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Articles

Humic fractions of soil carbon under agroforestry system in altitude swamp Pernambucano

Frações húmicas de carbono do solo sob sistema agroflorestal em brejo de altitude Pernambucano

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ABSTRACT

MOS (soil organic matter) is a natural carbon reservoir, and divided into different stages of decomposition according to its solubility and structural complexity. In view of this context, this work aimed to quantify the carbon content in the humic fractions of the soil organic matter under an agroforestry system in three toposequences in the swamp of altitude in Pernambuco, Brazil. The study was carried out on the Yaguara farm, and the studied areas were native forest and three toposequences of agroforestry system. Soil samples were collected in trenches 1.5 x 1.5 m, at depths 0-20, 20-40 and 40-60 cm, with four replications. The carbon concentrations in the humic fractions of the soil decreased with increasing depth. The area with agroforestry system had the highest concentrations of carbon in the humic fractions. The stocks of humic fractions found in the agroforestry system area showed higher average values in the top area 5.62, 9.72 and 22.53 Mg ha^{-1} in relation to native forest 4.84, 8.28 and 19.20 Mg ha^{-1}, respectively for fulvic acid, humic acid and humine. Among the evaluated areas, the soil with agroforestry system top area has great potential to increase the carbon storage in the humic fractions of the soil.

Keywords: Soil organic matter; Fulvic acid; Humic acid; Humine

RESUMO

A MOS (matéria orgânica do solo) é um reservatório natural de carbono e dividida em diferentes estágios de decomposição conforme sua solubilidade e complexidade estrutural. Diante desse contexto, este trabalho teve como objetivo quantificar os teores de carbono nas frações húmicas da matéria orgânica do solo sob sistema agroflorestal em três topossequências no brejo de altitude de Pernambuco, Brasil. O estudo foi desenvolvido na fazenda Yaguara, e as áreas estudadas foram mata nativa e três topossequências de sistema agroflorestal. As amostras de solos foram coletadas em trincheiras 1,5 x 1,5 m, nas profundidades 0-20, 20-40 e 40-60 cm, com quatro replicações. As concentrações de carbono nas frações húmicas do solo diminuíram com o aumento da profundidade. A área com sistema agroflorestal teve as maiores concentrações de carbono nas frações húmicas. Os estoques das frações húmicas encontradas em área de sistema agroflorestal apresentaram maiores valores médios em área de topo 5,62, 9,72 e 22,53 Mg ha^{-1} em relação à mata nativa 4,84, 8,28 e 19,20 Mg ha^{-1}, respectivamente para ácido fúlvico, ácido húmico e humina. Dentre as áreas avaliadas, o solo com sistema agroflorestal área de topo tem grande potencial para aumentar o armazenamento de carbono nas frações húmicas do solo.

Palavras-chave: Matéria orgânica do solo; Ácido fúlvico; Ácido húmico; Humina

1 INTRODUCTION

The largest carbon reservoir on the Earth's surface is MOS, being considered fundamental for the maintenance of the physical, chemical and biological characteristics of the soil. The concept of humus is related to the classification of a set of organic and organomineral horizons of the superficial layer of the soil, which reflects morphologically distinct phases of the litter and the decomposition of the organic matter of the soil, but not to the fractions of the organic matter of the soil (Chertov; Nadporozhskaya, 2018).

Chemically, MOS is the main source of macronutrients and micronutrients essential to plants, it acts indirectly on the availability of the elements and carbon is the one with the highest amount (Cotrufo; Ranalli; Haddix; Six; Lugato, 2019). Physically, it improves the structure, reduces plasticity and cohesion, and increases the water retention and aeration capacity, allowing greater penetration and distribution of the roots in the soil (Williams; Blanco-Canqui; Francis; Galusha, 2017). Basically, MOS is divided into light and heavy fractions, the light fraction in general consists of organic materials derived mainly from plant remains, but containing reasonable amounts of microbial and microfauna residues (Chen; Wang; Liu; Zhao; Lu; Zhou; Li, 2017). The heavy fraction consists of organic materials in an advanced stage of decomposition and not visually identifiable. This fraction is represented by humic substances which are fulvic acids, humic acids and humines, where they have a higher percentage of total organic carbon of 70 to 80% in most soils (Olk; Bloom; Perdue; Mcknight; Chen; Farenhorst; Senesi; Chin; Schmitt-Koplin; Hertkorn; Harir, 2019).

