



Assessment of carbon storage under rainforests in Humic Hapludox along a climosequence extending from the Atlantic coast to the highlands of northeastern Brazil



Jane Kelly Silva Araujo^a, Valdomiro Severino de Souza Júnior^{a,*}, Flávio Adriano Marques^b, Paul Voroney^c, Regilene Angelica da Silva Souza^d

^a Departamento de Agronomia, Universidade Federal Rural de Pernambuco, Av. Dom Manoel de Medeiros, s/n, 52171-900 Recife, PE, Brazil

^b EMBRAPA Solos/UEP Nordeste, Empresa Brasileira de Pesquisa Agropecuária, Rua Antônio Falcão 402, 51020-240 Recife, PE, Brazil

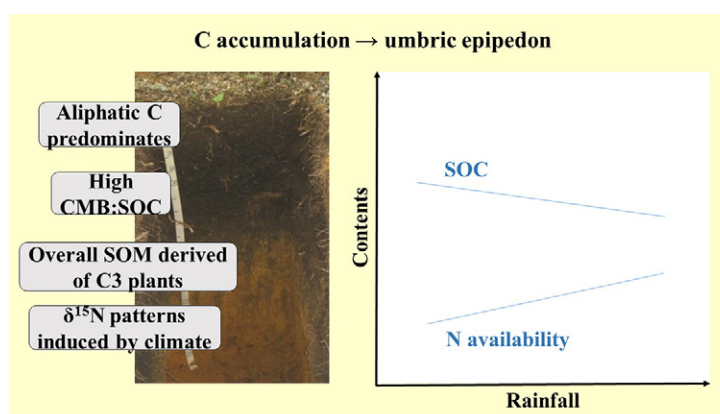
^c School of Environmental Sciences, University of Guelph, 50 Stone Road East, N1G 2W1 Guelph, ON, Canada

^d Instituto de Ciências Agrárias, Universidade Federal Rural da Amazônia, Av. Presidente Tancredo Neves 2501, 66077-830 Belém, PA, Brazil

HIGHLIGHTS

- SOM was assessed in thick umbric epipedon in areas surrounded by semi-arid region.
- Soil carbon storage contrasts with the hot and humid tropical climate.
- The climate and recalcitrant SOM do not determine the umbric epipedon formation.
- ¹⁵N patterns suggest that the low availability of N favors the accumulation of C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 October 2015

Received in revised form 4 June 2016

Accepted 5 June 2016

Available online 11 June 2016

Editor: D. Barcelo

ABSTRACT

An understanding of the stock of soil organic carbon (SOC) in the umbric epipedon of Oxisols located in the tropical forests surrounded by a semi-arid region is limited but essential because of their importance in the global cycle of carbon (C). The purpose of this study was to assess the effects of climatic (temperature and rainfall), soil organic matter (SOM) composition and litter on the stability of C in surfaces and subsurfaces in five Humic Oxisols along a 475-km climosequence from 143 to 963 m a.s.l. in a tropical environment in northeastern Brazil. We assessed vertical changes in SOC; soil total nitrogen (N); C from the microbial biomass; $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and the humified composition of SOM; the composition of the humin (HUM) fraction by Fourier Transform Infrared (FTIR); and Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) at depth. The elemental and isotopic

Abbreviations: SOC, soil organic carbon; SOM, soil organic matter; HO, Humic Oxisols; CMB, C from the microbial biomass; HA, humic acids; FA, fulvic acids; HUM, humin; FTIR, Fourier Transform Infrared; DSC-TG, Differential Scanning Calorimetry and Thermogravimetry; TNS, total nitrogen in the soil; TCL, total C in the litter; TNL, total N in the litter; $\delta^{13}\text{C}_l$, $\delta^{13}\text{C}$ in the litter; $\delta^{15}\text{N}_l$, $\delta^{15}\text{N}$ in the litter; C:N_l, C:N ratio in the litter; 1Exo, first exothermic reaction; 2Exo, second exothermic reaction; Exo1%, percentage loss during the first exothermic reaction relative to the total loss of organic material; FLONA, Araripe-Apodi National Forest.

* Corresponding author.

E-mail addresses: janeksaraujo@gmail.com (J.K.S. Araujo), valdomiro.souzajunior@ufrpe.br (V.S. de Souza Júnior), flavio.marques@embrapa.br (F.A. Marques), pvoroney@uoguelph.ca (P. Voroney), regilene.angelica@ufra.edu.br (R.A. da Silva Souza).

Keywords:

Deep carbon
Semi-arid
FTIR
Soil nitrogen
Litter
Microbial biomass

composition of the litter samples were analyzed in all areas studied. The results indicated that the current climate and recalcitrant organic compounds are not preponderant factors in the formation of the umbric epipedon, as suggested by the partial influence of temperature and rainfall on SOM. In addition, SOM was dominated by easily decomposable compounds, as indicated by the predominance of aliphatic C–H groups in the HUM fraction in the FTIR spectra; by the thermal oxidation through DSC-TG, which revealed that approximately 50% of the HUM was composed easily decomposable compounds; and by the high proportion of organic C present in the microbial biomass. Values of $\delta^{13}\text{C}$ showed a predominance of C3 plant-C in SOM whereas $\delta^{15}\text{N}$ patterns indicated that N dynamics differ among the profiles and drive the accumulation of C. These findings can help to characterize the susceptibility of these soils to changes in climate and land use and the implications for the sequestration of soil C.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Forest ecosystems account for more than 70% of terrestrial soil organic carbon (SOC) (Jandl et al., 2007), and the majority of SOC (approximately 60%) is present in the subsoil below a depth of 20 cm (Rumpel et al., 2002; Chabbi et al., 2009; Batjes, 2014). However, subsoil carbon (C) has drawn increasing attention in recent years (Fontaine et al., 2007; Sanaullah et al., 2011; Rumpel and Kögel-Knabner, 2011; Mora et al., 2014; Marín-Spiotta et al., 2014). Studies have shown that the stability of subsoil-C is related to the scarcity of fresh C in the subsurface (Fontaine et al., 2007), the physical protection of soil organic matter (SOM) in soil aggregates (von Lützow et al., 2006), the chemical composition influenced by pedological processes (Spielvogel et al., 2008; Mikutta et al., 2009), and labile and resistant C pools responding similarly to changes in soil temperature (Fang et al., 2005). Furthermore, the majority of these studies were conducted on soils containing low SOM concentrations at depth. The chemical composition and the factors regulating the stabilization of SOM in the umbric epipedon (>1.0 m) of Oxisols in tropical areas has rarely been studied.

The C stocks (0–30 cm) in the umbric epipedon of Brazilian Oxisols are in the order of 30.0 kg m^{-2} (Andrade et al., 2004). In contrast the adjacent soils in the Brazilian northeast (NE) semi-arid region are characterized by low C stocks ($2.0\text{--}3.0 \text{ kg C m}^{-2}$), which indicates the critical influence of climatic on C accumulation influence (Bernoux et al., 2002). Thus, Humic Oxisols (HO), represent an important C sink and/or source and are a significant component of the global C (Poulter et al., 2014).

The occurrence of HO is common in southern and southeastern Brazil (humid tropical and subtropical environments); HO are associated with highland environments with mean temperatures below 18°C (Lepsch and Buol, 1986; Brasil, 1972; Ker, 1997; Silva and Vidal-Torrado, 1999). The majority of HO studies are concentrated in these regions because the stability of SOM in these soils has, in part, been empirically linked to the mild climate. However, the identification of the effects of the current climate on the C stocks in these soils has been neglected. Contrary to expectations, in the NE region of Brazil in which the semi-arid climate prevails, these soils also have a thick umbric epipedon (>1.0 m), and this is not consistent with current climate conditions. These soils are under ecological tension (enclaves or ecotones) between the Dense Ombrophilous Forest and the Seasonal Semideciduous Forest and *Caatinga*, commonly located in the upper portion of a water basin/slope (Brasil, 1972). In this region, altitudes range from 150 m to 1200 m, with orographic rain that ensures precipitation above $1000 \text{ mm year}^{-1}$ (Araújo Filho et al., 2000; Velloso et al., 2002) and causes the emergence of tropical forests.

The variations in altitude show a variety of local climates that influence C stock (Garcia-Pausas et al., 2007). In addition, the climate determines plant communities, which can also influence SOM content and quality (Vinton and Burke, 1997). A recent theoretical model suggests that the limitation of nitrogen (N) to plants and to decomposing microorganisms, mediated by mycorrhizal fungi, would lead to an increase in soil C stock (Lindahl et al., 2010; Averill et al., 2014). There is also evidence that C from the roots, which could be more chemically recalcitrant because of the higher lignin content, significantly contributes to subsoil-SOM (Jobbágy and Jackson, 2000; Lorenz and Lal, 2005). In

general, the chemical recalcitrance of subsoil-C has been supported because of the increase in the mean residence time of ^{14}C in subsurfaces (Paul et al., 1997).

C stability in HO remains partially understood and has been related to cold climates, acidity, high Al saturation and the association between C and the mineral fraction of the soil, particularly poorly crystallized forms of Al (Queiroz Neto and Castro, 1974; Lepsch and Buol, 1986; Ker, 1997; Marques et al., 2011) and crystalline Fe (Fontes et al., 1992) in addition to the redistribution of carbonized material (charcoal) in the soil over time by biological activity (Silva and Vidal-Torrado, 1999). These materials would be paleosoils formed during the Holocene under conditions favorable to the accumulation of SOM in the subsurface (Lepsch and Buol, 1986).

We hypothesize that C accumulation in the umbric epipedon increases with an increase in altitude because microbial activity is inhibited at low temperatures (Garcia-Pausas et al., 2007). We also hypothesize that the stability of the C in this horizon is due to the complex chemical nature of the SOM. The purpose of this study was to assess the effects of climate (temperature and rainfall) on the accumulation and composition of SOM and litter in the surface and subsurface HO soils using isotopic, spectroscopic and thermal degradation techniques.

2. Materials and methods

2.1. Study areas

The selection of study areas was based on the occurrence of HO in NE Brazil, as indicated in previous pedologic studies (Brazil, 1972; 1973; Araújo Filho et al., 2000; Marques et al., 2011; Embrapa, 2012) and the knowledge of the pedologists of the region. The study was conducted along a 475-km climosequence to encompass the bioclimatic variation of occurrence of HO in the NE region of Brazil, extending from the sedimentary coastline toward the inland semi-arid region in NE Brazil and at altitude ranging from 143 to 963 m a.s.l (Fig. 1). The locations of soil profiles, soil classification, altitude, rainfall, air temperature, parent material and vegetation in the studied areas are shown in Table 1.

