

SOIL ATTRIBUTES AND C AND N VARIATION IN HISTOSOLS UNDER DIFFERENT AGRICULTURAL USAGES IN THE STATE OF RIO DE JANEIRO, BRAZIL

ATRIBUTOS EDÁFICOS E VARIAÇÃO DE C E N EM ORGANOSSOLOS SOB DIFERENTES USOS AGRÍCOLAS NO ESTADO DO RIO DE JANEIRO, BRASIL

Paula Fernanda Chaves SOARES¹; Fernando ZUCHELLO²;
Lúcia Helena Cunha dos ANJOS³; Marcos Gervasio PEREIRA³; Ana Paula Pessim de OLIVEIRA⁴

1. Pós-Doutoranda CPGA-CS, Universidade Federal Rural do Rio de Janeiro - UFRRJ, Seropédica, RJ, Brasil. pfernanda07@gmail.com; 2. Professor, Doutor, Instituto Federal Catarinense - Campus Concórdia, Concórdia, SC; 3. Professor, Doutor, Departamento de Solos, Universidade Federal Rural do Rio de Janeiro - UFRRJ, Seropédica, RJ, Brasil; 4. Pós-Doutoranda PPGCTIA, Universidade Federal Rural do Rio de Janeiro - UFRRJ, Seropédica, RJ, Brasil.

ABSTRACT: Histosols are a natural reservoir of C in the soil, and their drainage followed by other farming practices leads to subsidence and soil organic matter transformations. The objective of this study was to evaluate the influence of use and management of Histosols, by means of: characterizing chemical and physical properties, and the content of SOM and humic fractions; and quantifying C and N stocks. In addition, to obtain preliminary data on greenhouse gas emissions (CO₂, N₂O) in Histosol areas with different agricultural practices. Three areas were selected with similar soil and environment, two in Macaé municipality, under pasture, and with bean annual crop rotation, and the third in Santa Cruz, Rio de Janeiro city, cultivated with cassava (*Manihot esculenta*). The attributes evaluated were: physical - bulk density (BD), particle density (Dp), organic matter density (OMD), mineral matter (MM), mineral residue (MR), aggregate stability; and chemical - pH, exchangeable cations, soil organic matter (SOM), carbon in the humin (HUM-C), humic acid (HAF-C) and fulvic acid (FAF-C) fractions; stocks of C and N; and flux of CO₂ and N₂O. In general, the area cultivated with cassava had the highest values for exchangeable cations, as a result of fertilizer and soil management practices. The cassava site showed the highest values of BD and Dp; total volume of pores; MM, MR and OMD and higher degree of transformation of SOM; indicating higher alteration of Histosols properties under this usage. In all sites, the C levels indicated dominance of humin fraction. The SOM and C and N stocks were highest in the pasture, indicating preservation of organic matter, with values from 115.92 to 99.35 Mg ha⁻¹ of C e 8.35 to 4.45 Mg ha⁻¹ for N. The values of CO₂-C flux were within the range proposed by the IPCC, where the highest emission was 0.09 Mg CO₂ ha⁻¹ day⁻¹ in the pasture site. The values of N₂O-N flux were lower than proposed by the IPCC, with the highest value (270 g N₂O-N m⁻² day⁻¹) in the area under beans (crop rotation). In general, the multivariate analyses discriminated the sites and the pasture was the usage that least affected the Histosols properties.

KEYWORDS: Humic Substances. C and N stocks. CO₂ and N₂O emissions.

INTRODUCTION

The use and occupation of Histosols should be planned rationally in order to avoid negative environmental impacts on natural resources (MOURA et al., 2013; NOGUEIRA et al., 2012). They are important to environmental changes, and it is estimated that to a depth of one meter, in global terms, the soil contains 2200 Pg C, corresponding to about four times the C in vegetation (560 Pg) and three times C in the atmosphere (750 Pg). The C stored in soil is composed of organic C (1500 Pg C) and mineral C (700 Pg C) (BATJES, 1996). However, the soil organic matter is easily decomposed through cropping (CIPRIANO-SILVA et al., 2014) thus aggravating the release of gases such as CO₂ (CERRI et al., 2007).

When drainage for agriculture is implemented the subsidence process of Histosols starts and the content of soil organic matter changes rapidly (EBELING et al., 2013). In Histosols the mineralization of organic matter and release of gases can be greater than in other soils, and it is enhanced by drainage and cropping. In flooded areas, SOM decomposes anaerobically and produces compounds like CH₄. In Histosols, drainage promotes aerobic decomposition of soil organic matter (SOM), generating CO₂, which is later released by diffusion to the atmosphere. The N₂O is the second most abundant form of N in the atmosphere and is highly stable, with residence time of approximately 110 to 150 years (BATJES et al., 1996). In comparison with CO₂, N₂O has 298 times the warming potential, while CH₄ has 25 times as much (IPCC, 2007; YAO et al., 2012).

Histosols are different from other soils, and they are defined in the Brazilian Soil Classification System (SiBCS) (EMBRAPA, 2013) as less developed soils with high organic carbon ($\geq 80 \text{ g kg}^{-1}$). Among their distinctive edaphic characteristics are the dark colors and high moisture retention, susceptibility to subsidence, acidity and cation exchange capacity (CEC), as well as presence of plant material at different stages of decomposition.

In contrast, the increase in the SOM stock is slow and needs adequate soil management, particularly in tropical regions where decomposition is faster due to the higher biological activity (SIX et al., 2002). In Serra de Espinhaço Meridional region of Minas Gerais, Silva et al. (2007) found Histosols acidic and with high concentrations of exchangeable Al^{3+} and potential acidity; with high CEC as a function of deprotonation or protonation of carboxyl and phenyl radicals.

In Histosols, the properties and characteristics of the organic matter determine the rate of mineralization and emissions of C and N to the atmosphere in the form of gases. The objective of this study was to evaluate the influence of use and management of Histosols, by means of: characterizing chemical and physical properties, and the content of SOM and humic fractions; and quantifying C and N stocks. In addition, to obtain preliminary data on greenhouse gas emissions (CO_2 , N_2O) in Histosol areas with different agricultural practices.

