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Humic fractions as support for the classification of high-mountain *Organossolos* in the southeast of Brazil

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ABSTRACT: Brazilian Soil Classification System (SiBCS) adopts a hierarchical approach to classify soils using specific diagnostic attributes. *Organossolos* (Histosols) class is differentiated according to its genesis, especially because the parent material is organic, thus requiring diagnostic attributes that describe the unique properties of soil organic matter (SOM). This study aimed to propose the use of labile organic carbon and the C and N contents of humic fractions and their ratios for the family and series levels of the Brazilian Soil Classification System for *Organossolos* in high mountainous regions. Quantitative chemical fractionation of SOM was performed to obtain the humic fractions and determine the labile oxidizable carbon in 16 *Organossolos* profiles from Itatiaia National Park, RJ. Carbon and nitrogen contents of the humic acid, fulvic acid, and humin fractions were obtained, as well as the percentages of these fractions in relation to the total carbon and nitrogen in the soil. Carbon and nitrogen ratios were calculated for each fraction. Results showed little variation in the levels of labile organic carbon between the profiles but a large variation in total carbon and nitrogen levels, especially in the *Organossolo Fólico Hêmico lítico* profile. The ratios between the carbon and nitrogen of humic acids and fulvic acids (means of HAC/FAC = 1.61 and AHN/FACN = 1.05), carbon and nitrogen of the alkaline extract and humin (means of AEC/HUMC = 0.71 and AEN/HUMN = 0.38), carbon and nitrogen of the alkaline extract, and total carbon and total nitrogen (means of AEC/TC = 0.28 and AEN/TN = 0.19) were effective in determining the humification level of the profiles. This study proposes that the attributes evaluated, especially the ratio between the carbon of the alkaline extract of the humic substances (carbon of the fulvic acid fraction + carbon of the humic acid fraction) and the total soil carbon, as well as the ratio between the C and N of the humin fraction, should be used to define lower categorical levels of *Organossolos*. This new approach could facilitate the classification of these soils and contribute to a better understanding of the composition of *Organossolos* in Brazil.

Keywords: humic acid, fulvic acid, humin, SiBCS, categorical levels.

INTRODUCTION

Brazilian Soil Classification System (SiBCS) is a hierarchical soil classification system to systematize the soil classes found in the country. Soil classes were established using diagnostic attributes and horizons (surface and subsurface) that must be found within a specific control section (soil depth or thickness). The SiBCS is a morphopedogenetic classification system. Therefore, the main pedogenetic processes that acted in its genesis can be determined by analyzing the morphology of the profile in the field (Santos et al., 2018).

The SiBCS structure was defined using six categorical soil classification levels (order, suborder, large group, and subgroup) that are well-defined. Categorical levels for the 5th (families) and 6th (series) are intended to adopt specific diagnostic attributes to differentiate the soil classes; however, the attributes are not defined (Santos et al., 2018).

Processes related to the transformation (decomposition, mineralization, and humification) of soil organic matter (SOM) are benefited in Brazil due to its hot and wet climatic conditions. Formation of soils with high carbon content is limited to a few areas that favor the organic matter accumulation over time, such as high mountains and hydromorphic and limestone environments (Valladares et al., 2003; Pereira et al., 2013). To be considered a soil with an organic constitution, the properties of the organic material must predominate over those of the soil's mineral material, according to the SiBCS (Santos et al., 2018). As a result, two different types of horizons can be formed: (i) the O horizon formed under good drainage conditions and does not remain saturated with water for more than 30 consecutive days during the rainy season; and (ii) H horizons that are formed under conditions of excess water over a long period.

Organossolos are defined as poorly developed soils with a black, very dark grey, or burnished color and more than 80 g kg^{-1} of organic carbon in their diagnostic histic horizons. When formed by an O horizon, this horizon must be 0.20 m or more when an overlying lithic or fragmentary lithic contact occurs, or even under gravel, pebbles, or boulders, or 0.40 m or more when overlying horizons A, B, and/or C occur. The H horizons must be 0.40 m or more, continuously or cumulatively, within the first 0.80 m of the surface (Santos et al., 2018). In addition, H horizons can be found in other soil classes such as *Cambissolos*, *Espodossolos*, *Gleissolos*, and *Neossolos*.

Accumulation of organic material in mountainous regions is the result of reduced biological activity in the humification and mineralization processes of MOS, which is related to low temperatures and variable rainfall conditions that negatively affect the enzymatic activity of microorganisms (Pereira et al., 2005). Most of the time, these areas are covered by preserved natural vegetation (such as high-altitude grasslands) that continuously add organic material to the soil (Barreto, 2013).

Organic matter that comprises *Organossolos* is formed from different organic origins and, when deposited, can be at different stages of decomposition. An important part of this soil organic matter is the humic fraction, which represents a material that has already undergone a transformation process, such as humification. Humic fractions of MOS play an important role in the formation, differentiation, and transformation of soil profiles. In the formation of humic horizons, the processes involved in the humification of organic materials can vary and are affected by environmental variables that determine the transformation rate of the material.

Chemical fractionation of SOM is used to obtain the humic fractions of organic material through sequential extractions based on the different solubilities of the organic fractions obtained: fulvic acid (FA), humic acid (HA), and humin (HUM) (Benites et al., 2003). These fractions represent an important component of the carbon stock in the soil and the supply and dynamics of nutrients. Sum of these fractions generally represents more than 80 % of the total soil carbon and is differentiated by color, molecular mass, functional groups (e.g., carboxylic and phenolic), and the level of polymerization (aliphaticity, aromaticity, and condensation) (Stevenson, 1994).

The persistence or mobility of humic fractions in the soil profile can indicate different diagnostic horizons resulting from certain soil pedogenetic processes (Fontana et al., 2008a,b). Few studies aimed to understand the distribution patterns of humic fractions along the profile to classify them. Fontana (2009) summarizes some of these studies, including those by Benites (1998, 2002), Gomes et al. (1998), Benites et al. (2000), Lima (2001), Schaefer et al. (2002), Melo (2002), and Valladares et al. (2007). Valladares et al. (2003) and Fontana et al. (2008a,b) were the first to develop organic soil classification studies using humic fractions of the soil. Fontana et al. (2008a,b) established a standard for humic fractions in classifying soils at lower hierarchical levels, proposing C-FAF and C-FAH contents in addition to the C-EA/C-HUM humic index.