Fulvic acids are soluble in alkaline medium and in diluted acid, consisting of polysaccharides, amino acids and phenolic compounds, which are more reactive than the other two fractions due to the greater amount of carboxylic and phenolic groups (Stevenson, 1994). Humic acids are soluble in alkaline medium and insoluble in diluted acid medium, with dark coloring, composed of macromolecules of relatively high molecular weight. Humic acids have a higher carbon content, less oxygen and a similar hydrogen content than fulvic acids (Stevenson, 1994). Humine is insoluble in alkaline and acidic media and can have a varied composition, with reduced reaction capacity. It has high hydrophobicity and strong interaction with inorganic components and also because it contains lipid compounds, carbohydrate and aromatic structures in different proportions. In comparison to fulvic and humic acids, it has a strong association with minerals and causes insolubility in an alkaline aqueous medium (Stevenson, 1994).

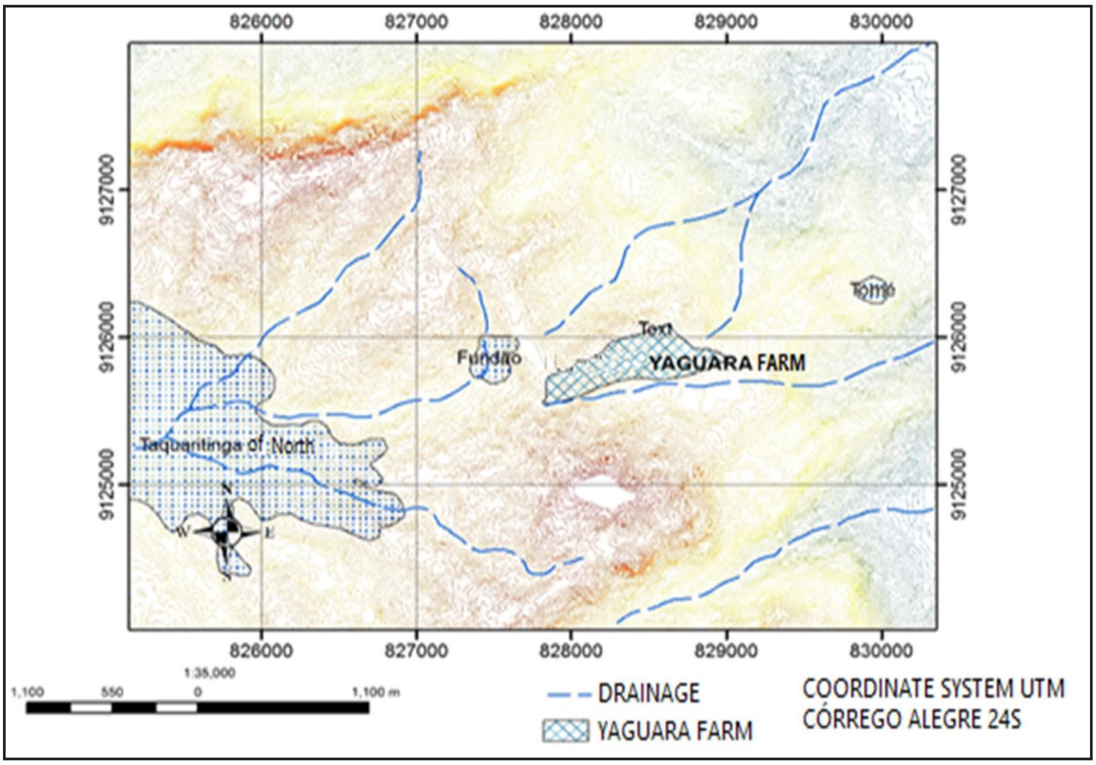
Thus, the conversion of areas of natural vegetation into agroforestry systems can cause positive or negative changes in the carbon reserve in humic fractions, caused by the change in land use, a reason that has become a frequent focus of research. In view of this, this work aimed to quantify the carbon content in the humic fractions of the soil organic matter under an agroforestry system in three toposequences (top, hillside and downhill) in the swamp of altitude in Pernambuco, Brazil.