MATERIAL AND METHODS

Location and Characterization of the Areas and Soil Sampling

The study was conducted in three areas with soils classified as Histosols, according to the SiBCS (EMBRAPA, 2013), in floodplain regions of Rio de Janeiro State and with different tillages and cover crops. The first area (1), in the municipality of Macaé, has been cultivated with mixed pasture consisting of *Brachiaria brizantha* and leguminous, for beef cattle production. The water table level is controlled by channels along the Macaé and São Pedro rivers, at a depth of approximately 60 cm. The second area (2) is adjacent to the first; this area is planted with corn (*Zea mays*), rice (*Oryza sativa*), and beans (*Phaseolus vulgaris*) for seed production, in a crop rotation system. The cultivation practices are by conventional tillage, consisting of plowing and harrowing the surface layers. The drainage channels are deeper (approximately 1.5 m) and closer than in the first area. The third area (3), in Santa Cruz district, in the western part of Rio de

Janeiro city, has been planted with cassava (*Manihot esculenta*) since the 1980s. The soil is mechanized and the cassava is planted in raised beds about 30 cm high, and dolomitic lime was applied during the period of cultivation. The drainage channels are 80 cm deep. The third area has been cultivated for the longest period, as part of a settlement project starting in the 1940s, which included the macro-drainage of the region.

The soil was sampled in 2009 and 2010, in areas 1 and 2 in April and in area 3 in May. In each location there were three sites selected for trenching, and in each trench samples were collected at depth intervals of 0-10 and 10-20 cm.

Analytic Characterization

The air dry soil samples were analyzed for Ca, Mg, Na, K, Al, H+Al, pH and C according to Embrapa (1997), and the N according to Tedesco et al. (1995). The pH was determined in a soil-liquid suspension of 1:2.5, in water, CaCl_2 0.01 mol L^{-1} and KCl 1 mol L^{-1} . The soil total C and N contents were determined in a Tru-Spec CHN elemental analyzer, which was calibrated with the 'Acetanilide' standard ($\text{C}_8\text{H}_9\text{NO}$) part 501-053, lot 1010 (the respective values of CHN were 71.09%, 6.71% and 10.36%). This methodology was an adaptation of Smith & Myung (1990).

The stocks were calculated based on the C and N amounts determined by the CHN analyzer, in the soil sections at the depths of 0-10 and 10-20 cm. The soil density values were homogeneous in the soil samples, thus the equation, without mass correlation, was used: $S_s = \text{BD} \cdot P \cdot X$, according to Embrapa (1997); where: S_s is the total stock of carbon/nitrogen in Mg ha^{-1} , BD is the soil bulk density in Mg m^{-3} , P is the thickness in cm, and X is the carbon/nitrogen concentration in Mg ha^{-1} .

The soil organic matter was determined by quantitative combustion method in a muffle furnace for 6 h at 600°C , according to Embrapa (2013). The soil mass lost by combustion in relation to oven-dried sample corresponds to the soil organic matter (SOM). The mineral matter percent (%MM), organic matter density (OMD) and mineral residue (MR) was calculated according to Embrapa (2013). The humic substances were chemically fractionated using the differential solubility technique based on Kononova (1966) and adapted by Benites et al. (2003). The organic C was fractionated in the following: fulvic acid (FAF-C), humic acid (HAF-C) and humin (HUM-C). From these values the HAF-C/FAF-C was calculated.

Measurements of CO_2 and N_2O emission rates from the soil were also collected in 2009 and

2010 at the end of year. The N_2O was measured according with Alves et al. (2012) and is expressed in $kg\ ha^{-1}\ year^{-1}$. A portable infrared gas analyzer (IRGA) from PP Systems Company (2010) was used for measuring CO_2 . Samples were taken once a day, in the morning, at each site, for four consecutive days; there were six readings taken per day plus a reference measurement.

The soil bulk density was measured according to Embrapa (1997). The distribution of the aggregate classes was determined by sifting samples in water in a Yooder device, using sieves with mesh sizes of 2.0, 1.0, 0.5, 0.25 and 0.105 mm, following Embrapa (1997).

Statistical Analyses

To evaluate the data, each area was considered as a treatment (identified by the coverage/crops: pasture, beans and cassava) and treated as completely randomized experimental design, with three field replicates in each area. The data were submitted to homogeneity (Bartlett) and normality (Lilliefors) tests. The data was submitted to variance analysis (ANOVA), and when significant the Tukey test ($p < 0.05$) was applied. The data was compared for the areas, depths and samplings, with their interactions serving as a variation source. Multivariate analysis was also performed, using the principal components analysis (PCA) tool of the Canoco 4.5 program (VAN DEN BRINK; TER BRAAK, 1999).

RESULTS AND DISCUSSION

Characterization of the Sorption Complex, pH and Organic Matter Content

The concentrations of elements of the sorption complex were, in general, high in both sampling years (Table 1). In the first year, the values of Al^{3+} ranged from 1.2 to 2.7 $cmol_c\ kg^{-1}$, and there was no difference between areas or depths. H^+ ions predominate in the sorption complex, varying from 22.4 to 32.7 (0-10 cm) and from 23.9 to 32.1 (10-20 cm) $cmol_c\ kg^{-1}$ and the values showed differences when comparing the areas, with highest values in cassava site, followed by pasture, then beans, at both soil depths. High H^+ values were reported for Ebeling et al. (2008; 2011) and Silva et al. (2009), working with Histosols in floodplain and in highland environments. In 2008, Ebeling et al. observed H^+ values in floodplain soils from 10 to 83.6 $cmol_c\ kg^{-1}$, and in highland well-drained soils from 11.9 to 83.6 $cmol_c\ kg^{-1}$. In 2009, Silva et al. found in highland soils H^+ values higher than 100 $cmol_c\ kg^{-1}$ at the depth of 10-20 cm.