According to the SiBCS, the 5th categorical level of *Organossolos* includes attributes that distinguish the nature of the material found below the organic layer or the characteristics and proportions of the organic material that constitutes it. The suggested differentiating characteristics for the 6th categorical level are the thickness, state of decomposition of the organic material, presence of water to define the potential for subsidence, and better management of these soils (Santos et al., 2018). Therefore, for *Organossolos*, as already discussed by Valladares et al. (2003) and Fontana et al. (2011), the humic fractions and their ratios can be useful diagnostic attributes for differentiating the lower classification levels. Classification suggestions for the lower categorical levels proposed by Fontana et al. (2008b) and Valladares et al. (2003) adopted the C content of the AF (=20.0 g kg^{-1}: hypofulvic; >20.0 g kg^{-1}: fulvic) and AH (=90.0 g kg^{-1}: hypohumic; >90.0 g kg^{-1}: humic) fractions, and the index obtained from the CEA/HUM ratio (=1.0: hypoalkaline-soluble; >1.0 alkaline-soluble). Fontana et al. (2011) proposed the C-FAH/C-FAF ratio to categorize soils with O and H histic horizons at lower hierarchical levels of family and series.

Quantifying the labile and humic compartments of SOM is fundamental for understanding the carbon and nitrogen dynamics in the environment. This information is essential for understanding the mechanism of SOM stabilization under low-temperature conditions and for the preservation of natural vegetation. This greater detail of information may help to restructure and include new classes for the less generalized or more homogeneous categorical levels (family and series) for the classes *Organossolos Fólicos* and *Organossolos Háplicos*.

This study aimed to (a) quantify the labile organic carbon content in *Organossolos* profiles formed in mountainous regions, (b) quantify the carbon and nitrogen content of the humic substances in the SOM of these profiles, (c) evaluate the relationships between the carbon and nitrogen of the humic fractions based on the stoichiometric ratio (C/N), and (d) propose criteria for the lower categorical levels for the *Fólicos* and *Organossolos Háplicos* classes.

MATERIALS AND METHODS

Physical environment and sampling

Profiles were described and collected in the Itatiaia National Park (INP) located in the Serra da Mantiqueira in southeast Brazil, in the highlands where the vegetation is characterized by high-altitude grasslands (Barreto, 2013). The PNI has approximately 28,000 ha, and the extent of high-altitude grasslands present in the PNI is a small portion of this total (Ibama, 1997; Barreto, 2013). Altitudinal grasslands are located above 2.000 m and are composed of small, endemic undergrowth predominantly formed by grasses adapted to local climatic conditions, low availability of nutrients, and large variations in temperature throughout the day and year (Barreto, 2013).

Specific environmental conditions in the upper part of the INP resulted in the formation of shallow autochthonous soils with low levels of pedogenesis. In addition, low temperatures often result in the accumulation of organic material, forming mineral horizons with high organic carbon levels and horizons of organic constitution. Occasionally, the significant accumulation of organic carbon associated with the increased thickness of these horizons contributes to the formation of *Organossolos* (Santos et al., 2018). In this environment, two classes of *Organossolos* were identified, namely, *Organossolos Fólicos* (OO) formed in areas of good drainage and *Organossolos Háplicos* (OX) observed in conditions where drainage is impeded or limited, the occurrence of which is greater in the valley bottoms.

Sixteen *Organossolos* profiles were evaluated, and samples from the surface layer (0.00–0.20 m) were used for analysis. Further information on these profiles can be found in Costa (2019). Samples were obtained from a combination of horizons that comprised each profile up to an established depth. Highland field vegetation and a climate classified as Cwb (moderately hot and rainy summers) influenced all profiles. Among the profiles studied (Table 1), 13 were classified as OO and differentiated into two large groups (3rd categorical level): *Organossolos Fólicos Sápricos* (OOs) and *Organossolos Fólicos Hêmicos* (OOy). The OX corresponded to three soil profiles represented by three major groups (sapric, hemic, and fibric) with the same suborder (typical).

Chemical and physical attributes of the soils were also used, namely, pH, active acidity; P, available phosphorus; Na^+, exchangeable sodium; K^+, exchangeable potassium; Ca^{2+}, exchangeable calcium; Mg^{2+}, exchangeable magnesium; Al^{3+}, exchangeable aluminum; H+Al, potential acidity; SB, base sum; CEC, cation exchange capacity at pH 7.0; CECef, effective cation exchange capacity; BS, Base saturation; and SD, soil density, obtained from Costa (2019).

Chemical fractions of soil organic matter

After the soil was collected, the samples were air-dried, crushed, and passed through a 2.00 mm sieve to obtain fine air-dried soil. Total carbon and nitrogen contents were determined using the dry combustion method in a Perkin Elmer 2400 CHN elemental analyzer at the Carbon and Nitrogen Biotransformation Research Laboratory (LABCEN, Santa Maria, Brazil). Analyses were carried out using 1.0 (± 0.1) mg of soil sample macerated in a mortar and passed through a 100-mesh sieve (149 µm) (Nelson and Sommers, 1996; Sato et al., 2014). Stoichiometric C/N ratio was then calculated.

Labile organic carbon was quantified via oxidation with a 0.02 mol L^{-1} $KMnO_4$ solution (POXC) (Weil et al., 2003; Culman et al., 2012). Approximately 1.00 g of fine air-dried soil was weighed and transferred to a 50 mL polypropylene centrifuge tube, after which 20 mL of $KMnO_4$ 0.02 mol L^{-1} was added. Tubes were then homogenized for 2 min on a horizontal shaker at 240 oscillations $minute^{-1}$. Subsequently, the tubes were left to stand vertically for 10 min. After stabilization, 0.50 mL of the supernatant was pipetted off and transferred to another 50 mL centrifuge tube containing 49.50 mL of distilled water. Absorbance of each sample was measured colorimetrically at 550 nm using a spectrophotometer. The POXC (mg kg^{-1}) was calculated using equation 1 and converted to g kg^{-1} of soil.

$$POXC = [0.02\ mol\ L^{-1} - (a+b\ Abs)] \times (9000\ mg\ C\ mol^{-1}) \times (0.02\ L\ Wt^{-1}) \qquad \text{Eq. 1}$$

in which: POXC is the labile organic carbon extracted with $KMnO_4$; 0.02 *mol* L^{-1} is the initial concentration of the $KMnO_4$ solution; *a* is the intercept of the standard curve; *b* is the slope of the standard curve; *Abs* is the absorbance reading of the sample at 550 nm; 9000 mg is the amount of C oxidized by 1 mol of MnO_4 with Mn^{7+} being reduced to Mn^{4+}; where 0.02 L is the volume of the $KMnO_4$ solution that reacted with the soil, and *Wt* is the mass of the sample (kg) used in the reaction.

