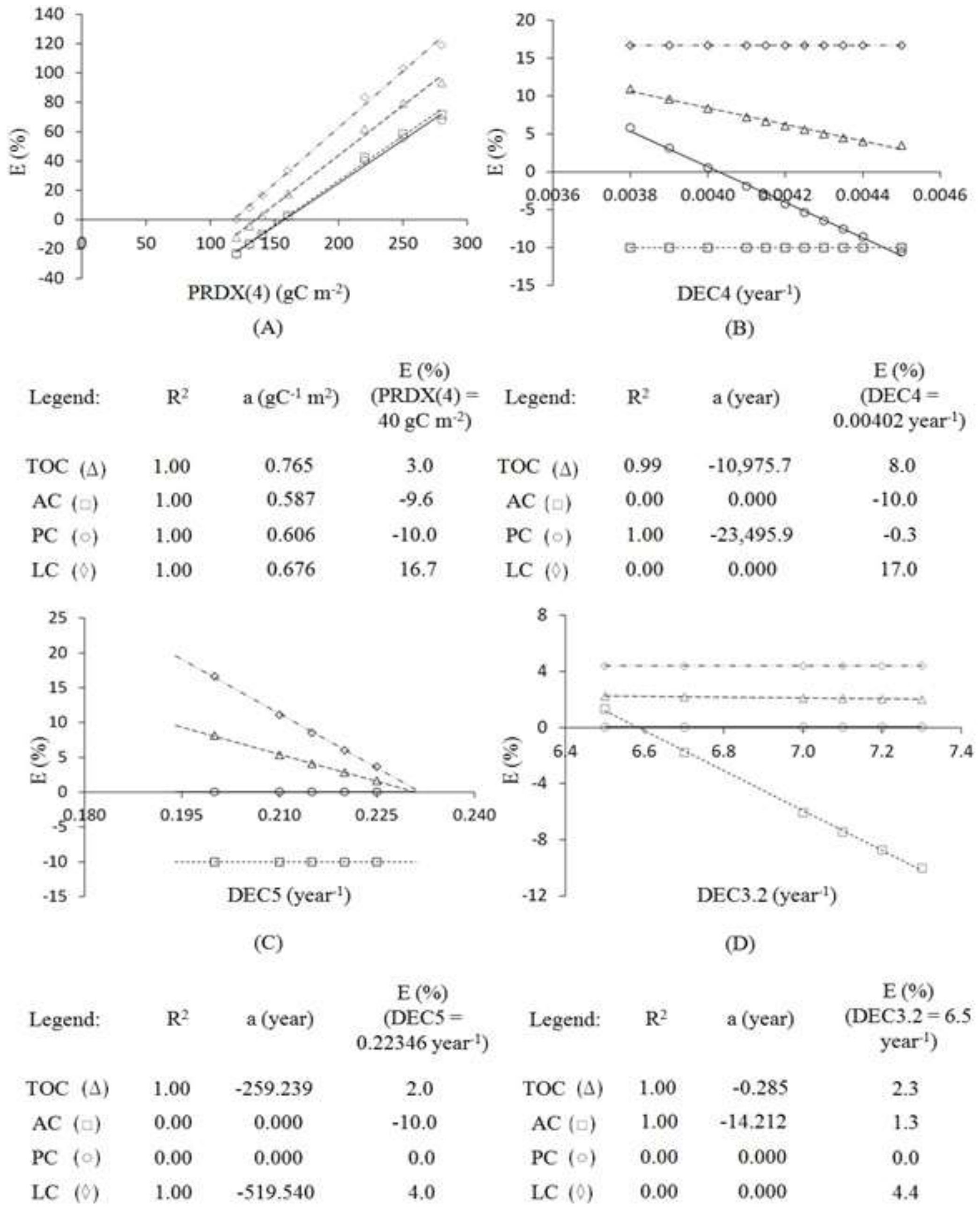
The underestimation of the TOC in the passive compartment is consistent with the results obtained by Silva and Mendonça (2007). According to these authors, the underestimation in the passive compartment in tropical soils dominated by kaolinite arises from the interference of the Fe and Al contents in the stabilisation of SOM.