2.2. Sampling and processing soil and litter

The five study site were selected using the map of soils in Brazil (Embrapa, 2012). One pit was dug at each site, after soil sampling with an auger to identify a representative soil of the area, and studied according to the Brazilian protocol of soil science (Embrapa, 2013) and each profile was located on top of a slope under natural vegetation (Table 1). Soil samples were collected from profiles at depth intervals from 10 cm to 100 cm for SOC analysis, total soil N (TNS), $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. An identical sampling procedure was repeated to collect samples for analysis of microbial biomass C (CMB). In the field, soil samples were immediately cooled and then kept at 4°C until they were analyzed. Additional soil samples was taken for morphological description of profiles (data not shown) according to Embrapa (2013) to identify the umbric epipedon, which was subsequently verified by chemical

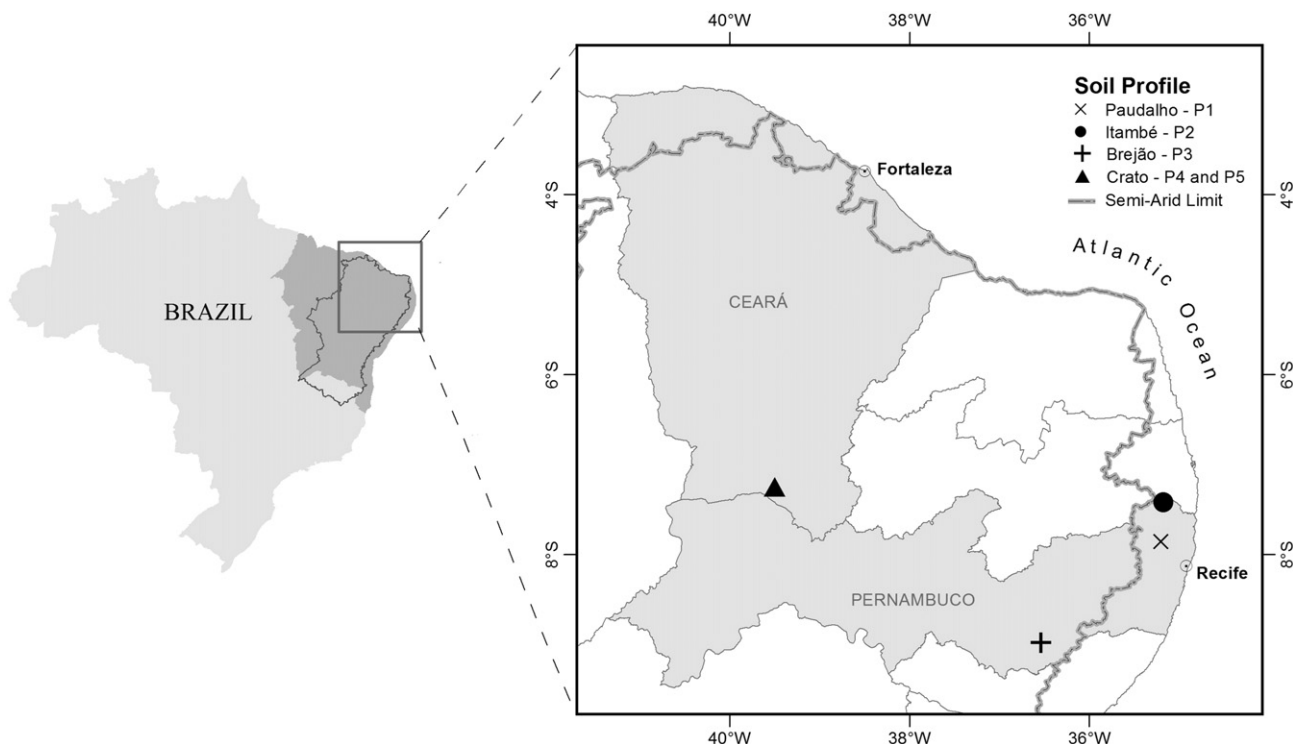


Fig. 1. Location of the study areas in northeastern Brazil.

analysis, as shown in Araujo (2014). This allowed definition of the soil sampling depth for this study.

Soils from three profiles, P2, P3 and P4 from depths 0–5, 5–10, 30–40 and 80–90 cm, were selected for characterization of humic substances. These profiles were selected based on the different climatic regions, vegetation types and parent materials spanning the occurrence of HO, to address the major factors that influence the accumulation and stability of SOM in natural ecosystems (Jenny, 1980).

All of the samples were collected when the profiles were opened. After collection, soil samples were stored in polyethylene bags and transported to the laboratory. The soil samples were air dried and passed through a 2 mm sieve, except samples collected for analysis CBM. SOC, TNS, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ concentrations were measured in ground soil samples and sieved (mesh <0.15 mm); samples for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were dried in an oven (60 °C) for 24 h before being ground and

processed in the same manner before drying prior to the encapsulation of the samples.

Surface layers were defined to a depth of 30 cm; hereafter, “surface layers” will refer to these horizons. Subsurface horizons varied from 30 to 100 cm; both correspond to the umbric epipedon in all of the profiles. The umbric epipedon showed the following thicknesses and sequence of horizons to 100 cm: P1: A1 (0–20 cm), A2 (20–50 cm), A3 (50–88 cm), AB (88–115 cm); P2: A1 (0–20 cm), A2 (20–45 cm), A3 (45–75 cm), A4 (75–97 cm), A/B (97–120 cm); P3: A1 (0–15 cm), A2 (15–35 cm), A3 (35–67 cm), AB (67–100 cm); P4: A1 (0–20 cm), A2 (20–40 cm), AB (40–70 cm), BA (70–110 cm); and P5: A1 (0–28 cm), AB (28–55 cm), BA (55–80 cm), Bw1 (80–120 cm).

In all areas studied, a sampling area of approximately 0.5 ha (plot) was delimited. Litter samples (organic debris reaching the forest floor, as the leaves, branches and bark of the trees, seeds, forest floor plants

Table 1
Soils and characteristics of the study areas.

Profile	Location	Soil ^a	Altitude m	MAP ^b mm	MAT ^c °C	PM ^d	Vegetation
P1	Paudalho, PE 07°51'58" S 35°12'17,1" W	Humic Xanthic Hapludox ^e	143	1700	25	Clayey-sandy sediments	Deciduous Submountainous Seasonal Forest
P2	Itambé, PE 07°25'23" S 35°10'51" W	Humic Xanthic Hapludox ^f	178	1200	24	Clayey-sandy sediments	Deciduous Submountainous Seasonal Forest
P3	Brejão, PE 07°32'12" S 37°13'69" W	Humic Xanthic Hapludox ^e	820	1400	22	Clayey-sandy sediments	Dense Mountainous Ombrophylous Forest
P4	Crato, CE 07°14'24" S 39°29'15" W	Humic Xanthic Hapludox ^f	947	1100	23	Sandy sediments	Savanna woodland
P5	Crato, CE 07°14'54" S 39°29'50" W	Humic Xanthic Hapludox ^f	963	1100	23	Sandy sediments	Savanna woodland

^a According to the US Soil Taxonomy (Soil Survey Staff, 2014).

^b Mean annual precipitation.

^c Mean annual temperature.

^d Parent material.

^e Latossolo Amarelo distrocoeso húmico, according to the Brazilian System of Soil Classification-SiBCS (Embrapa, 2013).

^f Latossolo Amarelo distrófico húmico, according to SiBCS (Embrapa, 2013).

debris (Jonczak, 2013)) were collected at points randomly distributed throughout the area of the plot (zigzag pattern), considering that the variability of the area is uniformly distributed in the plot. The mean representative sample comprised of at least 5 subsamples, each stored in a polyethylene bag (3000 cm³ capacity). The litter samples were homogenized, air dried, ground and sieved (mesh <0.15 mm); litter samples for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis were oven dried (60 °C) for 24 h before being milled and prior to encapsulation of the samples.

2.3. Soil and litter analyses

All soil samples were acidic (pH from 4.8 to 5.8, data not shown) and carbonate-free, therefore measurement of total soil C was equivalent to the SOC concentration. The ground and homogenized samples were placed in 8 × 5 mm tin capsules (Elemental Microanalysis Ltd., Okehampton, United Kingdom). The amount of each soil sample ranged from 13 to 40 mg; litter samples were 3 mg. These provide sample weights between 300 and 540 µg (420 µg average) of the organic C required for analysis. The samples in the tin capsules were carefully sealed, compressed (to remove trapped CO₂) and stored in cell culture plates (Polystyrene 96-well Costar® [Corning Costar Corp., Corning, NY]). SOC and TNS concentrations in samples of soil and litter were determined by dry combustion on an elemental analyzer – LECO (furnace at 1350 °C in pure oxygen). The isotope composition of C and N in the soil and litter were determined by the continuous flow-isotope ratio mass spectrometry (CF-IRMS) using a combined elemental analyzer (ANCA-GSL). Isotope ratios are expressed in V-PDB and atmospheric N standards (Gonfiantini, 1978; Gonfiantini et al., 1995). Reproducibility of the determinations is better than 0.2 ‰ for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.

CMB was measured by the irradiation–extraction method (Brookes et al., 1982; Islam and Weil, 1998; Mendonça and Matos, 2005). Soil samples (20 g 60% of gravimetric SWC) were extracted in 50 mL 0.5 M K₂SO₄ for 30 min on automatic shaker. Simultaneously with the extraction, another sample (20 g 60% of gravimetric SWC) was irradiated with a domestic microwave oven. Subsequently, irradiated samples were extracted in a manner similar to non-irradiated samples. CMB was determined from the difference between C in the extracts of irradiated and non-irradiated samples using the colorimetric method (Bartlett and Ross, 1988) and the recovery factor (K_{EC}) of 0.41.

The extraction of soil humic acids (HA), fulvic acids (FA) and humin (HUM) was performed according to Swift (1996), using 3 g of soil samples in 30 mL 0.1 M NaOH for 16 h on automatic shaker under inert atmosphere (N₂). Total C was analyzed by dry combustion (950 °C) in an elemental analyzer (Flash EA 1112 NCS Soil Analyzer) in subsamples of the humic fractions. The remaining HUM fraction was purified with 10% HF according to Gonçalves et al. (2003). The HF treatment was performed by adding 10 mL of 10% HF to 1 g of HUM. The suspension was shaken for 10 min, centrifuged (3000 rpm) and the supernatant removed; this procedure was repeated 6 times. The samples were then washed 5 times with deionized H₂O to remove residual HF. The samples were oven-dried (45 °C).

The infrared spectra of the HUM fraction purified with 10% HF were obtained in the range of 4000–400 cm⁻¹, using KBr pellets (1 mg of HUM + 200 mg of dry KBr), using a Fourier Transform Infrared (FTIR) spectrometer, FTIR Spectrum Two, Perkin-Elmer. Each spectrum was obtained using 16 scans, with a resolution of 4 cm⁻¹. Readings were performed in Transmittance compared with Wavenumber (in cm⁻¹).