Chemical fractionation of MOS was also performed to extract the humic fractions, i.e., fulvic acid (FA), humic acid (HA), and humin (HUM), using a method from Swift (1996) adapted by Matos et al. (2017). Each sample was extracted following the concept of the differential solubility of humic substances established by the International Humic

Table 1. *Organossolos* profiles in the upper part of Itatiaia National Park and their chemical and physical attributes (Costa, 2019)

Symbols			SiBCS	Geological Formation
OO (13 profiles)	OOs (8 profiles)	OOscamb1	*Organossolos Fólicos Sápricos cambissólicos*	Nepheline-syenites-phyrite
		OOsfragmen	*Organossolos Fólicos Sápricos fragmentários*	Magnetic slit
		OOslitico2	*Organossolos Fólicos Sápricos líticos*	Magnetic slit
		OOstipico1	*Organossolos Fólicos Sápricos típicos*	Nepheline-syenites-phyrite
		OOstipico2		Brecha magmática
		OOstipico5		Alkaline granite
		OOstipico6		Quartz syenites
		OOstipicoX		Nepheline-syenites-phyrite
	OOy (5 profiles)	OOylitico2	*Organossolos Fólicos Hêmicos líticos*	Nepheline-syenites-phyrite
		OOylitico3		Nepheline-syenites-phyrite
		OOylitico4		Nepheline-syenites-phyrite
		OOylitico5		Quartz syenites
		OOylitico6		Quartz syenites
OX (3 profiles)	OXfi (1 profile)	OXfitipico	*Organossolos Háplicos Fíbricos típicos*	Nepheline-syenites-phyrite
	OXs (1 profile)	OXstipico	*Organossolos Háplicos Sápricos típicos*	Alluvial sediments
	OXy (1 profile)	OXytipico2	*Organossolos Háplicos Hêmicos típicos*	Alluvial sediments

SiBCS	pH	P	Na^+	K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	SB	CEC	CECef	BS	SD
OOscamb1	4.96	6.84	0.04	0.27	0.22	0.35	1.95	20.30	0.88	21.18	2.83	4.17	0.57
OOsfragmen	3.79	7.14	0.03	0.18	0.26	0.65	8.05	32.35	1.12	33.47	9.17	3.35	0.43
OOslitico2	4.55	19.03	0.02	0.12	0.04	0.75	0.77	12.50	0.92	13.42	1.69	9.20	0.60
OOstipico1	4.08	9.52	0.15	0.24	0.20	0.25	2.15	21.29	0.83	22.12	2.98	3.77	0.46
OOstipico2	4.27	7.55	0.06	0.24	0.11	0.49	4.65	21.70	0.89	22.59	5.54	3.95	0.52
OOstipico5	3.91	4.94	0.04	0.23	0.00	1.24	5.10	21.30	1.51	22.81	6.61	6.62	0.51
OOstipico6	4.40	4.54	0.02	0.17	0.39	1.06	3.70	23.75	1.64	25.39	5.34	6.37	0.50
OOstipicoX	5.06	3.50	0.33	0.46	0.70	1.30	7.90	25.10	2.80	27.90	10.07	10.00	0.41
OOylitico2	4.34	11.00	0.04	0.38	0.17	0.43	2.95	23.60	1.02	24.62	3.97	4.15	0.39
OOylitico3	5.04	13.33	0.10	0.59	0.66	0.69	4.00	27.59	2.04	29.63	6.04	7.08	0.34
OOylitico4	4.29	14.15	0.08	0.45	0.00	0.45	6.00	31.00	0.98	31.98	6.98	3.06	0.32
OOylitico5	4.21	11.51	0.03	0.17	0.38	0.42	3.00	15.00	1.00	16.00	4.00	6.25	0.69
OOylitico6	4.18	5.21	0.08	0.15	0.17	1.28	4.20	17.60	1.68	19.28	5.88	8.71	0.33
OXfitipico	5.22	5.14	0.05	0.26	0.15	0.40	2.45	15.69	0.86	16.55	3.31	5.22	0.29
OXstipico	4.64	8.43	0.05	0.06	0.17	0.58	2.20	13.15	0.85	14.00	3.05	6.19	0.65
OXytipico2	5.41	7.43	0.05	0.13	0.15	0.43	1.50	13.09	0.76	13.85	2.26	5.51	0.12

pH, active acidity; P, available phosphorus; Na^+, exchangeable sodium; K^+, exchangeable potassium; Ca^{2+}, exchangeable calcium; Mg^{2+}, exchangeable magnesium; Al^{3+}, exchangeable aluminum; H+Al, potential acidity; SB, base sum; CEC, cation exchange capacity at pH 7.0; CECef, effective cation exchange capacity; BS, Base saturation; and SD, soil density (Costa, 2019).

Substances Society. Carbon and N contents of each humic fraction were determined using the humidity method described by Matos et al. (2017).

Once these procedures were completed, the C and N contents of the fulvic acid (FAC and FAN), humic acid (HAC and HAN), and humin (HUMC and HUMN) fractions were obtained, as well as the percentage of each of these fractions (%FAC, %HAC, %HUMC, %FAN, %HAN, and %HUMN) in relation to the total carbon and nitrogen contents of the soil and non-humified carbon and nitrogen (%NHC and %NHN). After obtaining the carbon and nitrogen contents of the humic fractions of MOS, the stoichiometric ratios (C/N) were calculated for each fraction to obtain the C/N ratios of fulvic acid (FA-C/N), humic acid (HA-C/N), and humin (C/N-HUM). Humic indices were obtained from the ratios of carbon and nitrogen in humic acids and fulvic acids (HAC/FAC and HAN/FAN), carbon and nitrogen in the alkaline extract and humin (AEC/HUMC and AEN/HUMN), carbon and nitrogen in the alkaline extract, and total carbon and total nitrogen (AEC/TC and AEN/TN). The alkaline extract (AE) is the sum of the carbon and nitrogen contents of the FA and HA fractions. Humic indices are numerical values (without units) obtained from the relationships between the humic fractions of the SOM.