2 MATERIALS AND METHODS

2.1 Study area

The research was carried out at the Yaguara farm (Figure 1), inserted in the municipality of Taquaritinga do Norte, belonging to the geoenvironmental unit of the Planalto da Borborema, State of Pernambuco, in the geographical coordinates 7°53’17”S and 36°5’33” W. The area is inserted in the relief called Altitude Swamp, and the soil classified as Ultisols (SOIL SURVEY STAFF, 2014). The climate of the region was classified as Aw, of tropical climate with dry winter, mountainous relief with deep and narrow valleys. The highest rainfall was recorded between February and August, with an annual average of 721 mm and an annual average temperature of 21°C and altitude between 736 m and 1,100 m according to Koppen (1948).

Figure 1 – Location map of the study area, ecological Yaguara farm in the municipality of Taquaritinga do Norte - PE



Source: Authors (2021)

Inside the farm were studied two areas, one with native vegetation as a control and the other with an agroforestry system with planting coffee under thinned native forest called agroforestry system. The Native vegetation area has 4.57 ha, with large swamp species between 20 and 35 m high. Through the floristic survey, the experimental site presented the following forest species: *Galezia gorazema* Moq., Rubus sp., *Inga subnuda* Salzm. ex Benth., *Caesalpinia leiostachya* Benth. Ducke, *Copaifera trapezifolia* Hayne, *Roupala cearaensis* Sleumer, *Cedrela* sp., *Terminalia* sp., *Oreopanax capitatum* Decne et Planch. var. multiflorum (DC.) E. March, *Manilkara rufula* (Miq.) Lam, *Aspidosperma pyricollum* Muell. Arg., *Tabebuia avellanedae* Lorentz ex Griseb (Silva, 2017).

Agroforestry system: The cultivation used was the rustic with little alteration of the forest, used area was 25.59 ha and more than ten years of Coffea arabica L. The percentage of shade of the projections of the canopies of native vegetation for the coffee was in around 75%. Coffee seedlings were planted in open holes with dimensions 0.40 x 0.40 m in width and depth, with a distance of 2 m from one of the others. The organic fertilization was made using bovine and poultry manure. In addition, tree pruning and thinning with a manual cutter were carried out.

2.2 Soil sampling

Four trenches were opened in each area, with a distance between them of 50 m, with dimensions of 1.5 x 1.5 m and depth of 0.80 m, in three slopes: mountainous (45% to 75%), undulating (8% 20%) and smoothly wavy (3% to 8%), according to classification EMBRAPA (1979). In each trench, deformed and undisturbed soil samples were collected, at depths of 0–20, 20–40 and 40-60 cm, for physical and chemical analysis.

2.3 Physical Analysis

Soil density was obtained using the volumetric ring method described by Grossman and Reinsch (2002), and the particle size analysis of solid soil particles was performed using the densimeter method (Gee; Or, 2002).

2.4 Chemical analysis

The chemical fractionation of humic substances was carried out according to the method suggested by the International Humic Substances Society (Swift, 1996). Fulvic acids (FA), humic acids (HA) and humine (HUM) were obtained, based on the solubility in acids and bases. After fractionation, the samples were frozen and lyophilized to determine C in humic fractions by the dry combustion method (CHNS/O) in an elemental analyzer (Model PE-2400 Series II Perkin Elmer).

The C (carbon) concentrations were converted into soil carbon stock (SCS) in Mg ha^{-1} for each depth sampled as follows (Veldkamp, 1994):

$$Stock\ C = (C \times SD \times VPD) \times 1000 \quad (1)$$

Where: *Stock C* = carbon stock in the soil layer, in Mg ha^{-1}; *C* = concentration of carbon in the soil sample, in kg Mg^{-1}; *SD* = density of the soil in the layer, in Mg m^{-3}; *VPD* = volume of the sampled depth, in (m^3).