Thermal analytical measurements were simultaneously performed in the HUM fraction purified with 10% HF through Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG), using the thermal analyzer Netzsch STA 449. HUM samples were heated from room temperature (approximately 23 °C) to 950 °C at a linear velocity of 10 °C min⁻¹ in N₂ atmosphere. Twenty milligrams of HUM were used as samples, and an empty alumina crucible was used as a reference sample. The amount of more thermally labile material (associated with the first exothermic reaction) was expressed in a percentage relative to the total loss of

organic material (1°Exo%). These measurements quantified the fractions that have a different thermal stability, according to Dell'Abate et al. (2002, 2003).

2.4. Statistical analyses

We conducted polynomial regression analysis based on a second order model to test for effects of climatic parameters (temperature and rainfall) on the SOC, CMB, C:N, TNS and $\delta^{15}\text{N}$ values in surface layers and subsurfaces. In addition, SOC, CBM, and $\delta^{13}\text{C}$ e $\delta^{15}\text{N}$ values were regressed against one another and against TNS and C:N ratio; we presented only best-fit models. All regressions were tested for homocedasticity. STATISTICA 7.0 (Statsoft) software was used for statistical tests.

3. Results

3.1. Elemental composition and values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ at depths in the soil profile

SOC concentrations in surface layers (0–30 cm) were quadratically related to mean annual rainfall ($r = 0.70, p < 0.001$) and temperature ($r = 0.67, p < 0.001$). In the subsurface, SOC was weakly related to rainfall and temperature ($r = 0.34, p < 0.001$ and $r = 0.35, p < 0.001$, respectively) (Table 2).

The TNS concentrations decreased from 2.7 to 0.4 g kg⁻¹ in the subsurface (Table 3). Temperature and rainfall explained 41% and 38%, respectively, of the variation of TNS in surface layers whereas the relation of these concentrations to the climatic parameters was even lower in the subsurface (Table 2). SOC and TNS were linearly related in surface layers ($r = 0.77, p < 0.001$) and subsurfaces ($r = 0.91, p < 0.001$) (Table 4), and the slope of the model referring to the surface layers shows a soil C:N ratio of 13.9:1. This ratio increased in subsurfaces in all of the profiles, increased slightly in P3 and increased substantially in P4 and P5, compared with the other profiles.

Soil $\delta^{13}\text{C}$ values varied slightly in P1 (–24.0‰ to –25.5‰) and P2 (–27.1‰ to –26.1‰) along the depth whereas in P3, P4 and P5, $\delta^{13}\text{C}$ values increased from –26.4 to –21.0‰, –23.8 to –20.2‰ and –26.0 to –17.5‰ along the depth, respectively (Fig. 2). Temperature and C:N ratio were closely related ($p < 0.001$) to the changes in soil $\delta^{13}\text{C}$ values below a depth of 30 cm (Tables 2 and 4) whereas in surface layers, the variation in $\delta^{13}\text{C}$ was related only to TNS ($p = 0.005$) (Table 4).

In general, ¹⁵N-isotope abundance tended to increase in the subsurface, showing $\delta^{15}\text{N}$ values between 4‰ and 8‰ (Fig. 3), with greater variations in surface layers. The greatest variation amplitudes of $\delta^{15}\text{N}$ concentrations were equal to 4.63‰ (7.97–3.34) in P5; 3.77‰ (3.54–7.31) in P4; and 3.33‰ (4.68–8.01) in P3. In general, ¹⁵N concentrations were more impoverished in areas at higher altitudes than in lower areas. $\delta^{15}\text{N}$ values were related to rainfall, temperature and C:N ratio ($p < 0.005$) in surface layers. Conversely, in the subsurface, temperature and TNS were significantly related to the $\delta^{15}\text{N}$ values (Tables 2 and 4). According to the isotopic data ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$), P3, P4 and P5 were the most enriched profiles in the subsurface, compared with the other profiles.

3.2. Elemental composition, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in the litter

The concentrations of total C in the litter (TCL) ranged from 427 to 506 g kg⁻¹ in all of the studied areas (Table 5). The mean concentrations of total N in the litter (TNL) was equal to 15.2 g kg⁻¹, and the amount of N in the litter added to the soil tended to be higher in P2 and P3, 18 and 19 g kg⁻¹, respectively (Table 5). The values of $\delta^{13}\text{C}$ in the litter ($\delta^{13}\text{C}_l$) ranged from –28.77‰ to –30.62‰, and the profiles P4 (–30.62‰) and P5 (–30.38‰), located in the Araripe Plateau, showed $\delta^{13}\text{C}$ values more impoverished than the values in the other areas. The values of

Table 2

Regression analysis between qualitative variables of SOM and climatic parameters in surface layers and subsurface.

Depth	X	Model	R ²
Surface layers	Rainfall	SOC = 19.899 – 8.376***x + 3.98x ²	0.70
		CMB = 546.878 – 301.785***x – 92.749x ²	0.66
		C:N = 13.01 – 1.394**x + 1.91x ²	0.54
		TNS = 1.586 – 0.401**x + 0.0015x ²	0.38
		δ ¹⁵ N = 5.902 + 0.789**x – 0.227x ²	0.30
		Temperature	SOC = 31.615 – 3.330x – 13.765***x ²
Subsurface	Rainfall	CMB = 758.836 – 194.633**x – 405.086***x ²	0.66
		TNS = 2.04 – 0.086x – 0.705***x ²	0.41
		δ ¹⁵ N = 0.345 + 0.344**x – 0.644x ²	0.48
		SOC = 12.54 – 3.77***x – 0.514x ²	0.34
		CMB = 178.536 – 83.54***x – 44.465x ²	0.35
		C:N = 17.682 – 1.747***x – 0.460x ²	0.51
	Temperature	TNS = 0.729 – 0.152***x – 0.044x ²	0.19
		SOC = 16.22 – 1.290x – 6.155***x ²	0.35
		CMB = 207.380 – 87.070***x – 80.638***x ²	0.43
		C:N = 18.597 – 1.90***x – 1.664***x ²	0.66
		δ ¹³ C = –23.860 – 4.041***x + 1.731***x ²	0.85
		TNS = 0.883–0.007x–0.287***x ²	0.22
δ ¹⁵ N = 6.264–0.580***x + 0.855***x ²	0.41		

** $p < 0.01$.*** $p < 0.001$.

δ¹⁵N in the litter (δ¹⁵N_l) ranged from –2.97‰ to 4.39‰. The C:N ratio in the litter (C:N_l) was higher in the areas of the profiles P1, P4 and P5 (Table 5).

3.3. CMB, microbial quotient and humic substances

CMB was considered an estimate of labile C to assess the contribution of that fraction C in depth, which was higher in the majority of the umbric epipedon and decreased in subsurface in all of the profiles, with mean values of 806 mg kg^{–1} for the layer of 0–20 cm, disregarding P1 (221.8 mg of CMB kg^{–1} soil in the layer of 0–10 cm) (Table 3).

Regression analyses indicated that CMB concentrations in the entire profile were related to rainfall, temperature (Table 2), SOC ($p < 0.001$) and TNS ($p < 0.001$) (Table 4). CMB variability is more influenced by the climatic conditions in surface layers, as evidenced by the values of temperature ($r = 0.66$, $p = 0.016$) and rainfall ($r = 0.66$, $p < 0.001$), and weakly affected in subsurface horizons ($r = 0.35$, $p < 0.001$ for rainfall and $r = 0.43$, $p < 0.001$ for temperature).

The relation between CMB and SOC can represent a simple, efficient indicator of the impoverishment of the soil with respect to biological quality. The values of the microbial quotient (CMB:SOC) in the profiles varied substantially in an interval of 3.6%–0.2% (Table 3).

The highest values of microbial quotient were observed in surface layers in all of the profiles, except P1, which showed the lowest values (1.1% and 0.2%) in all evaluated layers, compared with the other profiles, following the low values of SOC. The contribution of the microbial biomass to SOC was noticeable in the entire umbric epipedon, particularly in profiles P3, P4 and P5, in which CMB represented approximately 2% of soil C in the majority of the umbric epipedon, and this value reached the depth of 90 cm in P4.

HUM was the most significant fraction as a reserve of organic C in all of the evaluated profiles (Table 6). The C concentration in the HUM fraction (C-HUM) ranged from 5.6 to 27.3 g kg^{–1} in the studied profiles, corresponding, on average, to 49% of SOC in P2 whereas in P3 and P4, this proportion tended to be slightly higher, reaching up to 57% of SOC. The C concentrations in the extracts of humic acid (C-HA) decreased with depth in P4 and P3, ranging from 3.3 to 12.6 g kg^{–1} and 3.3 to 9.9 g kg^{–1}, respectively. Conversely, in P2, the C-HA fraction increased from 2.3 to 9.7 g kg^{–1} in the middle portion of the umbric epipedon (5–10 and 30–40 cm). Among the analyzed fractions, FA showed the lowest concentrations of C (C-FA). The concentrations of C-FA were, on

average, 3.0 g kg^{–1} in profiles P2 and P3, and 5.3 g kg^{–1} in P4, decreasing in the subsurface of all of the profiles (Table 6).

The C-HA/C-FA ratio is an indicator of humus quality. Except for the most superficial layer of P2, C-HA/C-FA values were higher than 1.0 in all of the studied layers and profiles, indicating a predominance of the HA fraction over FA.

3.4. FTIR of HUM

The FTIR spectra of HUM in all analyzed profiles were quantitatively similar and are shown in Fig. 4. The interpretation of FTIR spectra was conducted according to numerous authors (Stevenson, 1994; Silverstein et al., 2005; González-Pérez et al., 2004). HUM showed stronger aliphatic peaks in all of the evaluated profiles and layers at absorptions of approximately 1082 cm^{–1} and peaks at 1261 cm^{–1}, attributed to the C–O stretch and vibration of groups COOH and C–N of amines. These compounds were absorbed more intensely in the surface layers of P2, unlike P3, in which they appeared with higher expression in the subsurface, and P4, between layers of 5–10 and 80–90 cm. Absorptions from 1172 to 1164 cm^{–1} can be attributed to C–O stretches of polysaccharide structures and Si–O vibrations of mineral impurities (Stevenson, 1994), indicating the presence of mineral materials that were not completely removed during the purification process. Another strong peak at approximately 797 cm^{–1} can be attributed to out-of-plane bends of aromatic C–H compounds, which showed frequencies between 900 and 690 cm^{–1}. The most intense signals were observed between 80 and 90 cm of depth, except for P2, in which the signals occurred more intensely between 30 and 40 cm.

The broad band at 3400 cm^{–1} is associated with the OH stretch of OH groups. Peaks at approximately 2922 cm^{–1}, characteristic of the absorption of methylene and methyl groups, are present in P2 and P3 in all of the studied layers, and the intensity of the peaks increased slightly in the layers of 5–10 and 30–40 cm. In P4, the peaks occurred only in surface layers and were also more expressive in the layer of 5–10 cm. Additionally, there was absorption at 2851 cm^{–1}, also attributed to aliphatic C–H but characteristic of CH₂ groups, such as the alkanes. The occurrence of these compounds followed the same tendency observed for the groups at 2922 cm^{–1}.