Statistical analysis

R were analyzed using descriptive statistics using the Tableau Public Tool. The averages of three replicates were calculated, and boxplots were constructed to evaluate the distribution of carbon, nitrogen, and POXC contents, and the distribution of the C and N contents of the humic fractions. Cumulative bar charts were created in Excel to show the percentage of each humic fraction in relation to the total C and N content of the soil. RStudio was used to carry out multivariate analyses using the “Openxlsx,” “FactoMineR,” “Factoextra,” “Stats,” “Dendextend,” “Igraph,” and “Ggplot2” packages, allowing the relationships between the variables studied and the soil profiles evaluated to be observed.

The distribution of the labile organic carbon and humic fractions of the MOS was analyzed in terms of the quantitative and qualitative values that stood out for their magnitude and/or participation, as well as the ability to form distinct groups in each diagnostic horizon to propose the separation of the diagnostic horizons for the 5th categorical level. Pearson’s correlation between the labile organic carbon content, humic fraction values and indices, and the chemical and physical attributes of each diagnostic horizon was also used as an auxiliary analysis for decision-making. Significance values of 5 and 10 % were used in this analysis.

For comparison in the established classes, the data were analyzed for normality of errors using the Shapiro–Wilk test and for homoscedasticity of variances using the Bartlett test. Variables that did not show a normal distribution or homoscedasticity were transformed according to the Box-Cox test and tested again. The data were evaluated using an analysis of variance (ANOVA) when the assumptions were satisfied (variables were transformed or not). In cases where data transformation was inefficient, the Kruskal–Wallis test, followed by Fisher’s minimum significant difference criterion, was used as a non-parametric analysis. These tests were conducted at a 10 % significance level, as confidence was sufficient to establish the classification classes in this study. All statistical data processing was performed using R Software (R Development Core Team, 2020).

RESULTS

Total carbon (TC) and total nitrogen (TN) contents ranged from 81.0 to 292.0 g kg^{-1} and 4.0 to 16.0 g kg^{-1}, respectively (Table 2). The highest TC value (292.4 g kg^{-1}) was observed in the OOstipicoX profile, which did not fall within the quartile range of the *Box Plots* (Figure 1). This was considered an “outlier”. The POXC values ranged from 0.87 to 2.22 g kg^{-1} in the OOylitico3 and OXytipico2 profiles, and no outliers were observed (Table 2).

Table 2. Total carbon (TC) and total nitrogen (TN) of the soil and carbon (FAC, HAC and HUMC) and nitrogen (FAN, HAN, and HUMN) contents of the humic fractions and labile organic carbon (POXC) in *Organossolos* profiles from Itatiaia National Park, southeastern Brazil

SiBCS	POXC	TC	TN	FAC	FAN	AHC	HAN	HUMC	HUMN
					g kg^{-1}				
OOscamb1	1.60	140.2	8.80	18.40	0.99	21.49	0.86	48.20	4.21
OOsfragmen	1.97	200.4	13.20	15.93	0.90	30.75	1.08	53.12	4.15
OOslitico2	0.97	150.7	12.50	11.07	0.56	21.18	0.96	55.67	7.07
OOstipico1	0.97	115.9	8.00	14.50	0.83	26.64	0.85	56.12	4.39
OOstipico2	1.50	163.4	10.30	18.70	1.26	29.76	1.11	76.06	5.48
OOstipico5	1.97	123.7	7.30	21.15	0.92	22.83	0.83	58.79	4.08
OOstipico6	1.86	171.5	10.40	15.68	0.58	21.51	0.67	47.62	3.59
OOstipicoX	1.75	292.4	11.70	18.66	0.76	40.43	1.32	121.48	7.28
OOylitico2	2.02	176.0	9.60	20.32	0.72	23.37	0.73	61.97	4.17
OOylitico3	0.87	221.7	12.70	23.66	0.90	33.99	1.17	96.67	6.81
OOylitico4	1.34	242.6	15.60	30.33	1.26	51.30	1.60	142.83	10.43
OOylitico5	1.25	81.3	4.40	14.50	0.83	26.64	0.85	56.12	4.39
OOylitico6	1.58	121.90	8.10	18.38	1.29	20.52	0.65	60.45	5.11
OXfitipico	1.06	158.20	10.10	16.70	1.93	30.11	1.20	60.21	4.40
OXstipico	1.01	129.00	8.90	4.51	0.42	15.11	0.45	17.49	2.17
OXytipico2	2.22	163.10	8.90	23.91	0.89	27.22	0.86	104.24	6.93
Mean	1.49	165.75	10.03	17.88	0.93	26.92	0.92	68.63	5.22

OOscamb1: *Organossolos Fólicos Sápricos cambissólico*; OOsfragmen: *Organossolos Fólicos Sápricos fragmentários*; OOslitico: *Organossolos Fólicos Sápricos líticos*; OOstipico: *Organossolos Fólicos Sápricos típicos*; OOslitico: *Organossolos Fólicos Hêmicos líticos*; OXfitipico: *Organossolo Háplico Fíbrico típico*; OXstipico: *Organossolo Háplico Sáprico típico*; OXytipico: *Organossolo Háplico Hêmico típico*.

The highest carbon content of the humic fractions was quantified in profile OOylitico4, with 30.33 g kg^{-1} FAC, 51.30 g kg^{-1} HAC, and 142.83 g kg^{-1} HUMC (Table 2). These variables in the OOylitic4 profile were different from those in the other profiles and were considered outliers in the Box Plots (Figure 1). The lowest carbon content in the humic fractions was observed in the OXstipico profiles, with FAC standing out (4.51 g kg^{-1}); this profile was also considered an "outlier" for this fraction (Figure 1). This profile also showed the lowest carbon contents for HAC and HUMC (15.11 and 17.49 g kg^{-1}, respectively). However, these fractions were not considered "outliers" when evaluating the profiles using Box Plots analysis (Figure 1) since they fell within the specific range defined by the quartiles of the data set.