For the second year, the Al^{3+} levels showed differences between the areas at the depth of 10-20 cm (Table 1). The highest values were found in pasture and the lowest in the cassava, reflecting the management (fertilization and liming). The concentrations of Al^{3+} did not differ according to depths or between the years. There were no differences for H^+ between the treatments and depths.

Ca^{+2} and Mg^{+2} showed high values in the first sampling year, and the Ca/Mg ratio was generally on the order of 3:1 (Table 1). The level of Ca^{+2} ranged from 9.3 to 19.4 (0-10 cm) and from 9.3 to 20.4 (10-20 cm) $cmol_c\ kg^{-1}$ and there were differences between the areas in both depths, with the cassava and pasture having the highest values, followed by the bean site. The levels of Mg^{+2} varied from 3.5 to 6.7 $cmol_c\ kg^{-1}$ in the first year sampling at 0-10 and 10-20 cm and there was no difference between areas. In the second year Ca^{+2} values varied from 4.4 to 9.8 $cmol_c\ kg^{-1}$ at 0-10 and 10-20 cm and there was no difference between values. For Mg^{+2} , the areas differed at the 10-20 cm depth, with the cassava field presenting the highest value in the second year; although there was no significant difference in values with depth or sampling years. The K value was relatively low and did not vary significantly with depth, in both years. The cassava is cultivated frequently with additions of fertilizer and liming, thus explaining the higher Ca^{+2} and Mg^{+2} levels in comparison to the other sites.

The pH values showed no variation in the first year (Table 1). The pH values were always higher when measured in water and lower in KCl solution (at least 0.8 units less than pH in water). These results are attributed to the effect of KCl solution, which in contact with the soil sample, induces exchange of cations due to the higher concentration of K^+ ions, releasing H^+ ions and Al^{3+} to the solution, resulting in increased acidity (EBELING et al., 2008).

In the second year, the pH in water showed significant differences for the sites at all depths, with higher values in the cassava, followed by beans, then pasture, in response to agricultural practices (Table 1). Similar results were observed in other regions of Brazil, with lower pH values in the upper layer of soils under pasture, compared to cassava and beans (MELO et al., 2010) and compared to areas with other crops (NOGUEIRA et al., 2012). According to these authors, the highest pH values in fruit crops are related to greater use of fertilizer and lime. The pH values in water are within the range reported by Ebeling et al. (2008; 2011) and Silva et al. (2009).

Table 1. Values of the elements of the sorption complex, and pH with different solutions, for the three treatments, in the first and second samplings, at depths of 0-10 and 10-20 cm

Area	Depth (cm)	Al ⁺³	H ⁺	Ca ⁺² (cmol _c kg ⁻¹)	Mg ⁺²	K ⁺	Na ⁺	pH values		
								H ₂ O	CaCl ₂	KCl
<i>First Sampling - 2009</i>										
Pasture		2.7Aa(a)	27.5ABa(a)	14.1Aba(a)	4.9Aa(a)	0.10Aa(a)	0.49Aa(a)	4.8Aa(a)	4.2Aa(a)	4.0Aa(a)
Bean	0-10	1.3Aa(a)	22.4Ba(a)	9.3Ba(a)	3.47Aa(a)	0.28Aa(a)	0.37Aa(a)	5.0Aa(a)	4.2Aa(a)	4.1Aa(a)
Cassava		1.2Aa(a)	32.7Aa(a)	19.4Aa(a)	6.73Aab(a)	0.66Aa(b)	0.73Aa(a)	4.8Aa(b)	4.1Aa(a)	3.9Aa(a)
Pasture		1.2Aa(a)	29.7ABa(a)	14.9Aba(a)	4.3Aa(a)	0.09Aa(a)	0.35Aa(a)	4.7Aa(a)	4.2Aa(a)	3.8Aa(a)
Bean	10-20	1.5Aa(a)	23.9Ba(a)	9.3Ba(a)	3.6Aa(a)	0.19Aa(a)	0.38Aa(a)	5.0Aa(a)	4.2Aa(a)	4.1Aa(a)
Cassava		1.8Aa(a)	32.1Aa(a)	20.4Aa(a)	5.7Ab(a)	0.20Aa(b)	0.73Aa(a)	4.8Aa(b)	4.1Aa(a)	3.9Aa(a)
<i>Second Sampling - 2010</i>										
Pasture		2.5Aa(a)	19.5Aa(a)	7.03Aa(a)	2.87Aa(a)	0.75Ba(a)	0.54Aa(a)	4.8Ba(a)	4.3Aa(a)	4.1Aa(a)
Bean	0-10	1.6Aa(a)	14.1Aa(a)	4.60Aa(a)	5.33Aa(a)	0.98Ba(a)	0.55Aa(a)	5.2Aba(a)	4.3Aa(a)	4.3Aa(a)
Cassava		0.6Aa(a)	13.3Aa(b)	9.83Aa(b)	6.63Aa(a)	4.54Aa(a)	0.53Aa(a)	5.5Aa(a)	4.3Aa(a)	4.5Aa(a)
Pasture		3.7Aa(a)	21.3Aa(a)	4.77Aa(b)	4.07Ba(a)	0.68Ba(a)	0.42Aa(a)	4.7Ba(a)	4.2Aa(a)	4.0Aa(a)
Bean	10-20	1.3ABa(a)	13.6Aa(a)	4.40Aa(a)	4.70ABa(a)	0.73Ba(a)	0.47Aa(a)	5.2Aba(a)	4.4Aa(a)	4.3Aa(a)
Cassava		0.8Ba(a)	13.6Aa(b)	9.60Aa(b)	8.67Aa(a)	4.36Aa(a)	0.66Aa(a)	5.5Aa(a)	4.2Aa(a)	4.4Aa(a)

The capital letter represents the treatments at the same depth; the small letter represents the depths within the same treatment; the letters in parentheses represent the sampling year.