Bands between 1632 and 1620 cm^{–1} are generally attributed to vibrations of aromatic C=C bonds from C=O groups of amines, quinones and conjugated ketones and to the asymmetric stretch of –COO– groups (Rovira et al., 2002). The intensity of absorption in these regions was higher in the subsurface in P3 and P4, and the latter showed the highest intensities in the layers of 30–40 and 80–90 cm, indicating that the humification is higher in the subsurface. However, P2 showed a similar pattern of intensity of absorption in this region, with lower intensity in the layer of 80–90 cm.

Only in P2 and P3 were peaks at approximately 1384 cm^{–1} observed, which were more expressive in the subsurface, particularly in the layer of 80–90 cm in P3. Lumsdon and Fraser (2005) attributed such absorptions to lignin fragments whereas Rovira et al. (2002) claimed that such absorptions are a deformation of –OH groups and stretches of C–O groups of phenolic groups and most such asly is the deformation of C–H bonds of CH₂ and CH₃ groups and asymmetric deformation of –COO– groups.

3.5. Thermal stability of HUM

The reactions evidenced by the low temperatures (~65 °C) correspond to loss of water. In the temperature interval between approximately 200 and 500 °C, two primary exothermic reactions occur, resulting from the thermal oxidation of organic compounds. The first reaction generally occurs because of the decomposition of aliphatic chains and functional groups, revealing an exothermic peak with a maximum of 344.3 °C (1Exo) whereas the second exothermic reaction of molecules containing aromatic rings occurred at higher

Table 3

Concentrations of soil organic carbon (SOC), total nitrogen in the soil (TNS), C:N ratio in the soil (C:N), C:N ratio in the litter (C:NL), carbon from the microbial biomass (CMB) and CMB:SOC ratio of studied soils.

Depth (cm)	SOC (g kg ⁻¹)	TNS	C:N	CMB (mg kg ⁻¹)	CMB:SOC (%)
P1 – Paudalho (143 m)					
0–10	21.3	1.8	12	221.8	1.0
10–20	13.9	1.0	13	109.7	0.8
20–30	11.0	0.7	15	115.9	1.1
30–40	10.0	0.7	15	79.7	0.8
40–50	10.0	0.6	16	70.9	0.7
50–60	9.4	0.6	17	75.3	0.8
60–70	7.9	0.5	15	14.6	0.2
70–80	8.1	0.5	16	36.8	0.5
80–90	6.9	0.5	14	15.0	0.2
90–100	6.6	0.5	14	15.1	0.2
P2 – Itambé (178 m)					
0–10	32.8	2.7	12	885.2	2.7
10–20	23.4	1.8	13	846.0	3.6
20–30	22.8	1.7	14	305.5	1.3
30–40	23.3	1.5	15	250.7	1.1
40–50	21.6	1.3	17	109.7	0.5
50–60	19.2	1.1	18	235.0	1.2
60–70	16.3	0.9	18	125.3	0.8
70–80	12.9	0.7	18	164.5	1.3
80–90	10.3	0.6	17	101.8	1.0
90–100	9.9	0.6	16	109.7	1.1
P3 – Brejão (820 m)					
0–10	24.3	1.8	14	736.1	3.0
10–20	18.4	1.3	14	550.7	3.0
20–30	18.2	1.3	14	388.3	2.1
30–40	13.7	0.9	16	245.9	1.8
40–50	13.9	0.8	18	315.5	2.3
50–60	12.5	0.7	19	255.0	2.0
60–70	12.9	0.7	19	189.5	1.5
70–80	10.6	0.5	20	229.9	2.2
80–90	10.1	0.5	19	133.4	1.3
90–100	8.4	0.4	19	97.8	1.2
P4 – Crato (947 m)					
0–10	34.8	2.2	16	859.1	2.5
10–20	31.8	1.9	17	794.5	2.5
20–30	26.9	1.5	18	561.1	2.1
30–40	24.6	1.2	20	343.9	1.4
40–50	21.9	1.1	20	281.0	1.3
50–60	17.5	0.9	20	370.3	2.1
60–70	13.9	0.7	19	50.9	0.4
70–80	12.0	0.6	19	290.7	2.4
80–90	11.8	0.6	19	241.0	2.0
90–100	9.9	0.5	19	94.8	1.0
P5 – Crato (963 m)					
0–10	26.0	1.5	17	942.1	3.6
10–20	38.7	2.3	17	833.7	2.2
20–30	36.9	2.3	16	591.9	1.6
30–40	22.4	1.2	19	375.2	1.7
40–50	18.0	0.9	19	350.1	1.9
50–60	17.4	0.8	21	291.8	1.7
60–70	14.6	0.7	19	141.7	1.0
70–80	12.2	0.6	19	241.8	2.0
80–90	10.2	0.5	20	116.7	1.1
90–100	9.5	0.5	19	83.4	0.9

temperatures, with a maximum peak of 527.1 °C (2Exo) (Czimeczik et al., 2002) (Table 7).

The intensity of exothermic reactions is expressed by the release of energy during such a reaction. Table 7 shows the energy released in the first exothermic reaction (1Exo) in μV/min, which, despite representing higher absolute values, indicates lower energy release compared with the second exothermic reaction (2Exo), which represents negative values. Thus, the greatest energy release is associated with the highest resistance to thermal degradation of SOM. Energy variations in the subsurface showed a slight increase in the resistance

to thermal degradation of the more labile compounds in all of the profiles, evidenced by the lower energy values in 1Exo.

In profiles P3 and P4, the more labile compounds of HUM showed higher resistance to thermal degradation, particularly in the superficial layers, which is evidenced by higher temperatures of the peaks. The highest mass loss in the thermal interval at approximately 300 °C was observed in P2 (1.21%) in the layer of 0–5 cm, which indicates that this profile has a higher proportion of labile compounds in surface layers compared with the other profile. According to the mass loss, P3 nevertheless showed a higher amount of labile compounds compared with P4. However, P3 was considered more humified, followed by P2 and P4, because of the greater amount of aromatic compounds, evidenced by the higher mass losses in the temperature interval at approximately 450 °C. The parameter Exo1% showed that the percentage loss during the first exothermic reaction was higher than 50 for P2 and P3 in surface layers whereas more recalcitrant structures prevailed in surface layers in P4. This parameter also showed that the most easily decomposable compounds decreased in the subsurface, except for P4.

4. Discussion

4.1. Effects of climate on the stability of C in surface and subsurface

The SOC accumulation not increase with altitude, since the highest SOC concentrations in the umbric epipedon were observed in profiles under lower rainfall (<1200 mm) located in coastal area (P2, at 178 m a.s.l) and uplands (P4 and P5, at 947 and 963 m a.s.l., respectively). Intermediate SOC concentration were observed in P3, at 820 m a.s.l., also with intermediate rainfall (1400 mm). The lowest C concentrations observed in P1 are attributed to the climate (As'), as reported by Marques et al. (2011). Furthermore, the anthropic action in this area, which shows secondary vegetation with signs of degradation, must be considered (Table 3). These accumulation is lower than most previous studies have suggested (Calegari, 2008), which shows that the majority of these soils are on hilltops, between 800 and 1200 m of altitude. However, the concentrations observed in the present study were higher than some HO of southeastern and northeastern Brazil (Fontes et al., 1992; Simas et al., 2005; Marques et al., 2011).

δ¹³C values can be related to an interaction of processes influenced by the mean annual temperature and rainfall of a region (Farquhar et al., 1989; Schuster et al., 1992). Soils under high temperatures showed a low δ¹³C enrichment ($r = 0.85, p < 0.001$) (Table 2), as in the profile P2, located in an area with a high mean annual temperature (25 °C), showed enrichment lower than 1.0‰ to a depth of 100 cm. Conversely, P3, located in an area with a lower mean temperature (22 °C), showed high enrichment in δ¹³C value (from -26.41‰ to -21.01‰) in depth, suggesting sparser vegetation with a predominance of C4 plants, which vary from -17‰ to -9‰ (O'Leary, 1988), before the establishment of the current forest. The profiles P4 and P5, located in areas with

Table 4
Relation among qualitative variables of SOM in surface layers and subsurface.

Depth	Model	R ²
Surface layers	SOC = 25.413 + 13.948(TNS)	0.77***
	SOC = 26.245 + 8.759*** (CMB) - 4.279(CMB) ²	0.58
	SOC = 26.450 - 9.145*** (δ ¹⁵ N) + 1.450(δ ¹⁵ N) ²	0.48
	CMB = 625.344 + 368.706*** (TNS) - 163.864(TNS) ²	0.49
	δ ¹³ C = -25.073 - 1.606*** (TNS) - 0.777(TNS) ²	0.50
Subsurface	δ ¹⁵ N = 5.101 - 0.974** (C:N) + 0.812(C:N) ²	0.39
	SOC = 17.764 + 9.774(TNS)	0.91***
	SOC = 14.035 + 5.731*** (CMB) + 0.052(CMB) ²	0.50
	δ ¹³ C = 13.604 - 4.330*** (δ ¹⁵ N)	0.28
	CMB = 277.969 + 85.983** (TNS) - 151.489*** (TNS) ²	0.47
	δ ¹³ C = -23.259 + 3.766(C:N)	0.43***
	δ ¹⁵ N = 6.025 - 0.773*** (TNS) + 0.788(TNS) ²	0.42

** $p < 0.01$.

*** $p < 0.001$.

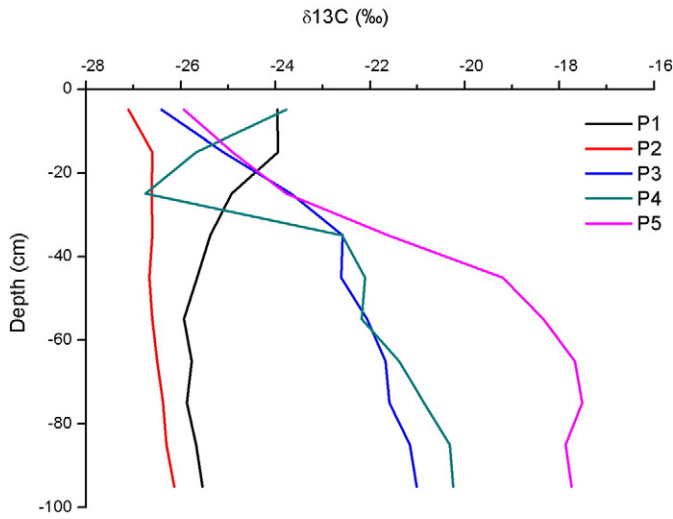


Fig. 2. Values of $\delta^{13}\text{C}$ at depth in the soil profiles.

an intermediate mean temperature (23 °C), showed higher ^{13}C enrichment in the subsurface. $\delta^{13}\text{C}$ variations in the profiles located in the Araripe-Apodi National Forest (FLONA), P4 and P5, also reflected changes in vegetation, suggested a mixture of C3 and C4 vegetation (Pessenda et al., 2010). The presence of C4 plants in areas currently covered by forests suggests that the climate was drier than the present conditions (Pessenda et al., 2010).