After calculating the C stock for each layer, the SCS was corrected, taking into account the differences in soil mass (Sisti; Santos; Kohhann; Alves; Urquiaga; Boddey, 2004). The total stock of C in the humic fractions at a depth of 0 to 60 cm was calculated by adding the values obtained in each sampled layer.

2.5 Statistical Analysis

The parameters evaluated concentrations and stocks of C in the humic fractions were subjected to the normality tests Shapiro and Wilk, then performed the analysis of variance to evaluate the differences between the uses of the soil in the depths. The comparison of means was performed by the Tukey test at 5% significance and using the statistical software SISVAR (Ferreira, 2011).

3 RESULTS AND DISCUSSIONS

The granulometric composition of the soil showed a predominance of medium texture classified as sandy loam clay (SOIL SURVEY DIVISION STAFF, 1993) in all soil depths of the analyzed areas (Table 1). According to Mendes Júnior, Tavares, Santos Júnior, Silva, Santos and Mincato (2018) the medium texture is suitable for the good development of the coffee plant, in addition, soils with medium texture, from 15% to 35% clay, allow good drainage and water retention capacity, and average erodibility index.

Table 1 – Physical average values of the soil in a swamp of altitude in the municipality of Taquaritinga do Norte - PE

Areas	Sand		Silt		Clay		Soil Density	Texture
			%				g cm^{-3}	
Depth 0-20 cm								
Agroforestry system								
Top	67,44	±0,91	6,76	±0,48	25,80	±0,43	1,29±0,12	Sandy-clay-loam
Hillside	64,74	±1,89	7,20	±0,56	28,06	±2,46	1,17±0,21	Sandy-clay-loam
Downhill	65,46	±0,93	7,45	±0,35	22,99	±2,27	1,34±0,38	Sandy-clay-loam
Native forest								
Top	64,10	±5,49	7,26	±0,43	28,63	±5,07	1,35± 0,10	Sandy-clay-loam
Hillside	67,87	±0,29	7,31	±0,95	24,82	±0,94	1,29± 0,08	Sandy-clay-loam
Downhill	66,24	±0,59	7,49	±0,54	26,26	±0,05	1,26± 0,16	Sandy-clay-loam
Depth 20-40 cm								
Agroforestry system								
Top	69,56	±2,62	7,45	±0,35	22,99	±2,27	1,29±0,23	Sandy-clay-loam
Hillside	63,66	±6,04	8,46	±0,83	27,89	±5,21	1,15±0,17	Sandy-clay-loam
Downhill	67,95	±0,02	8,07	±0,82	23,98	±0,84	1,38±0,34	Sandy-clay-loam
Native forest								
Top	65,06	±1,19	7,54	±0,10	27,40	±1,09	1,37± 0,08	Sandy-clay-loam
Hillside	65,92	±0,03	7,56	±0,20	26,52	±1,02	1,21± 0,14	Sandy-clay-loam
Downhill	69,21	±9,10	7,66	±0,13	23,13	±9,09	1,26± 0,12	Sandy-clay-loam
Depth 40-60 cm								
Agroforestry system								
Top	66,62	±1,14	8,86	±0,54	24,52	±2,01	1,26±0,27	Sandy-clay-loam
Hillside	66,12	±1,14	7,54	±0,07	26,34	±1,15	1,25± 0,11	Sandy-clay-loam
Downhill	64,98	±0,71	7,60	±1,08	27,42	±1,79	1,42±0,34	Sandy-clay-loam
Native forest								
Top	62,38	±1,25	8,21	±0,39	29,41	±1,64	1,23± 0,10	Sandy-clay-loam
Hillside	64,22	±1,75	7,27	±1,08	28,51	±0,72	1,16± 0,19	Sandy-clay-loam
Downhill	65,89	±0,12	7,22	±0,31	26,89	±0,43	1,22± 0,09	Sandy-clay-loam

Source: Authors (2021)

The soil density presented different average values between the studied areas and depths (Table 1). According to Jabro, Stevens, Iversen, Sainju and Allen (2021), the values obtained in Table 1, the agroforestry system indicated low compaction, and total porosity without restrictions for root growth and plant development.