In terms of the nitrogen content of the humic fractions, only one positive *outlier* was observed for FAN in the OXphytypic profile (1.93 g kg^{-1}) (Table 2 and Figure 1). Nitrogen content of the humic acid and humin fractions was the highest in the OOylitic4 profile for HAN (1.60 g kg^{-1}) and HUMN (10.43 g kg^{-1}). The OXstipico profile showed the lowest values for FAN (0.42 g kg^{-1}) and HUMN (2.17 g kg^{-1}). In the OOylitic5 profile, the lowest levels of this element were found in the HAN fraction (0.42 g kg^{-1}) (Table 2).

Humic indices were calculated to establish mathematical relationships between the carbon and nitrogen contents of the humic fractions (Table 3). The relationship between the carbon and nitrogen contents of the humic acid (HAC and HAN) and fulvic acid (FAC and FAN) fractions indicated values close to 1 for the HAC/FAC index (overall average of 1.61), except for the OOstipico6 (2.17) and Oxstipico (3.35) profiles (Table 3). For the HAN/FAN index, values ranged from 0.50 (Ooylitico6) to 1.74 (OostipicoX), with an overall average for all profiles of 1.05 (Table 3).

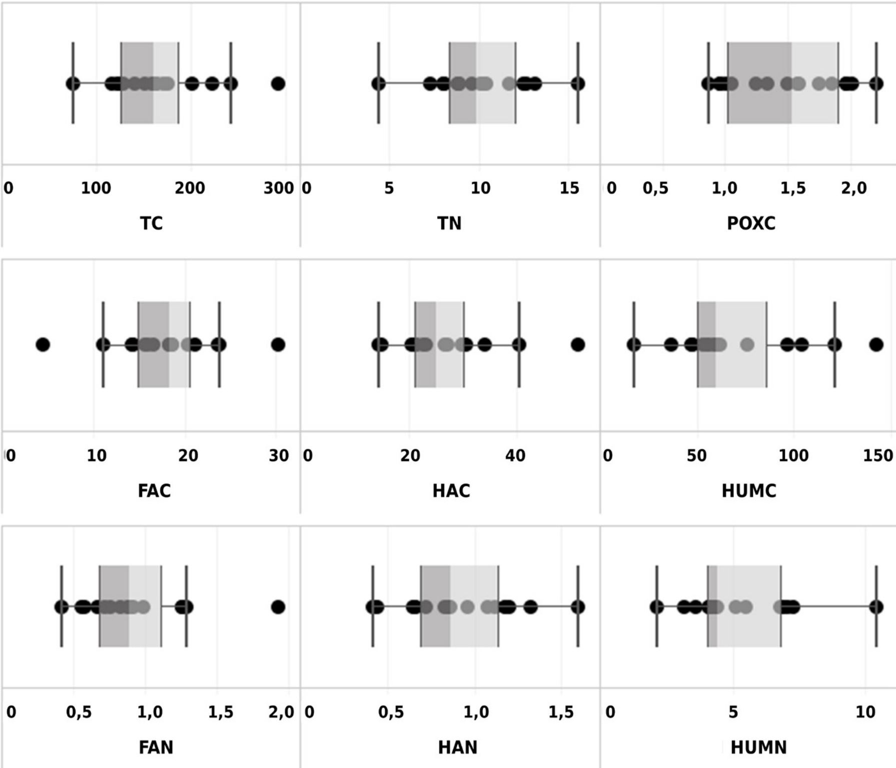

Figure 1. Box plot of the variables total carbon (TC), total nitrogen (TN), labile carbon (POXC), fulvic acid carbon (FAC), humic acid carbon (HAC), humin carbon (HUMC), fulvic acid nitrogen (FAN), humic acid nitrogen (HAN), and humin nitrogen (HUMN) in *Organossolos* profiles from Itatiaia National Park, Southeast Brazil.

The values observed for the AEC/HUMC ratio were lower than 0.88, except for the typical OX profile (1.12) (Table 3). For the AEN/HUMN ratio, the values ranged from 0.21 in the OOslitic2 to 0.71 in the OXtypical, with an overall average of 0.38 among the profiles. The EAC/TC ratio ranged from 0.15 (OXstyipico2) to 0.38 (OOylitico5), with an average of 0.28. The AEN/TN ratio ranged from 0.10 in the OXytipico2 profile to 0.31 in the OXfitipico profile, with an overall average of 0.19 (Table 3).

Proportional to TC and TN, the HUM fraction had the highest percentages of carbon and nitrogen among the humic fractions in the soil profiles evaluated (Figure 2). About the percentage, the lowest contribution of HUMC (14 %) was observed in the OXstipico profile, with most of the carbon in this profile being in the non-humified fraction of the MOS (%NHC, 71 %). The highest HUMC contribution (64 %) was observed in the OXytipico2 profile.

The percentages of nitrogen in the HUM fraction were lower than those in the non-humified fraction in only three profiles, namely OXstipico (24 % for %HUMN and 66 % for %NHN), OOsfragmen (31 % for %HUMN and 54 % for %NHN), and OOstipico6 (35 % for %HUMN and 53 % for %NHN) (Figure 2). This pattern showed a large portion of the nitrogen present in this soil was stored directly in the humin fraction.

In general, evaluating the stoichiometric ratios of carbon and nitrogen in the soil and humic fractions showed a decreasing pattern: HA-C/N > FA-C/N > C/N ≥ HUM-C/N (Table 4). The soil C/N ratio varied from 25 in the OOstipicoX profile to 12 in the OOslitico2 profile. The HUM-C/N ratios ranged from 8 (OOslitico2 and OXstipico) to 17 (OOstipicoX), whereas the HA-C/N ratios ranged from 22 to 36 in the OOslitico2 and OOylitico5 profiles (Figure 3).