The C:N ratio of the soil, as an indicator of substrate decomposability, was strongly related to $\delta^{13}\text{C}$ values in the subsurface (Table 4), which in turn was related to mean annual temperature, indicating changes in the decomposability of subsurface SOM influenced by temperature. Brunu et al. (2014) observed that the ^{13}C enrichment in SOM at a depth 10 cm of forests is related to temperature and rainfall and that vertical changes in $\delta^{13}\text{C}$ values combined with soil and litter C:N ratios indicated tendencies of decomposition driven by the climate. In the present study, although is not possible to clearly evaluate the effect of climate on $\delta^{13}\text{C}$ enrichment because the evaluated areas contained different plant species, the relationships between climatic parameters with the relation soil C:N and the CMB concentrations in surface and subsurface (Table 2) reinforce that there is an influence of climate on the decomposability of SOM.

It is interesting to note that in the P2, the SOM is easily decomposable, as suggested by the low values of C:N ratio and $\delta^{13}\text{C}$ in the soil profile. However, this profile has the highest accumulation of C in the

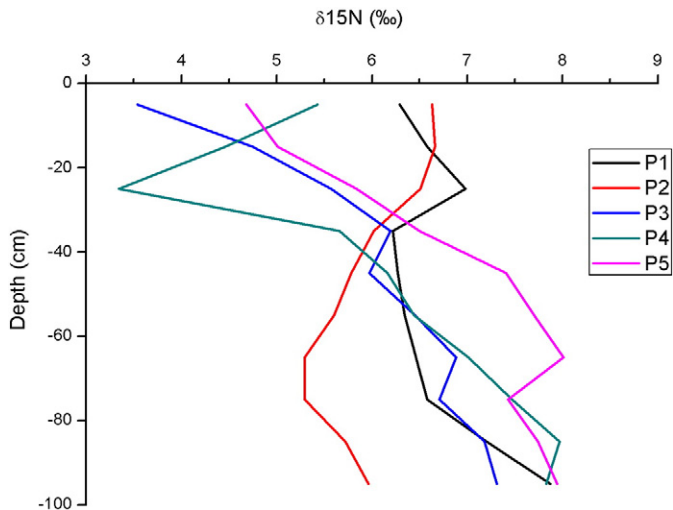


Fig. 3. Values of $\delta^{15}\text{N}$ at depth in the soil profiles.

Table 5

Values of litter $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_L$), litter $\delta^{15}\text{N}$ ($\delta^{15}\text{N}_L$), total carbon in the litter (TCL), total nitrogen in the litter (TNL) and C:N ratio in the litter (C:N_L) of all studied areas.

Profile	$\delta^{13}\text{C}_L$ ‰	$\delta^{15}\text{N}_L$ ‰	TCL g kg ⁻¹	TNL	C:N _L
P1 – Paudalho (143 m)	-29.40	3.37	434.4	12.9	34
P2 – Itambé (178 m)	-28.77	4.39	427.8	17.8	24
P3 – Brejão (820 m)	-29.43	3.02	447.6	18.9	24
P4 – Crato (947 m)	-30.62	-2.97	472.8	12.8	37
P5 – Crato (963 m)	-30.38	-0.86	506.7	10.6	48

studied profiles, despite of climate (hot and humid) and relative lability of SOM, which could favor high rates of decomposition of SOM and low C stock (Sanchez and Logan, 1992). Thus, changes in the decomposability of SOM induced by climate, does not seem to clearly explain the greater stability of C in this soil. However, the relations between the ^{15}N isotope and climatic parameters suggests that these areas, including P2, have N limitations, which could reduce the activity of free-living decomposers on SOM, according to Averill et al. (2014), and contribute to C accumulation.

The accumulation of ^{15}N , consistent with Martinelli et al. (1999) and Bustamante et al. (2004) for soils of tropical regions, has been appointed as a measure of the openness of the N cycle (Austin and Vitousek, 1988; Silfer et al., 1992; Eshetu and Högberg, 2000; Viani et al., 2011), a more open cycle having higher losses of the lighter isotope (^{14}N). The reduction of natural abundance of $\delta^{15}\text{N}$ in the subsurface in the soil profiles is possibly a result of the decomposition of organic residues. Because of SOM mineralization and the successive N assimilations by plants and microorganisms, the isotopic fractionation leads to higher losses of the lighter isotope (^{14}N), leaving the remaining SOM enriched in ^{15}N . This N loss in the subsurface is suggested by the relation between TNS and $\delta^{15}\text{N}$ ($r = 0.42, p < 0.001$) (Table 4). In surface layers, this enrichment is not clearly visualized although the reactions of mineralization, nitrification and denitrification may occur with greater intensity because of the constant supply of SOM.

The quadratic relation between temperature and $\delta^{15}\text{N}$ values in surface layers and subsurface (Table 2) indicates that soils under intermediate temperatures, as P4 and P5, has more closed cycle N, meaning less N loss, indicating restrictions N these soils, which may lead to increased C accumulation (Lindahl et al., 2010; Averill et al., 2014). This is also shown by the relations between SOC and $\delta^{15}\text{N}$ values in the entire soil (Table 4). Whereas the soils under higher and lower temperatures (P1 e P3), have more open N cycles and that in these soils, N losses are higher. This is consistent with the relation between soil $\delta^{15}\text{N}$ values and C:N ratio in surface layers (Table 4), which suggests that soils with low C:N ratios have more open N cycles and higher N losses. A negative relation between C:N ratio and soil ^{15}N values was reported by Amundson et al. (2003). These results were also indicated by the $\delta^{15}\text{N}$ values in the litter, which proved to be useful in expressing N dynamics in the soil. Martinelli et al. (1999) posited that systems without N limitations are subjected to higher N losses because of the open cycling, with higher $\delta^{15}\text{N}$ values, as observed in the areas of P1 and P3, with ^{15}N values of 3.37‰ and 3.02‰ in the litter, respectively. Conversely, the negative $\delta^{15}\text{N}$ values observed in the litter of Cerrado areas, -2.97‰ for P4 and -0.86‰ for P5, indicated systems with N restrictions (Fig. 3). In northeastern Brazil, in general, the isotopic patterns of soil N under montane forest and deciduous forest subhumid, are higher than in soils under coastal semideciduous forest (Freitas et al., 2015), in accordance with our study.

P2 showed high $\delta^{15}\text{N}$ values in surface layers in agreement with high value $\delta^{15}\text{N}$ litter (4.39‰) in this area, suggesting further loss of C surface. Whereas in the subsurface, this profile had the lowest $\delta^{15}\text{N}$ values between the studied profiles, which can be related to the stability of C, leading this profile to present the greatest accumulation of SOM. Mean annual temperature and total annual rainfall most likely affect N cycling

Table 6

Carbon concentrations of fulvic acids (C-FA), humic acids (C-HA), humin (C-HUM), and the C-HA/C-FA ratio in the studied profiles.

Profile	Depth Cm	C-FA g kg ⁻¹	C-HA	C-HUM	C-HA/C-FA
P2 – Itambé (178 m)	0–5	3.29	2.26	16.50	0.69
	5–10	3.57	6.78	14.01	1.90
	30–40	3.38	9.72	11.57	2.88
	80–90	1.72	5.10	6.58	2.97
P3 – Brejão (820 m)	0–5	3.59	9.88	16.05	2.75
	5–10	3.49	9.15	13.61	2.62
	30–40	2.77	4.66	7.13	1.68
	80–90	2.11	3.28	5.59	1.56
P4 – Crato (947 m)	0–5	7.77	12.58	27.26	1.62
	5–10	6.61	10.91	22.29	1.65
	30–40	3.79	6.38	13.30	1.68
	80–90	2.63	3.35	6.56	1.28

rates (Eshetu and Högberg, 2000); however, in the present study, a small effect of rainfall on $\delta^{15}\text{N}$ values was observed (Table 2). In a review performed by Amundson et al. (2003), the influence of temperature was stronger than the influence of rainfall on $\delta^{15}\text{N}$ values, even in colder environments.

Considering that SOM deposition is proportional to shoot biomass (Marín-Spiotta and Sharma, 2013) and that plant biomass above the soil in the deciduous forest is higher than in the savannah (Sampaio, 1996), in addition to other factors not considered in this study such as the high clay concentration in P2 (data not shown), these elements can be also related to the high C accumulation in this profile. However, even with a lower supply of organic residues in the soil compared with the other areas, the high C accumulation in profiles under savannah (P4 and P5) can be favored also by SOM quality, as indicated by the high C:N ratio in the soil (Table 3) and in the litter (Table 5), and the more recalcitrant SOM observed by spectroscopic and thermal gravimetric techniques (Sections 3.4 and 3.5, respectively). The P3, under humid montane forest, the lower temperatures compared with the other areas can reduce microbial activity (Kirschbaum, 1995), justifying the lower relative cycling and accumulation of C in this area. These results indicate that the current climate partially determines the balance between SOM deposition and mineralization.

These results show that the climate-C accumulation interaction observed along the climosequência shows that colder environments such as highlands or wet islands (Price et al., 2013) may be more susceptible to loss of soil C as a result of the intensification of the process of decomposition of SOM in land use changes or climate change, contributing to the emission of greenhouse gases to the atmosphere (Ceri and Cerri, 2007). This is particularly important for the Northeast region of Brazil, since these highland environments have privileged conditions as soil moisture and air, when compared to the surrounding semi-arid region, and therefore are under strong anthropic pressure. In addition, these environments constitute a large part of the Atlantic Forest remaining in this region (Brasil, 1972). At the national scale, although further studies are required to address the complexity of factors that control the stability of C in the soil, it is concerning that in a scenario of global climate change, the more unstable environments in relation to the loss of soil C coincide with the soils with larger store of this element as a result of the colder climatic influence (Bernoux et al., 2002).