The SOM content calculated from organic C values (EMBRAPA, 1997), varied from 142.9 to 292.3 g kg⁻¹ in the first year and from 142.1 to 303.2 g kg⁻¹ in the second (Table 2). The SOM values determined in the muffle furnace, considered as

standard method for Histosols (EMBRAPA, 2013), varied from 162.5 to 297.8 g kg⁻¹ in the first year and from 153.7 to 310.3 g kg⁻¹ in the second. The muffle values were generally greater than those calculated by the organic C method.

Table 2. Soil organic matter (SOM) values obtained by two methods, in the two years, for the treatments and depths

Area	Depth (cm)	SOM (g kg ⁻¹)			
		First Sampling 2009		Second Sampling 2010	
		Calculated	Muffle	Calculated	Muffle
Pasture		275.2Aa(a)	282.7Aa(a)	303.2Aa(a)	310.3Aa(a)
Bean	0-10	228.1ABa(a)	277.2ABa(a)	212.4ABa(a)	220.3ABa(a)
Cassava		142.9Ba(a)	162.5Ba(a)	145.4Ba(a)	153.7Ba(a)
Pasture		292.3Aa(a)	297.8Aa(a)	299.6Aa(a)	322.9Aa(a)
Bean	10-20	214.5ABa(a)	229.2ABa(a)	203.9ABa(a)	222.4ABa(a)
Cassava		152.2Ba(a)	163.5Ba(a)	142.1Ba(a)	155.0Ba(a)
CV%		39.81	28.82	34.27	26.28

The capital letters represents the treatments at the same depth; the small letters represent the depths within the same treatment; the letters in parentheses represent the samplings years. Calculated – SOM calculated from organic C values obtained from Embrapa (1997) and using a multiplication factor; Muffle – values obtained by the muffle furnace method of determining organic matter.

The distribution of SOM values in the surface reflected the soil management. The cassava presented the lowest SOM values in both methods and depths. In Histosols, Cipriano-Silva et al. (2014) found values between 175 and 181 g kg⁻¹ when cultivated with sugarcane and cassava; and Moura et al. (2013) found values of 122 and 126 g kg⁻¹ with cassava. These results indicate the effect of long period of cultivation and crop management, leading to intense SOM mineralization. According Moura et al. (2013), the decrease in SOM values were affected by drainage and soil tillage, influencing the temperature, humidity, soil aeration and supply of crop residues.

Physical Properties of Histosols

The particle density (Dp) values (Table 3) ranged from 1.31 to 1.91 Mg m⁻³; the total pore volume (TPV) varied between 50 and 69 % and the high TPV values are common in Histosols. The bulk density values ranged from 0.53 to 0.77 Mg m⁻³ at the two depths, and there was a difference between the areas in the second year. The properties bulk density (BD), minimum residue (MR) and mineral material (MM) are related to SOM content and degree of decomposition (CONCEIÇÃO et al., 1999). The physical properties of Histosols are strongly influenced by the organic matter content that is used as an indicator of soil degradation.

The cassava site showed the greatest values of BD, MR and MM (Table 3) and the lowest of SOM (Table 2). These results indicate that

agricultural practices in the cassava site had greatest soil impact in the SOM transformation and soil subsidence. Similar result was observed by Cipriano-Silva et al. (2014) in an area cultivated with sugarcane and cassava. The organic matter density (OMD) also is related to soil usage (Table 3). According to Kämpf & Schneider (1989), values higher than 0.15 Mg m⁻³ are associated with intensively cultivated areas. The OMD values were greater than or equal to this value in all sites, with a variation between 0.15 and 0.27 Mg m⁻³. However, no significant differences were observed among sites or depths.

For the soil aggregation, in the first year, the MWD showed a difference among the sites at 0-10 cm, with highest values in the cassava. The pasture showed variation in values of MWD, increasing with depth, and there were no differences in the other areas. The MWD ranged from 3.78 to 4.90 mm. These values were higher than the data found by Moura et al. (2013) in Histosols in Brasilia, DF (2.4 to 2.84 mm), and they are in accordance with Cardozo et al. (2008), studying Histosols in Nova Friburgo, RJ, under oleraceous crops (4.10 mm) and an area left fallow for 20 years (3.42 mm). The MWD values in all three studies are considered high when compared to other soils classes than Histosols, and this is attributed to the SOM, which is considered by many researchers as the primary agent stabilizing the aggregates (GANG et al., 1998).

Table 3. Values of Dp and BD, total pores volume, organic matter density, minimum residue, mineral matter, and aggregate indexes of three Histosol areas with different usages, first and second samplings, at depths of 0-10 and 10-20 cm

Area	Depth (cm)	Dp (Mg m ⁻³)	BD (Mg m ⁻³)	TPV (%)	OMD (Mg m ⁻³)	MR (cm cm ⁻¹)	MM (%)	Aggregate indexes	
								MWD (mm)*	GMD (mm)*
<i>First Sampling - 2009</i>									
Pasture		1.50 Aa(a)	0.68 Aa(a)	55 Aa(a)	0.26 Aa(a)	0.28 Aa(a)	61.0 Aa(a)	3.78 Bab(b)	0.10 Ba(b)
Bean	0-10	1.55 Aa(a)	0.57 Aa(a)	64 Aa(a)	0.20 Aa(a)	0.24 Aa(a)	63.9 Aa(a)	4.18 ABa(a)	0.26 ABa(a)
Cassava		1.67 Aa(a)	0.72 Aa(a)	57 Aa(a)	0.24 Aa(a)	0.32 Aa(a)	66.6 Aa(a)	4.90 Aa(a)	0.46 Aa(a)
Pasture		1.50 Aa(a)	0.67 Aa(a)	55 Aa(a)	0.27 Aa(a)	0.27 Aa(a)	59.9 Aa(a)	4.31 Aa(a)	0.09 Aa(b)
Bean	10-20	1.31 Aa(a)	0.64 Aa(a)	50 Aa(b)	0.19 Aa(a)	0.30 Aa(a)	71.0 Aa(a)	4.49 Aa(a)	0.18 Aa(a)
Cassava		1.65 Aa(a)	0.69 Aa(a)	58 Aa(a)	0.22 Aa(a)	0.31 Aa(a)	67.4 Aa(a)	4.86 Aa(a)	0.26 Aa(a)
<i>Second Sampling - 2010</i>									
Pasture		1.51 Aa(a)	0.53 Ba(a)	65 Aa(a)	0.24 Aab(a)	0.21 Ba(a)	57.1 Bab(a)	4.26 Aa(a)	0.26 Aa(b)
Bean	0-10	1.62 Aa(a)	0.50 Ba(a)	69 Aa(a)	0.16 Aa(a)	0.22 Ba(a)	67.9 ABa(a)	4.14 Aa(a)	0.33 Aa(a)
Cassava		1.91 Aa(a)	0.76 Aa(a)	60 Aa(a)	0.15 Aa(a)	0.46 Aa(a)	81.6 Aa(a)	4.22 Aa(a)	0.13 Aa(b)
Pasture		1.51 Aa(a)	0.54 Ba(a)	64 Aa(a)	0.24 Aab(a)	0.18 Ba(a)	53.3 Bb(a)	4.37 Aa(a)	0.37 Aa(a)
Bean	10-20	1.61 Aa(a)	0.54 Ba(a)	66 Aa(a)	0.17 Aa(a)	0.22 Ba(a)	66.2 ABa(a)	4.45 Aa(a)	0.28 Aa(a)
Cassava		1.88 Aa(a)	0.77 Aa(a)	56 Aa(a)	0.16 Aa(a)	0.44 Aa(a)	80.7 Aa(a)	4.51 Aa(a)	0.16 Aa(a)