The stated that the high stability of the organo-minerals arises from the electrostatic interaction of the positive charges of the Fe and Al oxides and the negative charges of the SOM, thereby hampering microbial access to the organic substrate. The oxides are responsible for the disorganisation of the clay particles on a microscopic scale, thus hampering the face-to-face orientation of the kaolinite crystals. This disorientation prevents the formation of the deoxy plasma and favours the onset of the formation of the granular structure, which ensures greater resistance to anthropogenic interference and to changes in soil management (Silva and Mendonça, 2007).

The X-ray diffractogram (Figure 3) shows intense peaks that identify the X-ray powder diffraction pattern of Kaolinite-Aluminum Silicate Hydroxide ($Al_2Si_2O_5$ $(OH)_4$), Silicon Oxide (SiO_2), Titanium Oxide (TiO_2) and Goethite-Iron Oxide Hydroxide ($FeO(OH)$).

The distribution of the chemical elements identified in the x-ray fluorescence analysis confirms the diffraction results because the quantities shown add up to quantities that constitute the abovementioned clay type and minerals: the amounts of silicon oxides (SiO_2), aluminium oxides (Al_2O_3), iron oxides (Fe_2O_3) and titanium oxides (TiO_2), were respectively, 28.268, 19.717, 44.867 and 5.3415%.

Another aspect to be considered is that according to Gatto et al. (2010), the Latosols, which comprise the soils of the study area, generally display a high degree of clay flocculation, which provides greater physical protection of the TOC due to the formation of organo-minerals less



Legend:	R^2	a (gC^{-1} m^2)	E (%) (PRDX(4) = 40 gC m^{-2})
TOC (Δ)	1.00	0.765	3.0
AC (□)	1.00	0.587	-9.6
PC (○)	1.00	0.606	-10.0
LC (◊)	1.00	0.676	16.7

Legend:	R^2	a (year)	E (%) (DEC4 = 0.00402 $year^{-1}$)
TOC (Δ)	0.99	-10,975.7	8.0
AC (□)	0.00	0.000	-10.0
PC (○)	1.00	-23,495.9	-0.3
LC (◊)	0.00	0.000	17.0

Legend:	R^2	a (year)	E (%) (DEC5 = 0.22346 $year^{-1}$)
TOC (Δ)	1.00	-259.239	2.0
AC (□)	0.00	0.000	-10.0
PC (○)	0.00	0.000	0.0
LC (◊)	1.00	-519.540	4.0

Legend:	R^2	a (year)	E (%) (DEC3.2 = 6.5 $year^{-1}$)
TOC (Δ)	1.00	-0.285	2.3
AC (□)	1.00	-14.212	1.3
PC (○)	0.00	0.000	0.0
LC (◊)	0.00	0.000	4.4

Figure 2. Relative error (E) of the TOC and C concentrations in the active (AC), passive (PC) and slow (LC) compartments *vs.* PRDX (4) (A), DEC4 (B), DEC5 (C) and DEC3.2 (D). R^2: coefficient of determination; a: angular coefficient of the slope.

prone to decomposition. In the C dynamics, clay acts as a binder, protecting the organic C in the soil from heterotrophic decomposition. The type of clay may also affect the physical protection capacity, due to the effect of colloidal protection of the organic material. Soils with clays of greater specific surface area (SSA), such as smectite and vermiculite (2:1) with an SSA of 800 m^2 g^{-1}, adsorb greater amounts of humic substances than soils with clay of lower specific surface area, such as kaolinite, which has an SSA of approximately 39 m^2 g^{-1} (Dixon, 1977).

The authors therefore conclude that the absence of mineralogical aspects in the SOM dynamics model in *Century* can lead to underestimation in the passive compartment in soils with kaolinite and Fe and Al oxides, as observed in this study.