The C/N ratios were lower than the FA-C/N ratios in almost all profiles, except for OXstipico (11) and OXfitipico (11), where the C/N ratios were 14 and 16, respectively (Table 4). The C/N ratios of the humic SOM fractions showed that all profiles other than OXphytypic and

Table 3. Humic indices obtained from quantifying the C and N contents of the humic fractions of the SOM in *Organossolos* profiles from the Itatiaia National Park, southeastern Brazil

SiBCS	HAC/FAC	AEC/HUMC	AEC/TC	HAN/FAN	AEN/HUMN	AEN/TN
OOscamb1	1.17	0.83	0.28	0.87	0.44	0.21
OOsfragmen	1.93	0.88	0.23	1.20	0.48	0.15
OOslitico2	1.91	0.58	0.21	1.71	0.21	0.12
OOstipico1	1.84	0.73	0.35	1.02	0.38	0.21
OOstipico2	1.59	0.64	0.30	0.88	0.43	0.23
OOstipico5	1.08	0.75	0.36	0.90	0.43	0.24
OOstipico6	1.37	0.78	0.22	1.16	0.35	0.12
OOstipicoX	2.17	0.49	0.20	1.74	0.29	0.18
OOylitico2	1.15	0.71	0.25	1.01	0.35	0.15
OOylitico3	1.44	0.60	0.26	1.30	0.30	0.16
OOylitico4	1.69	0.57	0.34	1.27	0.27	0.18
OOylitico5	1.02	0.77	0.38	0.63	0.34	0.25
OOylitico6	1.12	0.64	0.32	0.50	0.38	0.24
OXfitipico	1.80	0.78	0.30	0.62	0.71	0.31
OXstipico	3.35	1.12	0.15	1.07	0.40	0.10
OXytipico2	1.14	0.49	0.31	0.97	0.25	0.20
Mean	1.61	0.71	0.28	1.05	0.38	0.19

HAC: Humic acid carbon; FAC: Fulvic acid carbon; AEC: Alkaline extract carbon (HAC+AFC); HUMC: Humin carbon; TC: Total carbon; AHN: Humic acid nitrogen; FAN: Fulvic acid nitrogen; AEN: Alkaline extract nitrogen (HAN+FAN); HUMN: Humin nitrogen; TN: Total nitrogen. OOscamb1: *Organossolos Fólicos Sápricos cambissólico*; OOsfragmen: *Organossolos Fólicos Sápricos fragmentários*; OOslitico: *Organossolos Fólicos Sápricos líticos*; OOstipico: *Organossolos Fólicos Sápricos típicos*; OOslitico: *Organossolos Fólicos Hêmicos líticos*; OXfitipico: *Organossolo Háplico Fíbrico típico*; OXstipico: *Organossolo Háplico Sáprico típico*; OXytipico: *Organossolo Háplico Hêmico típico*.

OXstypic followed a decreasing pattern (Figure 3). The HUM-C/N ratio (14) was higher than the FA-C/N ratio (11) in the OXphytypic profile, whereas the FA-C/N ratio (11) was lower than the soil C/N ratio (14) in the OXstypic profile.

Principal component analysis (PCA) correlating the soil profiles with the variables of carbon and nitrogen in the humic fractions and their respective stoichiometric ratios for the class *Organossolos Fólicos* (OO) (Table 5) revealed that PCA explained 62.7 % of the total variation in the data for the first two PC (Figure 3a). For the *Organossolos Háplicos* (OX) class, the percentage of total variation in the data was 100 % for the first two PCs (Table 5 and Figure 3b).

The PCA results of the *Organossolos Fólicos* (OO) (Figure 3a) revealed that axis 1 (PC1) contributed 42 % to the variation in the data, while dimension 2 (PC2) contributed 20.7 %. The variables humic acid carbon (HAC), humic acid nitrogen (HAN), humin carbon (HUMC), humin nitrogen (HUMN), total carbon (TC), total nitrogen (TN), and the ratio between humic acid nitrogen and humin nitrogen (HAN/FAN) showed positive correlations (Table 5) and were greater than 0.70 with PC1. Therefore, this component is directly related to the carbon and nitrogen content of the soil profiles. On the same axis, the AEC/HUMC variable showed a negative correlation of −0.70. For PC2, FAC, FAN, AEC/TC, and AEN/TN also showed positive correlation (0.70) (Table 5).

The PCA results of the *Organossolos Háplicos* (OX) (Figure 3b) indicated PC1 contributed 65.2 % of the variation in the data, while PC2 contributed 34.8 %. Variables with a positive correlation of 0.70 (Table 5) for PC1 of OX were TC, FAC, HAC, HAN, HUMC, HUMN, C/N, HUM-C/N, AEC/TC, and AEN/TN. On the same axis, the HAC/FAC and AEC/HUMC variables showed a negative correlation of −0.90. For PC2, the variables with a positive correlation above 0.70 were POXC, FA-C/N, and HA-C/N. It is worth noting that the variables TN, FAN, and AEN/HUMN were negatively correlated [−0.70 with PC2 (Table 5)].