Dp – particle density; Ds – bulk soil density; TPV – total pore volume, OMD - organic matter density; MR - minimum residue, MM - mineral matter; MWD – mean weight diameter; GMD - geometric mean diameter. # The capital letters represents the treatments at the same depth; the small letters represent the depths within the same treatment; the letters in parentheses represent the samplings. *CV (%) First Sampling: MWD – 13.47; GMD – 57.81 ; Second Sampling: MWD – 11.10; GWD – 51.32

The geometric mean diameter (GMD) varied from 0.09 to 0.46 mm. In the first year, the GMD showed a significant difference, with the largest diameter in cassava site at 0-10 cm. The low MWD and GMD values at 0-10 cm in the pasture may be related to cattle trampling. The highest values were observed in cassava site, where repetition of wet/dry cycles promoted by ridge planting and furrow irrigation leads to the formation of larger aggregates.

Fractionation of Humic Substances and Stocks of Carbon and Nitrogen in the Soil

The distribution of humic fractions of SOM at the sites indicate predominance of humin fraction

(HUM-C), followed by humic acid (HAF-C) and fulvic acid (FAF-C) (Table 4). The predominance of humin was also reported by others authors in Histosols and soils with high organic-matter content from different regions of Brazil (VALLADARES et al. 2007; FONTANA et al. 2008; CIPRIANO-SILVA et al, 2014). Two factors may explain the C dominance in the humin fraction in hydromorphic environments; the first is related to direct humidification of lignified tissues modified by demethylation processes, which is favored by reduction of insolubilization and mechanisms of microbial neossintese; and the second is related to presence of hereditary humin (ORLOV, 1985; TAN 2003).

Table 4. Carbon content in the humic substances fractions: humin (HUM-C), humic acid (HAF-C) and fulvic acid (FAF-C), and HAF-C/FAF-C ratio; and carbon and nitrogen stocks at 0-10 and 10-20 cm depth.

Area	Depth (cm)	HUM-C (g kg ⁻¹)	HAF-C (g kg ⁻¹)	FAF-C (g kg ⁻¹)	HAF-C/FAF-C (g kg ⁻¹)	Stock ¹ (Mg ha ⁻¹)	
						Carbon*	Nitrogen*
<i>First Sampling - 2009</i>							
Pasture		115.58 Aa(a)	29.80 Aa(b)	13.78Bb(b)	2.18 Aa(a)	115.92Aa(a)	8.35Aa(a)
Bean	0-10	90.64 Aa(a)	28.32 Aa(a)	13.34Bb(a)	2.19 Aa(a)	81.69Ba(a)	5.41ABa(a)
Cassava		77.26 Aa(a)	35.38 Aa(a)	22.67 Aa(a)	1.57 Aa(a)	104.98ABa(a)	1.86Ba(a)
Pasture		118.47 Aa(a)	26.52 Aa(a)	24.10 Aa(a)	1.22 Aa(a)	115.34Aa(a)	7.76Aa(a)
Bean	10-20	69.64 Aa(b)	29.03 Aa(a)	25.24 Aa(a)	1.24 Aa(a)	78.72Ba(a)	3.01ABab(a)
Cassava		75.68 Aa(a)	32.34 Aa(a)	29.28 Aa(a)	1.14 Aa(a)	97.27ABa(a)	2.34Ba(a)
<i>Second Sampling - 2010</i>							
Pasture		186.36 Aa(a)	82.50 Aa(a)	54.37 Aa(a)	1.54 Aa(a)	99.35Aa(a)	4.45Aa(b)
Bean	0-10	100.62 ABa(a)	49.34Ba(a)	17.62Ba(a)	2.21 Aa(a)	74.67Aa(a)	2.56Ba(b)
Cassava		79.05Ba(a)	44.56Ba(a)	15.90Ba(a)	2.80 Aa(a)	83.16Aa(a)	1.23Ba(a)
Pasture		135.36 Aa(a)	58.20 Aa(a)	35.87 Aa(a)	1.66 Aa(a)	113.65Aa(a)	5.32Aa(b)
Bean	10-20	125.79 Aa(a)	67.50 Aa(a)	42.86 Aa(a)	2.05 Aa(a)	70.62Ba(a)	1.97Ba(b)
Cassava		77.19Ba(a)	42.76 Aa(a)	17.00Ba(b)	2.54 Aa(a)	88.65Ba(a)	1.69Ba(a)

¹ Carbon and nitrogen determined by the dry combustion method in a CHN analyzer (LECO); # The capital letters represent the treatments at the same depth; the small letters represent the depths within the same treatment; the letters in parentheses represent the samplings. *CV (%) First Sampling: C – 33.20; N – 36.48; Second Sampling: C – 19.03; N – 22.85

There was a large variation in the HUM-C values for both depths; however, there was no difference among the sites in the first year. The HAF-C values did not differ, and FAF-C values only did so in the top layer (0-10 cm), with the highest value in the cassava site. There was no variation with depth for the C in SOM fractions (except for FAF-C in the first year), suggesting a similar SOM transformation processes of these Histosols.