There was also underestimation of the C in the active compartment, as shown in Figure (2e), by a relative error of 9.6%. There was underestimation (17%) of the C stock values in the active compartment, claiming that this result

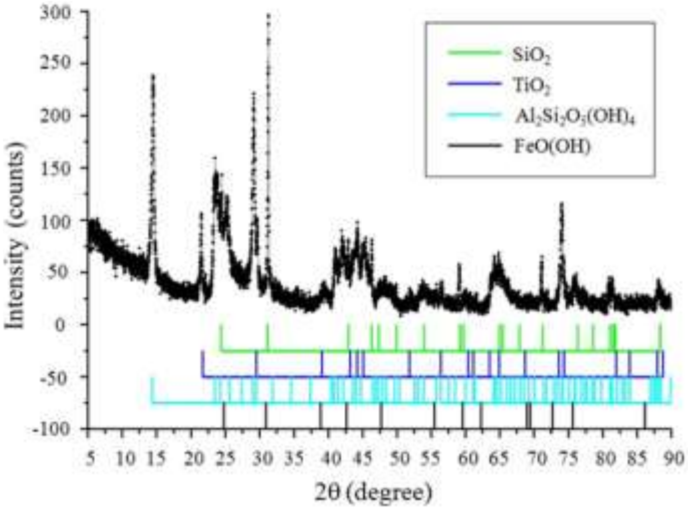


Figure 3. X ray diffractogram of the clay fraction. Θ: x ray incidence angle; Kt: kaolinite.

Table 2. Decay constant (K), adjusted constant (K*) and correction factor (A*) of the carbon decay rate in the passive (DEC4), slow (DEC5) and active (DEC3.2) compartments.

Parameter	K (year^{-1})	K* (year^{-1})	A*
DEC4	0.0045	0.00402	0.89
DEC5	0.2000	0.22500	1.12
DEC3.2	7.3000	6.50000	0.89

may be attributed to the absence in the model of the mechanisms controlling the exudation of C through the (Leite et al., 2004).

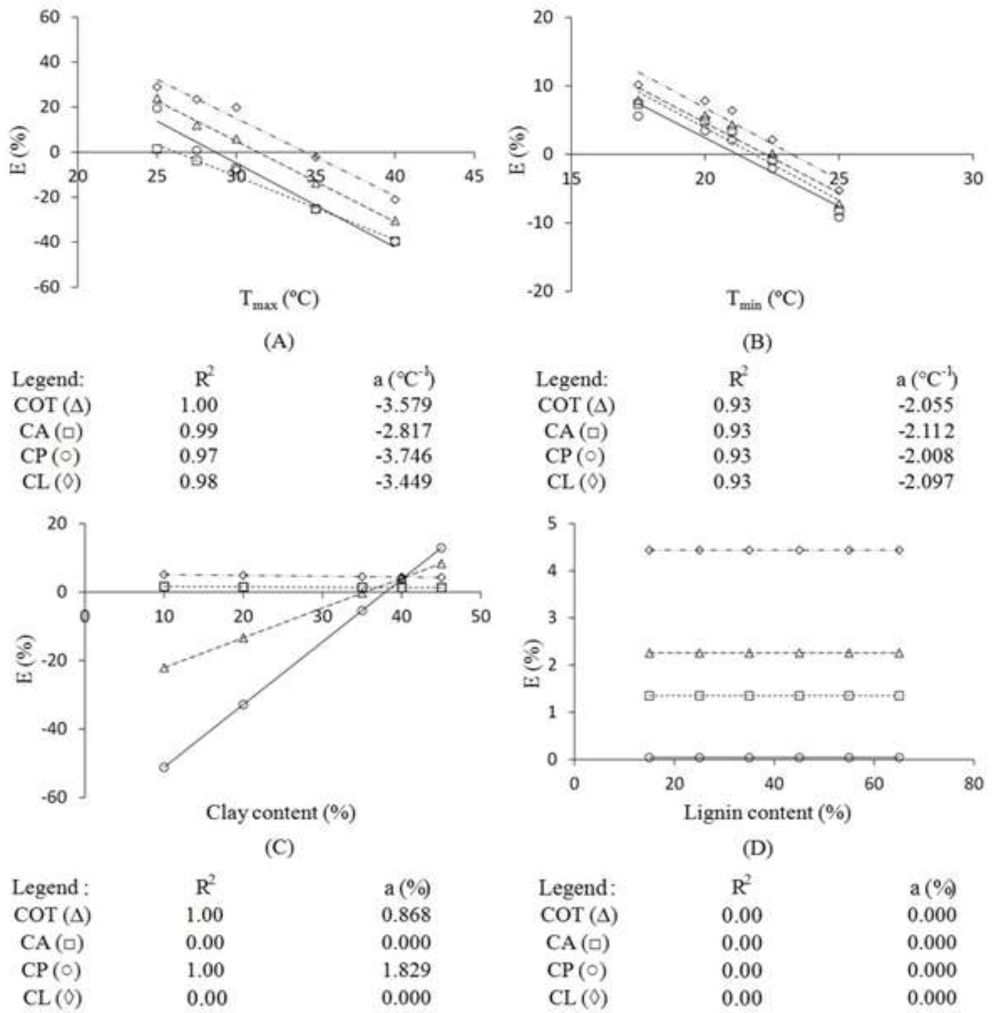
After correction of the C decay constants (K) in the passive (DEC4), slow (DEC5) and active compartments (DEC3.2), correction factors (A) were obtained, as shown in Table 2. This procedure was performed until absolute errors for the TOC values lower than 10% were obtained.