4.2. Characteristics of humified SOM on the stability of C in surface and subsurface

Our study shows that the contribution of aromatic-C is not the primary formation mechanism of the umbric epipedon in the studied soils. The HUM, as the most significant fraction of humified SOM in all studied profiles and the most important in terms of C sequestration (Stevenson, 1994), was dominated by aliphatic C-H groups that include carboxylic and polysaccharide groups (Stevenson, 1994) in the surface

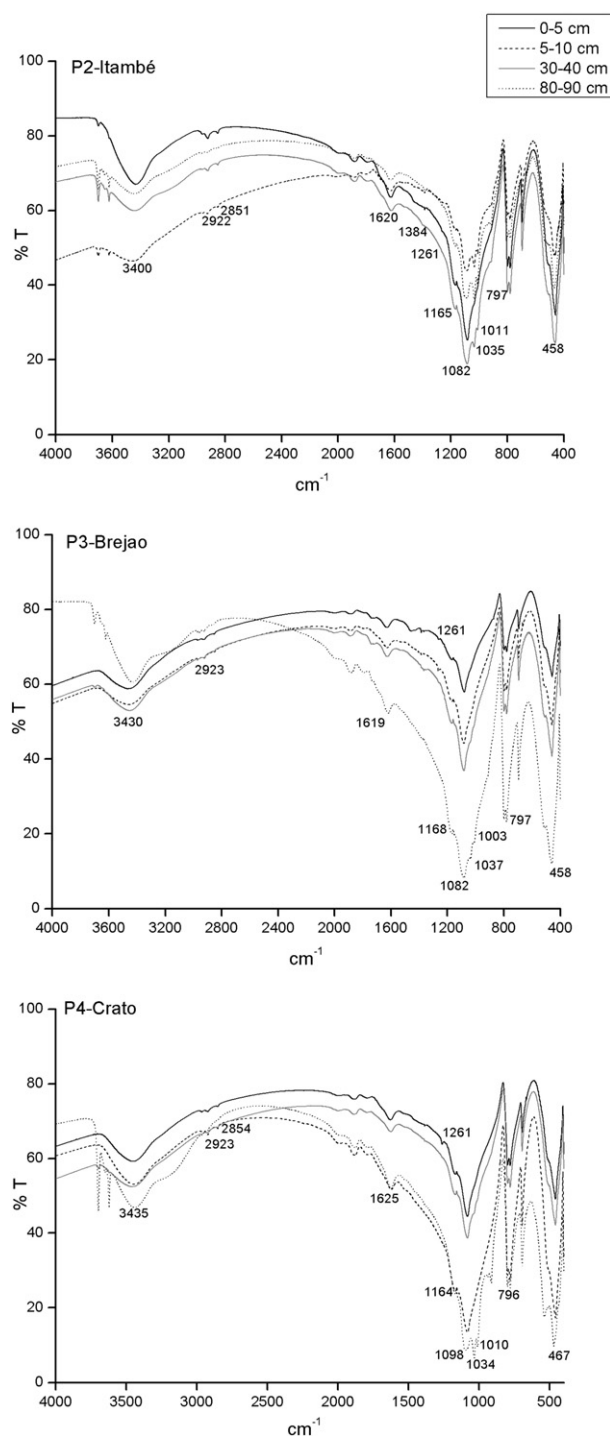


Fig. 4. FTIR spectra of humin at depth in the profiles.

layers and subsurface soil throughout the climosequência according to FTIR spectra (Fig. 4). These results are consistent with the DSC-TG data (Table 7), which are characterized by the prevalence of the oxidized fraction of the first exothermic reaction (1 Exo% approximately 50%), the thermally less stable fraction; thus, HUM was characterized by the substantial presence of a less stable fraction (100% – 1°Exo%). The HA fraction distinguished the profiles with regard to humification, which was lower in surface layers of soils developed in hotter areas (P2 and P4). The fastest cycling in a humid tropical environment (Sanchez and Logan, 1992) may explain the lower relative amount of aliphatic-C in this profiles. This lower humification is confirmed by the values of the C-HA/C-FA ratio, which, in general, are higher than 1.0 in

Table 7
DSC-TG data of humin extracted from profiles.

Profile	Depth Cm	DSC				TG			1°Exo ^a	
		Peak temperature °C			Energy (μV/min)		Mass loss %			
		End ¹	1Exo	2Exo	1Exo	2Exo	1Exo	2Exo		Total
P2	0–5	71.0	328.6	455.6	–	–	1.21	1.17	2.38	50.84
	5–10	68.7	329.3	465.4	0.04	–1.24	0.86	1.21	2.07	41.55
	30–40	66.5	326.7	462.6	–0.03	–0.98	0.51	0.94	1.45	35.17
	80–90	66.9	325.2	429.6	–0.50	–0.63	0.38	0.43	0.81	46.91
P3	0–5	66.7	340.0	469.6	0.07	–0.95	0.82	1.89	1.23	51.22
	5–10	66.0	337.5	489.2	0.07	–0.93	0.80	0.91	1.40	50.71
	30–40	67.9	337.4	440.7	–0.57	–0.49	0.53	0.47	0.90	46.67
	80–90	67.6	336.5	441.9	–0.73	–0.37	0.42	0.29	1.45	46.90
P4	0–5	68.5	344.0	527.1	0.23	–1.76	0.63	0.60	2.71	30.26
	5–10	74.9	344.3	458.3	0.19	–1.84	0.71	0.69	1.71	46.78
	30–40	66.4	340.1	455.7	–0.13	–1.14	0.42	0.48	1.00	53.00
	80–90	68.6	338.0	423.8	–0.72	–0.44	0.68	0.77	1.45	59.15

^a Percentage loss during the first exothermic reaction relative to the total loss of organic material.

all of the studied layers and profiles, indicating greater condensation of humic compounds (Leite et al., 2003). These results are consistent with the high values of the ratio CMB:SOC, which reinforce the concept that organic matter of epipedon umbric is dominated by easily decomposable compounds.

Previous studies identified polyaromatic hydrocarbons from charcoal degradation (black C) as an relevant factor for the C stability in HO under Cerrado (savanna), subtropical forests and tropical forests in southern and southeastern Brazil (Marques et al., 2015), in which the presence of coal in depth is identified in most profiles. These authors also suggested that the bioturbation and unfavorable conditions for decomposition determine the high reserve of subsoil-C. The soils described in the present study have not charcoal macroscopic lines in depth, which may indicate a different genesis of umbric epipedon, particularly the chemical nature of the organic material. This difference is suggested by the different chemical composition of the organic material in the surface layer of HO studied by Marques et al. (2015), in which the contribution of black C appears to be important only in depth, or even on HO (other) with small amounts of coal in the same study cited.

The general chemical composition of HUM in umbric epipedon provided by FTIR and DSC in this study is consistent with the results obtained by other methods of SOM analysis and confirms the high concentration on alkyl-C and polysaccharides in the subsoil-SOM mentioned by several authors (Skjemstad et al., 1992; Baldock and Skjemstad, 2000; Rumpel et al., 2004; Lorenz et al., 2007; Vancampenhout et al., 2012).

Considering the growing interest in C sequestration and the mitigation of climate change processes, our findings highlight the high concentration of easily decomposable HUM compounds, a significant fraction of C in umbric epipedon, suggesting the vulnerability of these C stocks and their potential to act as a source of CO₂. This finding may be relevant because C concentrations of HO are up to 5 times higher than Oxisols without umbric epipedon, and HO with a thick epipedon rich in SOM cover the 258,839 km² of the world (Lepsch and Buol, 1986; Andrade et al., 2004). In northeastern Brazil, in which 62% of the territory is semi-arid, the HO occur in areas of privileged climate, primarily favored by the orographic rain. Therefore, the HO are extensively used for agriculture and livestock, are extremely important to the regional economy (Andrade-Lima, 1966; Araújo Filho et al., 2000) and can increase the decomposition of SOM and compromise the C sequestration in these environments. Moreover, in the northeast, these soils have clay and Fe₂O₃ values significantly lower than HO located in other regions of Brazil (Araujo, 2014; Calegari, 2008), indicating that the association of SOM with the mineral phase may be an organic-matter-protection mechanism with less importance than in other HO in Brazil, reinforcing the idea of the susceptibility of these C stocks discussed previously because of the low chemical recalcitrance of HUM.

5. Conclusions

The Humic Oxisols have the potential to sequester larger amounts of C with thick umbric epipedons (>100 cm thickness). However, the occurrence of these soils in northeastern Brazil generates great interest because these soils are in tropical areas that favor the rapid decomposition of SOM in addition to composing privileged environments surrounded by semi-arid areas and being intensively used for agriculture and livestock. Thus, these soils are quite susceptible to degradation resulting in a potential source of C for the atmosphere.

C accumulation in the umbric epipedon of Oxisols in northeastern Brazil was not determined by the increase in altitude, the increase in rainfall and the reduction in temperature, as suggested by the high SOC concentrations in the majority of the studied profiles, including soils under hot and humid climates (P2 profile at coastal area). The abundance of the ¹⁵N isotope ($\delta^{15}\text{N}$) was related to temperature and the C:N ratio, indicating N restrictions in soils at high temperatures. This result suggests that the greater accumulation of C in the profiles P2 (178 m a.s.l.), P4 and P5 (>900 m a.s.l.) is influenced by the low availability of soil N. In general, $\delta^{13}\text{C}$ values showed a predominance of C3 plants at greater depths. CMB concentration was influenced by the climate in surface layers and the subsurface, indicating that the effect of temperature was greater than the effect of water availability. The microbial quotient (CMB:SOC) indicated that a high proportion of soil organic C is present as microbial biomass in the majority of the umbric epipedon. SOM aromaticity increased in the subsurface. FTIR spectra showed that HUM was dominated by aliphatic C–H groups in all of the evaluated profiles. The thermal gravimetric analysis revealed that approximately 50% of the HUM in the umbric epipedon composes aliphatic compounds in all of the studied soils.

This research area may be classified as poorly studied, and these results provide insights into the stability of SOM at surface layers and subsurfaces to provide a substantial soil C sink and to promote the health of the tropical forests remaining in South America.

Acknowledgments

We thank Mateus Rosas Ribeiro “in memoriam” for the supervision of this work, and José Fernando W. F. Lima for their assistance during the field activities. This work was partially financed by Coordination of Improvement of Higher Education Personnel - CAPES by Grants: PNPD #2888/2010 and PDSE-BEX #14700/12-3), and Foundation support to science and technology of Pernambuco (Facepe) by grants #APQ0044-5.01/11 and National Council for Scientific and Technological Development - CNPq for granting scholarships in Brazil.