In the second year (Table 4), the HUM-C fraction presented a significant difference in both

depths, in general with the same distribution and ranging from 77.19 to 186.36 g kg⁻¹. Pasture having the highest values, followed by bean and then cassava, a pattern that agrees with variation in SOM values. For HAF-C values, there was significative variation among sites only at 0-10 cm, and for FAF-C values in both depths, with the highest values in pasture site. The lowest values were in the cassava, and there was no variation with depth. The HAF-C/FAF-C ratio ranged from 1.14 to 2.19, similar to results found by Fontana (2008), and the values

higher than 2.0 indicate dominance of HAF-C in the Histosols.

There were differences in the carbon stocks (Table 4) for the first year, where the highest values were in pasture (115.92 and 115.34 Mg ha⁻¹, for 0-10 and 10-20 cm respectively), followed by cassava and then bean. The same sequence was observed in the second year, the pasture having the highest stocks at 10-20 cm (113.65 Mg ha⁻¹). The higher C stocks in pasture at the surface are related to the capacity of this system to add organic C to the soil by grass shoots and roots, leading to C increases in relation to other soil uses (D'ANDRÉA et al., 2002).

There were variations in the nitrogen stocks in the first year among the sites (Table 4). The pasture had the highest values, at depths of 0-10, 10-20 cm, followed by bean, then cassava. The variation for pasture was the same in the second year. Between the years, the pasture presented the highest values in the first sampling at both depths. In beans, the highest N stock was in the first sampling, at depths of 0-10 and 10-20 cm.

Since N is found in Histosols mainly in organic form, changes in SOM levels are accompanied by similar alterations in N stock. These attributes can help the development of sustainable technologies as well as help in the assessment of the soil's role as a source or sink of C-CO₂ and N-N₂O (CORAZZA et al., 1999).

Integration of Results for the Attributes of Histosols

To distinguish possible effects of soil management, a principal components analysis (PCA) was used to rank the attributes, which were summarized in a graph with perpendicular axes, representing multidimensional variation of a set of data as a function of soil usage. This analysis showed a strong effect of soil management by a clear separation of the three sites, shown by the position of the vectors in Figure 1a. In this respect, axis 1 was responsible for the separation of the bean site from the other two usages, with this site's data appearing above the horizontal line. The PCA presented good significance, with the sum of the eigenvalues reaching 74.1%.

The data in Figure 1b show variable results within the usages, separating the cassava site, but not clearly distinguishing the pasture and the bean sites. This figure presents all the values and variables analyzed in the form of vectors, showing

each variable's influence. Therefore, the nearest the attributes (variables) are, the more often they occur together. The pasture was associated with most of attributes related to C content as well as the state of organic matter transformation: C_CHN, H_CHN, N_CHN, soil SOM_muffle, N_distiller, OMD, Al³⁺, H⁺, HUM-C and FAF-C. These attributes are directly related to recent and steady influx of organic matter in the soil, added to those that indicate less intervention by soil preparation.

due to their fasciculate root system, with a high density of fine roots and constant root renewal. Thus, they are an important source of carbon for the soil. Addition of organic matter during decomposition process adds into the soil aminoacids, CO₂ and carboxylic acids, the main factors responsible for the increase of H⁺ ions in the soil solution. The bean field occupied an intermediate position with respect to the attributes and showed a direct relationship with C. But it stood out for attributes such as pH_KCl, FAH/FAF, HAF-C, SOM_WB, StC_WB, TPV, GMC, Al³⁺ and H⁺.

The levels of Al³⁺ and H_CHN were not specifically associated with any of the usages, but were instead found at the intersection between pasture and bean sites. Since these two were near each other, both in Macaé (RJ), these attributes may be related to characteristics inherited from the organic matter and mineral sediments that formed the Histosols. For the cassava site, there was a cluster of chemical attributes regarding soil fertility along with physical attributes indicative of the crop management. The attributes common to this usage were: Ca, Mg, Na, K, P, S, T, V, pH (water, CaCl₂), BD, Dp, MWD, GMD, MR and MM. The values related to soil fertility are explained by the greater usage of agriculture practices for a longer period. In turn, the physical attributes indicate an advanced subsidence and/or soil degradation process.

Grasses Promote Greater Addition of Carbon in Soil

The multivariate analysis was important to distinguish the usages. The values found and discussed separately above show that the soil management in the pasture site to a certain extent promotes conservation of organic carbon, while the management of the cassava is more aggressive, causing greater degradation and reducing the carbon stock.