Verifying the carbon concentrations, the soil humic fractions were evaluated: fulvic acid, humic acid and humine, according to Table 2.

Table 2 – Carbon concentrations in humic fractions in a swamp of altitude in the municipality of Taquaritinga do Norte – PE

Areas	FA	HA	HUM
		g C kg^{-1} Soil	
		Depth 0-20 cm	
		Agroforestry system	
Top	2,88Aa*	4,97Aa	11,52Aa
Hillside	2,03ABa	3,51ABa	8,13ABa
Downhill	1,90Ba	3,28Ba	7,60Ba
		Native forest	
Top	2,21ABa	3,81ABa	8,84ABa
Hillside	2,20ABa	3,78ABa	8,80ABa
Downhill	2,23ABa	3,86ABa	8,89ABa
		Depth 20-40 cm	
		Agroforestry system	
Top	2,45Aa	4,24Aa	9,82Aa
Hillside	1,82Aa	3,14Aa	7,28Aa
Downhill	1,58Aa	2,74Aa	6,35Aa
		Native forest	
Top	2,05Aa	3,55Aa	8,22Aa
Hillside	2,03Aa	3,50Aa	8,18Aa
Downhill	2,09Aa	3,59Aa	8,29Aa
		Depth 40-60 cm	
		Agroforestry system	
Top	1,58Aa	2,74ABb	6,34ABb
Hillside	1,29ABa	2,24ABa	5,18ABa
Downhill	0,74Bb	1,29Bb	2,98Bb
		Native forest	
Top	1,96Aa	3,39Aa	7,85Aa
Hillside	1,93Aa	3,33Aa	7,79Aa
Downhill	2,01Aa	3,43Aa	7,90Aa

Source: Authors (2021)

In where: *Significant differences are indicated by different letters by the Tukey test at 5% significance level ($p \leq 0.05$). Capital letters indicate differences between vegetation cover and lower letters indicate differences between soil layers.

The carbon concentrations in the humic fractions of the soil decreased with increasing depth, finding higher values in the superficial layers (Table 2). Among soil humic acids, it was possible to verify that cultivation reduced the H and O content. According to Stevenson (1994), the higher the humification stage of the SH, the higher the C content and the lower the H content lower H/C ratio. Thus, it can be inferred that the cultivation of anthropogenic soils favored conditions in the soil that resulted in an increase in the degree of humification of the HA. The increase in the degree of humification with cultivation was also reported by Bayer, Mielniczuk, Martin-Neto and Ernani (2002) and Pérez, Martin-Neto, Saab, Novotny, Milori, Bagnato, Colnago, Melo and Knicker (2004). The higher C content and the lower O content in the HA from the SAC group, compared to the SAF lower O/C ratio for SAC, corroborates and may explain the greater resistance to thermodegradation of the HA extracted from anthropogenic soils under cultivation.

Table 2, observed that the HUM prevailed with the highest average values in relation to the other humic fractions in each vegetation cover analyzed, in the superficial depths, with higher concentrations for the top area with agroforestry system, the value of 11.52 g C kg^{-1} followed by the slope area with a value of 8.13 g C kg^{-1} just after the downhill area with 7.6 g C kg^{-1}. Native forest considered as a control presented a value of 8.84 g C kg^{-1}.

The presented sequence of the humic fractions, with the HUM with a higher concentration, happens because of the lability of the fractions in the soil: while the FA denote the most labile and easily decomposed forms, the HUM represents the most recalcitrant and most persistent fraction in the soil and its main function is to act on the physical and chemical conditions of the soil, besides being fundamental in the sequestration of atmospheric C. That is, this predominance of the HUM fraction is related to its insolubility and resistance to biodegradation, favored by the formation of stable organomineral complexes (Poirier, Roumet; Munson, 2018).