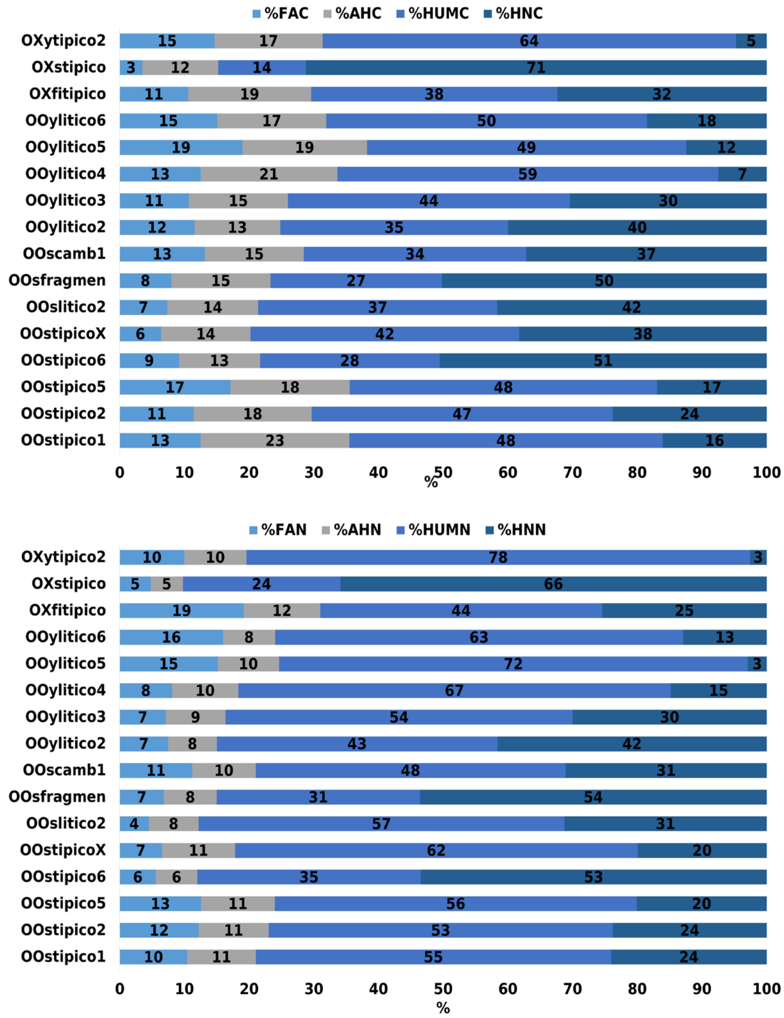

Figure 2. Percentage of non-humified carbon (%NHC) and humic fractions (%FAC, %HAC and %HUMC) in relation to total soil carbon in *Organossolos* samples in Itatiaia National Park. Percentage of non-humified nitrogen (%NHN) and humic fractions (%FAN, %HAN, and %HUMN) in relation to total soil nitrogen in *Organossolos* profiles from Itatiaia National Park, Southeast Brazil. OOscamb1: *Organossolos Fólicos Sápricos cambissólico;* OOsfragmen*: Organossolos Fólicos Sápricos fragmentários;* OOslitico*: Organossolos Fólicos Sápricos líticos;* OOstipico*: Organossolos Fólicos Sápricos típicos;* OOslitico*: Organossolos Fólicos Hêmicos líticos,* OXfitipico*: Organossolo Háplico Fíbrico típico;* OXstipico*: Organossolo Háplico Sáprico típico;* OXytipico*: Organossolo Háplico Hêmico típico.*

The PCA was carried out on the *Organossolos Fólicos Sápricos* (OOs) and *Organossolos Fólicos Hêmicos* (OOy) (Figure 4) to detail the pattern of carbon and nitrogen contents and their stoichiometric ratios within these classes (Table 6). The PCA of OOs explained 68.5 % (Figure 4a) of the variation in the data, and the PCA of OOy explained 86 % (Figure 4b) of the variation.

For OOs (Figure 4a), the variables with a positive correlation >0.70 with PC1 were TC, NT, HAN, HUMC, HUMN, HAC/FAC, and HAN/FAN. The variables AEC/HUMC and AEC/TC showed negative correlations above −0.70 for the same dimensions or axes. The PC1 explained 41.5 % of variation in the data. For PC2, the variables FAC, C/N, HUM-C/N, and AEN/TN showed positive correlations, with values higher than 0.70. PC2 explained 27 % of the variation in data (Table 6).

In the PCA of OOy (Figure 4b), the variables TC, TN, FAC, HAC, HAN, HUMC, HUMN, HAC/FAC, and HAN/FAN showed positive autovector values of greater than 0.90 PC1. This axis explained 62.8 % of the variation in the PCA data. On the same axis, the negative values of the eigenvectors of the HA-C/N, AEC/HUMC, AEN/HUMN, and AEN/TN variables

Table 4. Ratios between soil C and N (C/N) and soil humic fractions (FA-C/N, HA-C/N and HUM-C/N) in *Organossolos* in the upper part of Itatiaia National Park

SiBCS	C/N	FA-C/N	AH-C/N	HUM-C/N
OOscamb1	16	20	25	11
OOsfragmen	15	18	29	13
OOslitico2	12	20	22	8
OOstipico1	14	18	32	13
OOstipico2	16	16	27	14
OOstipico5	17	25	29	14
OOstipico6	16	27	33	13
OOstipicoX	25	25	31	17
OOylitico2	18	29	33	15
OOylitico3	17	26	29	14
OOylitico4	16	25	32	14
OOylitico5	17	21	36	12
OOylitico6	15	16	34	12
OXfitipico	16	11	26	14
OXstipico	14	11	35	8
OXytipico2	18	28	32	15
Mean	16	21	30	13

OOscamb1: *Organossolos Fólicos Sápricos cambissólico*; OOsfragmen: *Organossolos Fólicos Sápricos fragmentários*; OOslitico: *Organossolos Fólicos Sápricos líticos*; OOstipico: *Organossolos Fólicos Sápricos típicos*; OOslitico: *Organossolos Fólicos Hêmicos líticos*; OXfitipico: *Organossolo Háplico Fíbrico típico*; OXstipico: *Organossolo Háplico Sáprico típico*; OXytipico: *Organossolo Háplico Hêmico típico*.

Table 5. Autovector values of the variables in the principal component analysis (PCA) of the *Organossolos Fólicos* (OO) and *Háplicos* (OX) for dimensions 1 and 2 (Dim1 and Dim2), Itatiaia National Park in southeastern Brazil

Variables	OO				OX	
	PC1	PC2	PC3	PC4	PC1	PC2
POXC	0.21	−0.57	0.04	0.51	0.61	0.79
TC	0.94	−0.01	0.19	0.24	0.99	0.04
TN	0.87	−0.12	−0.27	0.15	0.41	−0.91
FAC	0.53	0.71	0.04	0.05	0.96	0.27
FAN	0.12	0.73	−0.53	0.30	0.66	−0.76
AHC	0.89	0.36	−0.12	0.11	0.96	−0.28
AHN	0.91	0.19	−0.29	0.14	0.84	−0.53
HUMC	0.90	0.43	−0.02	−0.09	0.91	0.42
HUMN	0.86	0.20	−0.33	−0.29	0.89	0.44
C/N	0.39	0.23	0.73	0.18	0.80	0.60
FA-C/N	0.38	−0.04	0.76	−0.21	0.58	0.81
AH-C/N	−0.20	0.53	0.54	−0.14	−0.69	0.72
HUM-C/N	0.36	0.53	0.60	0.39	0.99	0.09
AHC/FAC	0.68	−0.35	−0.25	0.12	−0.98	−0.20
AEC/HUMC	−0.71	−0.14	0.04	0.44	−0.93	−0.36
AEC/TC	−0.50	0.72	−0.21	−0.29	0.99	0.01
AHN/FAN	0.79	−0.53	0.04	−0.12	−0.56	0.82
AEN/HUMN	−0.54	0.24	−0.10	0.78	0.10	−0.99
AEN/TN	−0.49	0.74	−0.17	−0.01	0.79	−0.62

Labile organic carbon (POXC), total carbon (TC), total nitrogen (TN), fulvic acid carbon (FAC), fulvic acid nitrogen (FAN), humic acid carbon (HAC), humic acid nitrogen (HAN), humin carbon (HUMC), humin nitrogen (HUMN), soil C/N ratio (C/N), Fulvic acid C/N ratio (FA-C/N), humic acid C/N ratio (AH-C/N), humin C/N ratio (HUM-C/N), alkaline extract carbon (AEC) and alkaline stratum nitrogen (AEN).

of −0.70 stand out (Table 6). PC2 explained 23.2 % of the variation in the data with positive eigenvector values above 0.70 for the FAN and AEC/TC variables. In this same dimension, the C/N and FA-C/N variables showed a negative correlation of −0.70 (Table 6).