References

- Amundson, R., Austin, A.T., Schuur, E.A.G., Yoo, K., Matzek, V., Kendall, C., Uebersax, A., Brenner, D., Baisden, W.T., 2003. Global patterns of the isotopic composition of soil and plant nitrogen. *Glob. Biogeochem. Cycles* 17, 1031. <http://dx.doi.org/10.1029/2002GB001903>.
- Andrade, F.V., Schaefer, C.E.G.R., Correa, M.L.T., Mendonça, E.S., 2004. Carbon stocks in Brazilian Latosols (Oxisols) from different morphoclimatic regions and management systems. *Commun. Soil Sci. Plant Anal.* 35, 2125–2136. <http://dx.doi.org/10.1081/LCSS-200028959>.
- Andrade-Lima, D., 1966. Esboço fitoecológico de alguns “brejos” de Pernambuco (in Portuguese). Recife. Instituto de Pesquisas Agronômicas de Pernambuco. Boletim Técnico, 8.
- Araujo, J.K.S., 2014. Latossolos com Horizonte a húmico na província Borborema: caracterização de solos e da matéria orgânica (P.h.D. thesis) Universidade Federal Rural de Pernambuco, Recife.
- Araújo Filho, J.C., Burgos, N., Lopes, O.F., Silva, F.H.B.B., Medeiros, L.A.R., Melo Filho, H.F.R., Parahyba, R.B.V., Cavalcanti, A.C., Oliveira Neto, M.B., Silva, F.B.R., Leite, A.P., Santos, J.C.P., Sousa Neto, N.C., Silva, A.B., Luz, L.R.Q.P., Lima, P.C., Reis, R.M.G., Barros, A.H.C., 2000. Levantamento de reconhecimento de baixa e média intensidade dos solos do Estado de Pernambuco (in Portuguese). Embrapa Solos, Rio de Janeiro.
- Austin, A.T., Vitousek, P.M., 1988. Nutrients dynamics on a precipitation gradient in Hawaii. *Oecologia* 113, 519–529.
- Averill, C., Turner, B.L., Finzi, A.C., 2014. Mycorrhiza-mediated competition between plants and decomposers drives soil carbon storage. *Nature* 505, 543–545. <http://dx.doi.org/10.1038/nature12901>.
- Baldock, J.A., Skjemstad, J.O., 2000. Role of the soil matrix and minerals in protecting natural organic materials against biological attack. *Org. Geochem.* 31, 697–710.
- Bartlett, R.J., Ross, S.D., 1988. Colorimetric determination of oxidizable carbon in acid soil solutions. *Soil Sci. Am. J.* 52, 1191–1192. <http://dx.doi.org/10.2136/sssaj1988.03615995005200040055x>.
- Batjes, N.H., 2014. Total carbon and nitrogen in the soils of the world. *Eur. J. Soil Sci.* 65, 10–22. <http://dx.doi.org/10.1111/ejss.12114.2>.
- Bernoux, M., Carvalho, M.C.S., Volkoff, B., Cerri, C.C., 2002. Brazil's soil carbon stocks. *Soil Sci. Am. J.* 66, 888–896. <http://dx.doi.org/10.2136/sssaj2002.8880>.
- BRASIL. Ministério da Agricultura. Departamento Nacional de Pesquisa Agropecuária. Divisão de Pesquisa Pedológica, 1972a. Levantamento exploratório-reconhecimento dos solos do Estado de Pernambuco (in Portuguese). 2 vol. Recife. (DNPEA. Boletim Técnico, 28; SUDENE. Série Pedológica, 16).
- BRASIL. Ministério da Agricultura. Departamento Nacional de Pesquisa Agropecuária. Divisão de Pesquisa Pedológica, 1973b. Levantamento exploratório-reconhecimento dos solos do Estado do Ceará (in Portuguese). Recife. (MA/DNPEA Boletim Técnico, 28; SUDENE/DRN).
- Brookes, P.C., Powlson, D.S., Jendinson, D.S., 1982. Measurement of microbial biomass phosphorus in soil. *Soil Biol. Biochem.* 14, 319–326.
- Brunn, M., Petersen, S.L., Sauer, T., Oelmann, Y., 2014. Temperature and precipitation effects on $\delta^{13}\text{C}$ depth profiles in SOM under temperate beech forests. *Geoderma* 235–236, 146–153. <http://dx.doi.org/10.1016/j.geoderma.2014.07.007>.
- Bustamante, M.M.C., Martinelli, L.A., Silva, D.A., Camargo, P.B., Klink, C.A., Domingues, T.F., Santos, R.V., 2004. $\delta^{15}\text{N}$ natural abundance in woody plants and soils of central Brazilian savannas (cerrado). *J. Appl. Ecol.* 14, 200–213. <http://dx.doi.org/10.1890/01-6013>.
- Calegari, M.R., 2008. Ocorrência e significado paleoambiental do horizonte A húmico em Latossolos (P.h.d. thesis) Universidade de São Paulo, São Paulo.
- Cerri, C.C., Cerri, C.E.P., 2007. Agricultura e aquecimento global. *Bol. Soc. Bras. Ciênc. Solo* (in Portuguese), vol. 32 p. 40–44, 2007.
- Chabbi, A., Kögel-Knabner, I., Rumpel, C., 2009. Stabilised carbon in subsoil horizons is located in spatially distinct parts of the soil profile. *Soil Biol. Biochem.* 41, 256–271. <http://dx.doi.org/10.1016/j.soilbio.2008.10.033>.
- Czimczik, C.I., Preston, C.M., Schmidt, M.W.I., Werner, R.A., Schulze, E.D., 2002. Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood. *Org. Geochem.* 33, 1207–1223. [http://dx.doi.org/10.1016/S0146-6380\(02\)00137-7](http://dx.doi.org/10.1016/S0146-6380(02)00137-7).
- Dell'Abate, M.T., Benedetti, A., Trincera, A., Dazzi, C., 2002. Humic substances along the profile of two Typic Haploxerent. *Geoderma* 107, 281–296. [http://dx.doi.org/10.1016/S0016-7061\(01\)00153-7](http://dx.doi.org/10.1016/S0016-7061(01)00153-7).
- Dell'Abate, M.T., Benedetti, A., Brookes, P.C., 2003. Hyphenated techniques of thermal analysis for soil humic acids characterisation. *J. Sep. Sci.* 26, 433–440. <http://dx.doi.org/10.1002/jssc.200390057>.
- EMBRAPA – Empresa Brasileira de Pesquisa Agropecuária, 2013. Sistema brasileiro de classificação de solos. 3th ed. EMBRAPA, Brasília.
- EMBRAPA. Empresa Brasileira de Pesquisa Agropecuária. Ministério da Agricultura, Pecuária e Abastecimento. Mapa de Solos do Brasil - 1:5.000.000, 2012.
- Eshetu, Z., Höglberg, P., 2000. Effects of land use on ^{15}N natural abundance of soils in Ethiopian highlands. *Plant Soil* 222, 109–117. <http://dx.doi.org/10.1023/A:1004777301260>.
- Fang, C.M., Smith, P., Moncrieff, J.B., Smith, J.U., 2005. Similar response of labile and resistant soil organic matter pools to changes in temperature. *Nature* 433, 57–59. <http://dx.doi.org/10.1038/nature03138>.
- Farquhar, G.D., Ehleringer, J.R., Hubick, K.T., 1989. Carbon isotope discrimination and photosynthesis. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* 40, 503–537. <http://dx.doi.org/10.1146/annurev.pp.40.060189.002443>.
- Fontaine, S., Barot, S., Barre, P., Bdioui, N., Mary, B., Rumpel, C., 2007. Stability of organic carbon in deep soil layers controlled by fresh carbon supply. *Nature* 450, 277–280. <http://dx.doi.org/10.1038/nature06275>.
- Fontes, M.R., Weed, S.B., Bowen, L.H., 1992. Association of microcrystalline goethite and humic acid in some oxisols from Brazil. *Soil Sci. Am. J.* 56, 982–990. <http://dx.doi.org/10.2136/sssaj1992.03615995005600030050x>.
- Freitas, A.D.S., Sampaio, E.V.S.B., Ramos, A.P.S., Barbosa, M.R.V., Lyra, R.P., Araújo, E.L., 2015. Nitrogen isotopic patterns in tropical forests along a rainfall gradient in Northeast Brazil. *Plant Soil* 391, 109–122. <http://dx.doi.org/10.1007/s11104-015-2417-5>.
- García-Pausas, J., Casals, P., Camarero, L., Hugué, C., Sebastià, M.-T., Thompso, R., Romanyà, J., 2007. Soil organic carbon storage in mountain grasslands of the Pyrenees: effects of climate and topography. *Biogeochemistry* 82, 279–289. <http://dx.doi.org/10.1007/s10533-007-9071-9>.
- Gonçalves, C.N., Dalmolin, R.S.D., Dick, D.P., Klamt, E., Knicker, H., Kögel-Knabner, I., 2003. The effects of 10% HF treatment on the resolution of ^{13}C CP/MAS NMR spectra and on the quality of organic matter in Ferralsols. *Geoderma* 116, 373–392. [http://dx.doi.org/10.1016/S0016-7061\(03\)00119-8](http://dx.doi.org/10.1016/S0016-7061(03)00119-8).
- Gonfiantini, R., 1978. Standard for stable isotope measurement in natural compounds. *Nature* 215, 534–536.
- Gonfiantini, R., Stichler, W., Rozanski, K., 1995. Standards and intercomparison materials distributed by the International Atomic Energy Agency for stable isotope measurements. Reference and Intercomparison Materials for Stable Isotopes of Light Elements, IAEA-TECDOC-825. IAEA, Vienna.
- González-Pérez, M., Martín-Neto, L., Saab, S.C., Novotny, E.H., Milori, D.M.B.P., Bagnato, V.S., Colnago, L.A., Melo, W.J., Knicker, H., 2004. Characterization of humic acids from a Brazilian oxisols under tillage systems by EPR, ^{13}C NMR, FTIR and fluorescence spectroscopy. *Geoderma* 118 (3–4), 181–190. [http://dx.doi.org/10.1016/S0016-7061\(03\)00192-7](http://dx.doi.org/10.1016/S0016-7061(03)00192-7).
- Islam, K.R., Weil, R.R., 1998. Microwave irradiation of soil for routine measurement of microbial biomass carbon. *Biology and Fertility of Soils* 27, 408–416.
- Jandl, R., Lindner, M., Vesterdal, L., Bauwens, B., Baritz, R., Hagedorn, F., Johnson, D.W., Minkinen, K., Byrne, K.A., 2007. How strongly can forest management influence soil carbon sequestration? *Geoderma* 137, 253–268.
- Jenny, H., 1980. *The Soil Resource, Origin and Behavior*. Springer, New York.
- Jobbágy, E.G., Jackson, R.B., 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecol. Appl.* 10, 423–436. [http://dx.doi.org/10.1890/1051-0761\(2000\)10\[0423:TVDOSO\]2.0.CO;2](http://dx.doi.org/10.1890/1051-0761(2000)10[0423:TVDOSO]2.0.CO;2).
- Jonczak, J., 2013. Dynamics, structure and properties of plant litterfall in a 120-year old beech stand in Middle Pomerania between 2007–2010. *Soil Sci. Annu.* 64 (1), 8–13. <http://dx.doi.org/10.2478/ssa-2013-0002>.
- Ker, J.C., 1997. Oxisols of Brazil: a review (in Portuguese). *Geonomos* 5, 17–40 (<http://www.igc.ufmg.br/portaldoperiodicos/index.php/geonomos/article/view/187> (accessed 10 Jul. 2015)).
- Kirschbaum, M.U.F., 1995. The temperature dependence of soil organic matter decomposition and the effect of global warming on soil organic carbon storage. *Soil Biol. Biochem.* 27, 753–760. [http://dx.doi.org/10.1016/0038-0717\(94\)00242-S](http://dx.doi.org/10.1016/0038-0717(94)00242-S).
- Leite, L.F.C., Mendonça, E.S., Neves, J.C.L., Machado, P.L.O.A., Galvão, J.C.C., 2003. Total stocks of organic carbon and its pools in Acrisols under forest and under maize cultivated with mineral and organic fertilization (in Portuguese). *Rev. Bras. Ciênc. Solo* 27, 821–832.
- Lepsch, I.F., Buol, S.W., 1986. Oxisol-landscape relationship in Brazil. *International Soil Classification Workshop*, 13. Campinas: Papers SNLCS/EMBRAPA. University of Puerto Rico, USA, pp. 174–189.
- Lindahl, B.D., de Boer, W., Finlay, R.D., 2010. Disruption of root carbon transport into forest humus stimulates fungal opportunists at the expense of mycorrhizal fungi. *ISME J.* 4, 872–881.
- Lorenz, K., Lal, R., 2005. The depth distribution of soil organic carbon in relation to land use and management and the potential of carbon sequestration in subsoil horizons. *Adv. Agron.* 88, 35–66.
- Lorenz, K., Lal, R., Preston, C.M., Nierop, K.G.J., 2007. Strengthening the soil organic carbon pool by increasing contributions from recalcitrant aliphatic bio (macro) molecules. *Geoderma* 142, 1–10.
- Lumsdon, D.G., Fraser, A.R., 2005. Infrared spectroscopic evidence supporting heterogeneous site binding models for humic substances. *Environ. Sci. Technol.* 39, 6624–6631.
- Marin-Spiotta, E., Sharma, S., 2013. Carbon storage in successional and plantation forest soils: a tropical analysis. *Glob. Ecol. Biogeogr.* 22, 105–117. <http://dx.doi.org/10.1111/j.1466-8238.2012.00788.x>.
- Marin-Spiotta, E., Chaopricha, N.T., Plante, A.F., Diefendorf, A.F., Mueller, C.W., Grandy, A.S., Mason, J.A., 2014. Long-term stabilization of deep soil carbon by fire and burial during early Holocene climate change. *Nat. Geosci.* 7, 428–432. <http://dx.doi.org/10.1038/ngeo2169>.
- Marques, F.A., Calegari, M.R., Vidal-Torrado, P., Buurman, P., 2011. Relationship between soil oxidizable carbon and physical, chemical and mineralogical properties of umbric Ferralsols. *Rev. Bras. Ciênc. Solo* 35, 25–40. <http://dx.doi.org/10.1590/S0100-06832011000100003>.
- Marques, F.A., Buurman, P., Schellekens, J., Vidal-Torrado, P., 2015. Molecular chemistry in humic Ferralsols from Brazilian Cerrado and forest biomes indicates a major contribution from black carbon in the subsoil. *J. Anal. Appl. Pyrolysis* 113, 518–528. <http://dx.doi.org/10.1016/j.jaap.2015.03.016>.
- Martinelli, L.A., Piccolo, M.C., Townsend, A.R., Vitousek, P.M., Cuevas, E., McDowell, W., Robertson, G.P., Santos, O.C., Treseder, K., 1999. Nitrogen stable isotopic composition of leaves and soil: tropical versus temperate forests. *Biogeochemistry* 46, 45–65.
- Mendonça, E.S., Matos, E.S., 2005. Matéria orgânica do solo: métodos de análises (in Portuguese). UFV, Viçosa (In Portuguese).
- Mikutta, R., Schaumann, G.E., Gildemeister, D., Bonneville, S., Kramer, M.G., Chorover, J., Chadwick, O.A., Guggenberger, G., 2009. Biogeochemistry of mineral-organic associations across a long-term mineralogical soil gradient (0.3–4100 kyr), Hawaiian Islands. *Geochim. Cosmochim. Acta* 73, 2034–2060.
- Mora, J.L., Guerra, J.A., Armas-Herrera, C.M., Arbelo, C.D., Rodríguez-Rodríguez, A., 2014. Storage and depth distribution of organic carbon in volcanic soils as affected by environmental and pedological factors. *Catena* 123, 163–175. <http://dx.doi.org/10.1016/j.catena.2014.08.004>.