The HA predominated in relation to the FA especially in the depth 0-20 cm in the top area with agroforestry system, where there was an amplitude of 2.09 g C kg^{-1} between carbon HA, which presented a value of 4.97 g C kg^{-1} and FA, which presented a value of 2.88 g C kg^{-1} (Figure 2). Among the positions evaluated, the top one presented the highest concentrations of carbon compared to the other positions evaluated on the hillside and pediment with agroforestry system, as well as on the control area with native forest at all depths. As Pham, Nguyen and Kappas (2018) exemplifies in his work, topographic factors, such as the slope of the soil, generate a variety of environmental scenarios, for example: moisture gradients in the soil between the top and the bottom of the slope; favoring the transport of soil particles along the profile, causing variations in the angles of penetration and light distribution. Depending on the slope variation, water erosion contributes to the impoverishment resulting from the dragging of soil, water, nutrients and organic carbon associated with it.

According to El-Sayed, Khalaf, Gibson and Rice (2019), fulvic and humic acids play the role of transporting cations between organ mineral exchange complexes influencing the cationic exchange capacity of organic origin. Such behavior is reiterated by (Mi; Sun; Gao; Liu; Wu, 2019) who emphasize the greater stability of HUM and HA, with higher levels of C in these fractions, and greater lability of FA.

Fulvic acids are soluble in water, acidic and alkaline environments. Although HA has a structural similarity to AF, the latter exhibits less molecular weight, a greater amount of phenolic compounds and carboxylic groups and a lesser amount of structures with aromatic rings. These peculiarities provide better solubility in water, greater cation exchange capacity and mobility in the soil (Mendes Júnior; Tavares; Santos Júnior; Silva; Santos; Mincato, 2018).

Pham, Nguyen e Kappas (2018) studies evaluating the humic fractions in areas of native forest and reforested in a swamp of Paraiba altitude considering the position in the relief in areas with different forms of use found results similar to this study, where there was a predominance of HUM mainly in the more superficial horizon due to its little mobility and also reiterates the greater stability of the HUM in relation to the FA.

The top area was the one with the highest amounts of HUM (Table 3), which can be explained by the influence of the water movement at the top about the FA. In the area located on the hillside, the processes of pedogenesis are accentuated, and there is a greater distinction of horizons, which demonstrates the participation of HUM, as it is more stable, in differentiating horizons. The relief area, with less slope, of the relief allows the retention and vertical infiltration of water, favoring the mobilization of the FA (Canellas; Berner; Silva; Silva; Santos, 2000).

Carbon stocks in the FA fraction showed average values ranging from 3.78 to 5.62 to Mg ha^{-1}, HA fraction ranging from 6.53 to 9.72 Mg ha^{-1}, HUM fraction ranging from 15.15 to 22.53 Mg ha^{-1} (Table 3).

Table 3 – Carbon stocks in humic fractions in a swamp in altitude in the municipality of Taquaritinga do Norte – PE

Areas	**FA**	**HA**	**HUM**
		Mg ha^{-1}	
		Depth 0-60 cm	
		Agroforestry system	
Top	5,62A	9,72A	22,53A
Hillside	3,78C	6,53D	15,15D
Downhill	4,40B	7,61C	17,63C
		Native forest	
Top	4,84B	8,28B	19,20B
Hillside	4,79B	8,18B	19,10B
Downhill	4,91B	8,32B	19,29B

Source: Authors (2021)

In where: *Significant differences are indicated by different letters by the Tukey test at 5% significance level ($p \leq 0.05$). Capital letters indicate differences between vegetation cover and lower letters indicate differences between soil layers.

These values indicate that the carbon stocks in the HUM fraction have most of the carbon in its humidified, stabilized form, this fact can be seen by Clemente, Oliveira, Machado and Schaefer (2018) who state that HUM composes the part of organic matter most closely linked to the mineral fraction of the soil, which makes it more insoluble. The FA, on the other hand, has oxygenated functional groups, are mobile, soluble in acidic and basic media and are not associated with the mineral fraction of the soil.