In Figure 2b, while maintaining the PRDX(4) (Figure 2a) constant, it was observed that the adjustment of the C decay constant in the passive compartment (DEC4) from 0.0045 to 0.00402 year^{-1} decreased the discrepancies between the humic substance concentrations obtained experimentally and the simulated concentrations, thereby generating an error of only 0.04%, which is considered optimal for the study area. In contrast, this reduction in the K value decreased the C decay rate, resulting in increased TOC concentrations, with a consequent increase in the error between the measured and simulated values (from 3 to 8%). It is important to note that the reduction of the decay constant of the passive compartment in this study is justified by the mineralogy of the study area because the iron and aluminium oxides and kaolinite predominate in the FLONA soil and are responsible for the physical and colloidal protection of the SOM. This protection makes roots, of microbial metabolism in soils with intense organic fertilisation and the influence of the soil the SOM inaccessible to microorganisms and contributes to the formation of microaggregates (Sollins et al., 1996).

Another aspect to be considered refers to the fact that the adjustment of the K of the active compartment did not change the C concentrations in the active and slow compartments, showing that DEC5 and DEC3.2 are not sensitive to the DEC4 decay constant.

The lowest errors related to the LC concentration (3.7%) and TOC (1.7%) in the slow compartment (DEC5) (Figure 2c) were obtained by raising the K value from 0.20000 to 0.22500 yr^{-1} (Table 2). For DEC3.2, the lowest errors, that is, 2.3% for the TOC and 1.4% for the carbon of the active compartment were obtained when reducing K from 7.3 to 6.5 yr^{-1}.

Thus, the adjustments of the decay constants corrected the underestimations of the C concentrations in the active and passive compartments and the overestimation in the slow compartment. These adjustments also altered the value of the combined effect of temperature and moisture (A), which was assumed to equal to 1 in all compartments by default in *Century*. After the K adjustments, the A correction factors specific to the study area, herein represented by A*, were 0.89 for the active and passive compartments and 1.12 for the slow



(A)

Legend:	R^2	a (°C^{-1})
COT (Δ)	1.00	-3.579
CA (□)	0.99	-2.817
CP (○)	0.97	-3.746
CL (◊)	0.98	-3.449

(B)