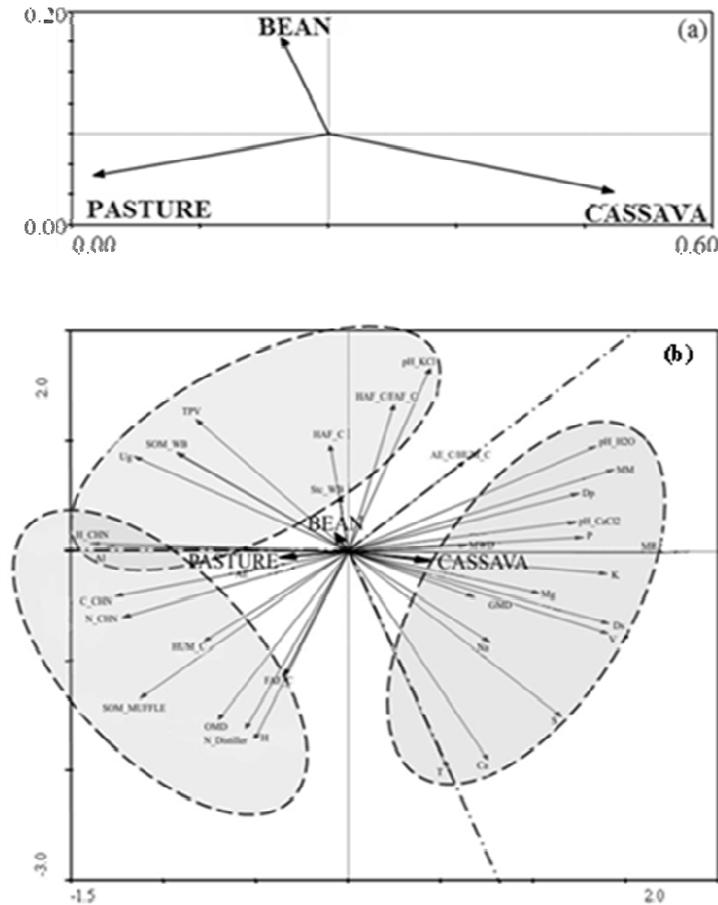


Figure 1. Principal components analysis of the soil attributes with emphasis on discrimination of the usages (a); and general analysis of influence of the soil attributes with emphasis on clustering as a function of usages (b) (Axis 1- 61.8% and Axis 2 – 12.3%).

Emission of CO₂ and N₂O from the Histosols

The emissions of CO₂ and N₂O were calculated from the data obtained in the field and analyzed by comparing against the greenhouse gas emission database of the IPCC (1997). Although the number of measurements was too small to be certain of the real emission pattern during the growing cycle, the data are still original and important because of the scarcity of studies in the literature on Histosols. The CO₂ flux (Figure 2-ab) was greatest in the first year in the bean site (0.09 Mg CO₂ ha⁻¹ day⁻¹) among all measurements during the four sampling days. This high CO₂ flux was possible due to addition of crop residue (leguminous N₂ fixer), causing a lower C/N ratio, which favored the OM decomposition by aerobic microorganisms, increasing the flux of CO₂. At the first sampling, the crop was in maturation stage, with a large proportion of leaves in senescence, increasing input of N in the soil. Giacomine et al. (2008) also observed a tendency for greater emissions after the

addition of plant material. The authors theorized that organic compounds, which decompose easily, are mineralized after microbial population adapts to the substrate, and in the process CO₂ is also emitted by root respiration.

For the second year, the highest CO₂ emissions were observed in the pasture, with high flux on all four measurement days and the highest value on the third day (0.10 Mg CO₂ ha⁻¹ day⁻¹). At that period, the bean and cassava fields had already been harvested and there were no plant residues, unlike the pasture, where the grass was about 80 cm tall and there was a layer of plant residues about 5 cm thick, thus a large proportion of biomass was steadily introduced in the soil to continue the process of transforming the SOM. Besides this, the dense grass root system intensified the emission of CO₂ by the respiration process. The CO₂ fluxes oscillated during the samplings, although with a tendency for higher values in the second year.