- O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. Fractionation techniques may reveal new aspects of carbon dynamics in plants. *Bioscience* 38, 328–336.
- Paul, E.A., Follett, R.F., Leavitt, S.W., Halvorson, A., Peterson, G.A., Lyon, D.J., 1997. Radiocarbon dating for determination of soil organic matter pool sizes and dynamics. *Soil Sci. Am. J.* 61, 1058–1067.
- Pessenda, L.C.R., Gouveia, S.E.M., Ribeiro, A.S., Oliveira, P.E.O., Aravena, R., 2010. Late Pleistocene and Holocene vegetation changes in northeastern Brazil determined from carbon isotopes and charcoal records in soils. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 297, 597–608.
- Poulter, B., Frank, D., Ciais, P., Myneni, R.B., Andela, N., Bi, J., Broquet, G., Canadell, J.G., Chevallier, F., Liu, Y.Y., Running, S.W., Sitch, S., Guido, R., van der Werf, G.R., 2014. Contribution of semi-arid ecosystems to interannual variability of the global carbon cycle. *Nature* 509, 600–603. <http://dx.doi.org/10.1038/nature13376>.
- Price, M.F., Byers, A.C., Friend, D.A., Kohler, T., Price, L.W., 2013. *Mountain Geography: Physical and Human Dimensions*. University of California Press, Berkeley.
- Queiroz Neto, J.P., Castro, S.S., 1974. *Formações Superficiais e Latossolos Vermelho-Amarelo Húmicos na área de Bragança Paulista*. Estado de São Paulo, Brasil. Congresso Brasileiro de Geologia, 18. Porto Alegre: Anais. SBG, Porto Alegre, pp. 65–83.
- Rovira, P.A.S., Brunetti, G., Pólo, A., Senesi, N., 2002. Comparative chemical and spectroscopic characterization of humic acids from sewage sludges and sludge-amended soils. *Soil Sci.* 167, 235–245.
- Rumpel, C., Kögel-Knabner, I., 2011. Deep soil organic matter — a key but poorly understood component of terrestrial C cycle. *Plant Soil* 338, 143–158. <http://dx.doi.org/10.1007/s11104-010-0391-5>.
- Rumpel, C., Kögel-Knabner, I., Bruhn, F., 2002. Vertical distribution, age, and chemical composition of organic carbon in two forest soils of different pedogenesis. *Org. Geochem.* 33, 1131–1142. [http://dx.doi.org/10.1016/S0146-6380\(02\)00088-8](http://dx.doi.org/10.1016/S0146-6380(02)00088-8).
- Rumpel, C., Eusterhues, K., Kögel-Knabner, I., 2004. Location and chemical composition of stabilized organic carbon in topsoil and subsoil horizons of two acid forest soils. *Soil Biol. Biochem.* 36, 177–190.
- Sampaio, E.V.S.B., 1996. Phytosociology. In: Sampaio, E.V.S.B., Mayo, S.J., Barbosa, M.R.V. (Eds.), *Northeastern Botanical Research: Progress and Prospects* (in Portuguese). Sociedade Botânica do Brasil, Recife, pp. 203–224.
- Sanaullah, M., Chabbi, A., Leifeld, J., Bardoux, G., Billou, D., Rumpel, C., 2011. Decomposition and stabilization of root litter in top- and subsoil horizons: what is the difference? *Plant Soil* 338, 127–141. <http://dx.doi.org/10.1007/s11104-010-0554-4>.
- Sanchez, P.A., Logan, T.J., 1992. Myths and science about the chemistry and fertility of soils in the tropics. In: Lal, R., Sanchez, P.A. (Eds.), *Myths and Science of Soil of the Tropics*. SSSA/ASA, Madison, pp. 35–46 (Special Publication, 29).
- Schuster, W.S.F., Sandquist, D.R., Phillips, S.L., Ehleringer, J.R., 1992. Comparisons of carbon isotope discrimination in populations of aridland plant species differing in lifespan. *Oecologia* 91, 332–337.
- Silfer, J.A., Engel, M.H., Macko, S.A., 1992. Kinetic fractionations of stable carbon and nitrogen isotopes during peptide bond hydrolysis: experimental evidence and geochemical implications. *Chem. Geol.* 101, 211–221.
- Silva, A.C., Vidal-Torrado, P., 1999. Gênese dos Latossolos Húmicos e sua relação com a evolução da paisagem numa área cratônica do sul de Minas Gerais. *Rev. Bras. Cienc. Solo* 23, 329–341.
- Silverstein, R.M., Webster, F.X., Kiemle, D.J., 2005. *Spectrometric Identification of Organic Compounds*. seventh ed. Hoboken, J. Wiley.
- Simas, F.N.B., Schaefer, C.E.G.R., Fernandes Filho, E.I., Chagas, A.C., Brandão, P.C., 2005. Chemistry, mineralogy and micropedology of highland soils on crystalline rocks of Serra da Mantiqueira, southeastern Brazil. *Geoderma* 125, 187–201. <http://dx.doi.org/10.1016/j.geoderma.2004.07.013>.
- Skjemstad, J.O., Waters, A.G., Hanna, J.V., Oades, J.M., 1992. Genesis of Podzols on coastal dunes in Southern Queensland. 4. Nature of the organic matter fraction as seen by C-13 nuclear-magnetic-resonance spectroscopy. *Aust. J. Soil Res.* 30, 667–681.
- Soil Survey Staff, 2014. *Soil Taxonomy: A basic system of soil classification for making and interpreting a soil survey*. 12nd ed. USDA-NRCS. U.S. Gov. Print. Office, Washington, DC.
- Spielvogel, S., Prietzel, J., Kögel-Knabner, I., 2008. Soil organic matter stabilisation in acidic forest soils is preferential and soil type-specific. *Eur. J. Soil Sci.* 59, 674–692.
- Stevenson, F.J., 1994. *Humus Chemistry: Genesis, Composition, Reactions*. second ed. Wiley, New York.
- Swift, R.S., 1996. Organic matter characterization. In: Sparks, O.L. (Ed.), *Methods of Soil Analysis Part 3: Chemical Methods*. Soil Science Society of America, Madison, pp. 1011–1020.
- Vancampenhout, K., De Vos, B., Wouters, K., Swennen, R., Buurman, B., Deckers, J., 2012. Organic matter of subsoil horizons under broadleaved forest: highly processed or labile and plant-derived? *Soil Biol. Biochem.* 50, 40–46.
- Velloso, A.L., Everardo, V.S.B., Sampaio, F.G., Pareyn, C., 2002. *Ecoregions proposed for the Caatinga biome* (in Portuguese). Associação Plantas do Nordeste, Instituto de Conservação Ambiental The Nature Conservancy do Brasil, Recife.
- Viani, R.A.G., Rodrigues, R.R., Dawson, T.E., Oliveira, R.S., 2011. Functional differences between woodland savannas and seasonally dry forests from South-Eastern Brazil: evidence from ¹⁵N natural abundance studies. *Aust. Ecol.* 36, 974–982. <http://dx.doi.org/10.1111/j.1442-9993.2010.02233.x>.
- Vinton, M.A., Burke, I.C., 1997. Contingent effects of plant species on soils along a regional moisture gradient in the Great Plains. *Oecologia* 110, 393–402.
- von Lützow, M., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions—a review. *Eur. J. Soil Sci.* 57, 426–445.