Legend:	R^2	a (°C^{-1})
COT (Δ)	0.93	-2.055
CA (□)	0.93	-2.112
CP (○)	0.93	-2.008
CL (◊)	0.93	-2.097

(C)

Legend :	R^2	a (%)
COT (Δ)	1.00	0.868
CA (□)	0.00	0.000
CP (○)	1.00	1.829
CL (◊)	0.00	0.000

(D)

Legend:	R^2	a (%)
COT (Δ)	0.00	0.000
CA (□)	0.00	0.000
CP (○)	0.00	0.000
CL (◊)	0.00	0.000

Figure 4. Relative error (E) of the TOC and C concentrations in the passive (C_{PC}), slow (C_{SC}) and active (C_{AC}) compartments *vs.* maximum temperature (A), minimum temperature (B), clay content (C) and lignin content (D). $R^{2:}$ coefficient of determination; a: angular coefficient of the slope.

compartment (Table 2). These results initially suggest a greater decay rate of the organic matter in the slow compartment, that is, the opposite of the expected decay rates of organic matter in the three compartments: high in the slow compartment, intermediate in the active compartment and low in the passive compartment.

However, the fact that A* is greater in the slow compartment may be attributed to the input of materials of slow biodegradation (such as lignin) from the structural compartments of the shoot and root. In this case, to compensate for the effect of the type of material allocated in this compartment such that the organic matter decay rate is intermediate compared to those of the other compartments, it is indeed necessary for the combined effect of temperature and moisture to be greater. In fact, the slow compartment includes other compounds in addition to C from the light fraction, with characteristics that result in an increase of the abiotic factor (Motavelli et al., 1994).

Sensitivity analysis

A sensitivity analysis was conducted after adjusting all parameters (Figure 4). The variations in the stocks of total organic C and C contents in the active, slow and passive compartments with temperature corroborate the results obtained by Leite et al. (2004). In that study, using *Century*, the author noted that changes in air temperature led to a 20% increase in the TOC stocks. The author also concluded that changes may occur in the output variables (carbon contents in the active, slow and passive compartments) based on changes in the input variables on the order of 10 to 30%.

Figure 4c shows that the clay contents interfere with the TOC and carbon contents in the passive compartment. This behaviour was expected because the organo-mineral interactions characteristic of soils with a predominance of kaolinite and iron oxides promotes physical and chemical protection, thereby hindering the stabilisation of SOM (Parton et al., 1987; Parfitt et al., 1997; Leite et al., 2004).

The environmental conditions in the study area are an important factor in the behaviour of SOM dynamics, particularly in tropical climates (Zech et al., 1997; Tornquist et al., 2009). However, they note that there is little information in highly weathered soils, such as Latosols, containing kaolinite.

None of the variables showed sensitivity to the amount of lignin (Figure 4d), which means that this input variable does not cause major modelling changes.

Based on the above findings, the adjustments in the decay constants and in the correction factors of the combined effect of temperature and moisture (A) in each compartment become essential when attempting to understand the C dynamics in weathered soils of semiarid regions with a predominance of kaolinite and Fe and Al oxides.

There is only one sensitivity analysis in the literature, specifically, the study by Leite (2002), that addresses the effects of the input data on the output variables in the *Century* simulator. However, that study was conducted on soils with different characteristics from the FLONA soil.

Conclusions

The application *Century* was found to have great potential for simulating the C dynamics of soil in semiarid regions with a predominance of kaolinite and iron and aluminium oxides after adjusting the decay constants. These adjustments allow the decay rates of the compartments to adequately simulate conditions in the study area (tropical conditions) because the default conditions in *Century* were developed for temperate climates.

The C in the active and passive compartments is more sensitive to environmental conditions in the study area than is the C in the slow compartment.

The sensitivity analysis revealed that the variables TOC, C_{PC}, C_{SC}, and C_{AC} are sensitive to the input variables of maximum temperature and minimum temperature. The clay contents affect the TOC and carbon contents in the passive compartment. The analysed variables displayed no sensitivity to lignin.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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