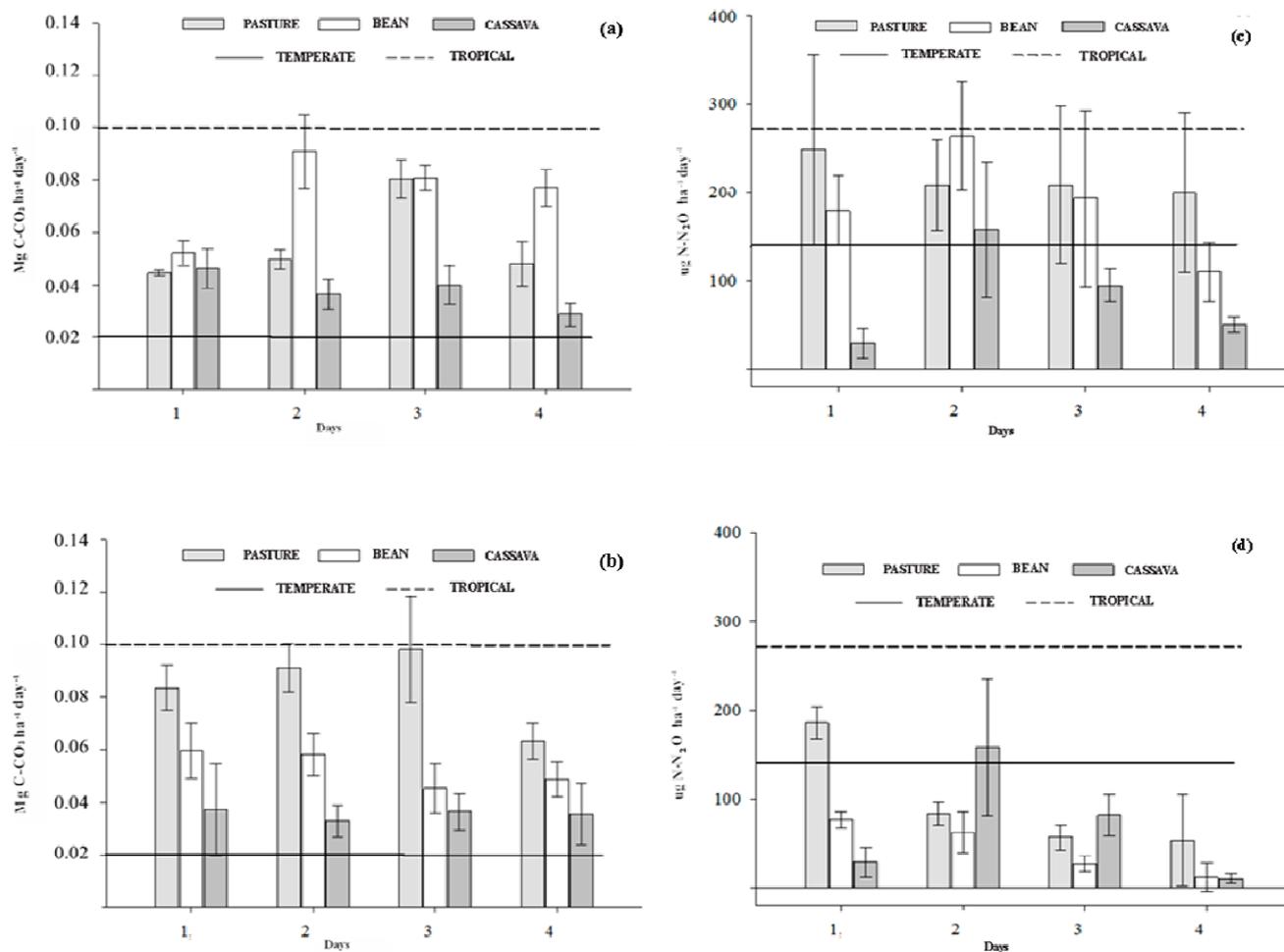


Figure 2. C₂CO₂ emissions on different sampling days (x-axis) in function of soil usage, first sampling (a) and second sampling (b). N₂N₂O emissions on different sampling days (x-axis) in function of soil usage, first sampling (c) and second sampling (d). The values were submitted to the Tukey test (0.05>p). The dotted line indicates the typical emission in a tropical climate and the solid line in a temperate climate.

Organic matter decomposes in tropical climates twice as fast as in temperate climates (IPCC, 1997). As a consequence, the CO₂ flux from Histosols is also greater in tropical regions, varying from 0.02 Mg C₂CO₂ ha⁻¹ day⁻¹ in temperate climates to 0.10 Mg C₂CO₂ ha⁻¹ day⁻¹ in tropical ones. The CO₂ flux values in this study are in accordance with IPCC data for Histosols in tropical regions.

Regarding N₂O (Figure 2-cd), for the first year the highest flux occurred in the bean site on the second day, at about 270 µg N-N₂O m⁻² day⁻¹. On the other days, the highest emissions came from the pasture. The N₂O fluxes in these two usages did not differ, while the lowest values occurred in the cassava site. The high values in the pasture are possibly related to the continuous addition of N (JANTALIA et al., 2006), and in the bean site due to releasing of N to the soil from decomposition of fallen leaves. For the second year the highest N₂O

flux occurred in the pasture on the first day, with values of 180 µg N-N₂O m⁻² day⁻¹. On the other days no variation or pattern was observed in the N₂O flux.

There are few published studies of gas emissions from Histosols in tropical regions, making comparison and validation of the data hard. However, the C-CO₂ flux values are within the emission range proposed by the IPCC, while the N-N₂O values are lower. Based on this study, although preliminary, nitrous oxide emission rates proposed for cultivated Histosols in tropical regions are overestimated.

CONCLUSIONS

The cassava site had the highest levels of sorption complex elements, as a direct influence of fertilization and soil management.

The physical properties: soil bulk density, particle density, mineral matter, mineral residue and organic matter density indicated highest alterations of Histosols properties with agricultural usage.

The cassava showed most transformation of soil organic matter.

In all sites, the carbon levels in the organic fractions indicated predominance of HUM-C. The SOM and the stocks of C and N were highest in the pasture, which was considered the best usage in terms of conserving SOM.

The clusters obtained through multivariate analysis allowed to stratify the three usages. The pasture stood out as showing the least alteration of soil properties.

Although C-CO₂ and N-N₂O flux data were obtained from a small number of samples, preliminary values of C-CO₂ emission were within the range proposed by the IPCC, while the N-N₂O values were lower.

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RESUMO: Os Organossolos são reservatório natural de C no solo e sua drenagem seguida por práticas agrícolas leva a subsidência e transformações na matéria orgânica do solo. O objetivo do estudo é avaliar a influencia do uso e manejo de Organossolos, através da: caracterização de propriedades químicas e físicas, conteúdo de matéria orgânica do solo e frações húmicas; e quantificação de estoques de C e N. Ainda, obter dados preliminares sobre emissão de gases de efeito estufa (CO₂, N₂O) em áreas de Organossolos com diferentes usos agrícolas. Foram selecionadas três áreas com solos e ambientes semelhantes, duas no município de Macaé, sob pastagem e feijão com rotação de lavouras, e a terceira em Santa Cruz na cidade do Rio de Janeiro, com mandioca (*Manihot esculenta*). Os atributos avaliados foram: físicos - densidade do solo (Ds), densidade de partículas (Dp), densidade de matéria orgânica (DMO), material mineral (MM), resíduo mineral (RM), estabilidade de agregados; químicos - pH, cátions trocáveis, matéria orgânica do solo (MOS), carbono nas frações húmica (HUM-C), ácido húmico (FAH-C) e ácido fúlvico (FAF-C); estoques de C e N; e fluxo de CO₂ e N₂O. A área de mandioca apresentou maiores valores de cátions trocáveis como resultado das práticas de adubação e manejo do solo. A área de mandioca apresentou Ds e Dp, volume total de poros, e valores de MM e RM e DMO mais elevados, e maior grau de transformação da matéria orgânica, indicando maior alteração das propriedades do Organossolo com esse uso. Em todas as áreas, os teores de C indicaram predomínio da húmica. Os valores de MOS e estoques de C e N foram maiores na pastagem, indicando melhor preservação da matéria orgânica, com valores variando de 115,92-99,35Mg ha⁻¹ de C e 8,35-4,45 Mg ha⁻¹ para N. Os valores de fluxo de CO₂ estão de acordo com o IPCC, sendo o mais elevado de 0,09 mg de CO₂ ha⁻¹ dia⁻¹ na pastagem. Para N₂O os fluxos foram menores que o proposto pelo IPCC, com o maior valor de 270 g N₂O -N m⁻² dia⁻¹ na área com feijão. Em geral, a análise multivariada discriminou as áreas e a pastagem foi o uso que menos afetou as propriedades dos Organossolos.

PALAVRAS-CHAVE: Substâncias Húmicas. Estoques de C e N, Emissões de N₂O e de CO₂.

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