The carbon stocks in the HUM fraction were higher in average values (Table 3). Humic substances, mainly HUM, have the ability to interact with the surface of minerals present in the soil through a wide variety of bonds, since it has several functional groups of C, which leads to the formation of organic mineral complexes (Samson; Chantigny; Vanasse; Menasseri-Aubry; Angers, 2020). The formation of organic mineral complexes assists in carbon stocks in the HUM fraction, considering that humic substances are associated with both clay and oxides, especially the most abundant ones such as iron oxide and aluminum oxide (Poirier, Roumet; Munson, 2018; Hanke; Dick, 2019). Zeng, Darboux, Man, Zhu and An (2018) observed that the accumulation of organic matter allows its binding agents to reduce soil toxicity, due to the organomineral complexation that humic substances perform with metals Once formed, these complexes can remain in solution or precipitate on mineral surfaces. Complexation, mono or multi-coordinated, can induce stereochemical changes, polarity and the electronic arrangement of organic compounds, which can reduce their accessibility to degradation and cause their half-life to be significantly increased (Hanke; Dick, 2019).

MOS also has the ability to complex with metals through covalent interaction, which forms a metal complex called chelate (Diarra; Kotra; Prassad, 2020). In addition to the organomineral interaction, MOS stabilization can occur through self-association, which consists of a “zonal structure” that involves the self-assembly of groups of organic matter in zones that vary with distance and with the strength of connection with the surface. It can also be stabilized by the hydrophobicity of the MOS and potential redox of the soil, aggregation and physical occlusion of the MOS, by the biochemical recalcitrance of the MOS (due to the aromatic compounds present in the HUM) and by the alteration of the environment caused by anthropic activities (liming, artificial drainage, plowing, harrowing, etc.) (Hanke; Dick, 2019). According to Zheng, Zheng, Tian, Yang, Jiang and Zhao (2018) the structure of the soil refers to the size and stability of the aggregates and which has a direct influence from the MOS.

The organomineral complexation of humic substances, especially HUM, causes the formation of macroaggregates that have large pores that facilitate the entry of water, air and the penetration of the plant root system. HUM optimizes the total volume and size of pores, which promotes greater infiltration, greater water retention and release to vegetables, with the ability to increase the water available in the soil by up to 25% in volume (Mi; Sun Gao; Liu; Wu, 2019).

In the case of native forest, there was a difference carbon stocks in relation to the other areas with agroforestry system. In general, there was an increase in the average values of carbon stocks of FA in the top, which can be seen in greater solubility and mobility (Table 3). A fact that was also observed by Pfleger, Cassol and Mafra (2017) where evaluating carbon stock and fractions of organic matter in areas under agroforestry systems and agriculture in the harsh Paraiba observed that the fulvic acid fraction showed a dynamic behavior because it is the most soluble and mobile among the three fractions, but in general it was decreasing in relation to the depth within each area, even though the FA is a fraction that presents high mobility in the soil profile. The slope influenced the carbon stock concentrations of FA, as explained by Canellas, Berner, Silva, Silva and Santos (2000) the relief area, with less slope, of the relief allows the retention and vertical infiltration of water, favoring the mobilization of the AF on the surface. In the top area, the increase in the carbon stock in the AF fraction can be explained due to a greater increase in partially decomposed OM.

The same trend was seen for carbon stocks in the HA fraction (Table 3). These variations and the absence of a regular pattern of distribution of carbon stocks can be seen in the work of Pfleger, Cassol and Mafra (2017). Stocks were higher in the HA fraction on the surface than in FA due to the stability and insolubility of AH in acidic environments (Mi; Sun; Gao; Liu; Wu, 2019).

CONCLUSIONS

- Areas with agroforestry system showed higher concentrations of carbon in the fractions of fulvic acid, humic acid and humine;

- Carbon from humic fractions decreased with depth and presented average values in increasing order for fulvic acid, humic acid and humine;

- Areas with agroforestry system showed greater capacity to store carbon, mainly in the top toposequence;

- Humic fractions of carbon proved to be an important variable to assess changes in carbon in the soil.

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