A hierarchical grouping analysis was performed on the studied profiles using the same variables (Figure 5). Four distinct groups with approximately 80 % dissimilarity were formed by grouping the soil profiles according to the variables studied. The first cluster was made up of the OOstipicoX, OOylitico3, and OOylitico4 profiles and differed the most from the other groups formed. In this group, the OOstipicoX profile differed from the others in that the two grouped profiles had the same classification (OOylitico) and were more similar.

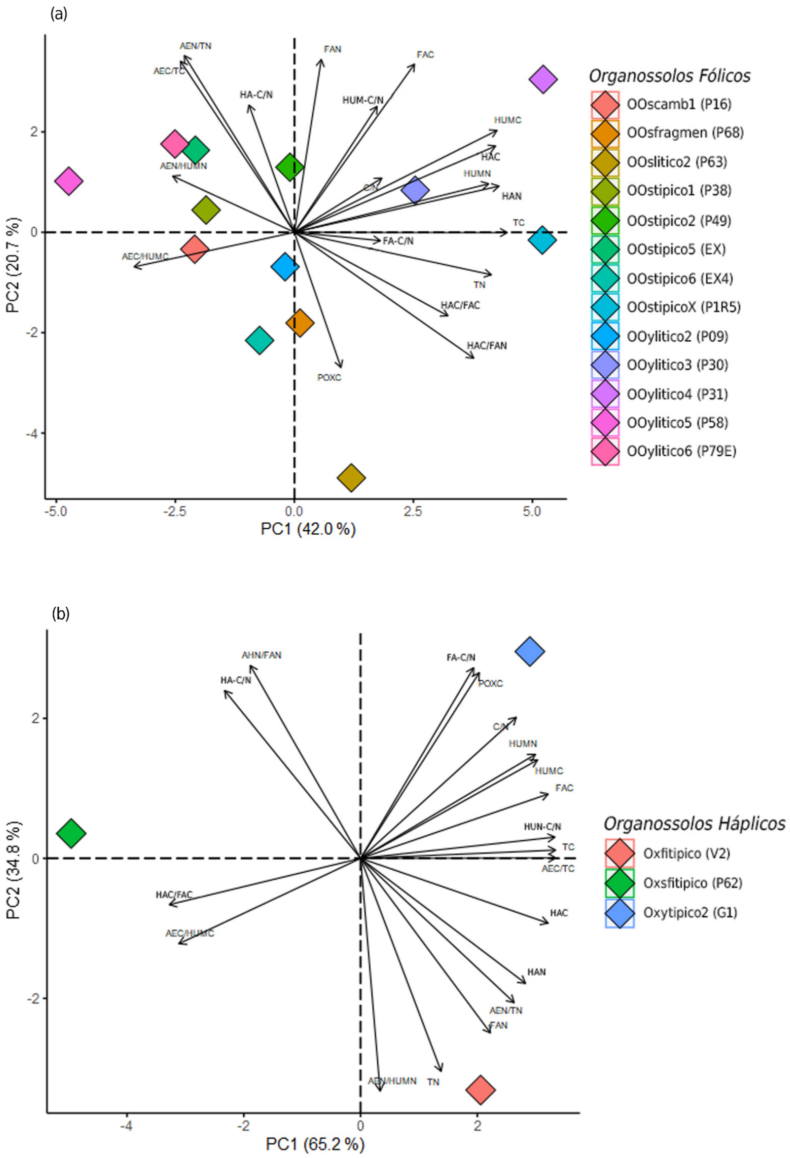

Figure 3. Principal component analysis of the variables labile carbon (POXC), total carbon (TC), total nitrogen (TN), fulvic acid carbon (FAC), fulvic acid nitrogen (FAN), humic acid carbon (HAC), humic acid nitrogen (HAN), humin carbon (HUMC), humin nitrogen (HUMN), soil C/N ratio (C/N), C/N ratio of fulvic acid (FA-C/N), C/N ratio of humic acid (HA-C/N), C/N ratio of humin (HUM-C/N) and ratio between the fractions HAC/FAC, AEC/HUMC, AEC/TC, HAN/FAN, AEN/HUMN, AEN/TN of soil profiles classified as *Organossolos Fólicos* (OO) (a) and Organossolos Háplicos (OX) (b), Itatiaia National Park in southeastern Brazil. OOscamb1: *Organossolos Fólicos Sápricos cambissólico*; OOsfragmen: *Organossolos Fólicos Sápricos fragmentários*; OOslitico: *Organossolos Fólicos Sápricos líticos*; OOstipico: *Organossolos Fólicos Sápricos típicos*; OOslitico: *Organossolos Fólicos Hêmicos líticos*; OXfitipico: *Organossolo Háplico Fíbrico típico*; OXstipico: *Organossolo Háplico Sáprico típico*; OXytipico: *Organossolo Háplico Hêmico típico*.

Table 6. Autovector values of the variables in the principal component analysis (PCA) of the *Organossolos Fólicos Sápricos* (OOs) *and Organossolos Fólicos Hêmicos* (OOy) for dimensions 1 and 2 (Dim1 and Dim2) found in the Itatiaia National Park

Variables	OOs				OOy			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
POXC	0.63	−0.35	0.10	0.57	−0.05	−0.31	0.79	0.53
TC	0.86	0.38	−0.14	0.30	0.99	−0.12	0.08	−0.03
TN	0.76	−0.36	0.20	0.48	0.99	0.08	0.10	0.01
FAC	−0.28	0.84	−0.10	0.12	0.97	0.17	0.04	0.15
FAN	−0.40	0.60	0.63	0.17	0.42	0.77	0.48	−0.06
AHC	0.67	0.66	0.16	0.16	0.95	0.25	-0.08	0.16
AHN	0.73	0.46	0.49	0.09	0.97	0.21	−0.07	0.05
HUMC	0.73	0.66	0.04	−0.20	0.95	0.28	−0.04	0.10
HUMN	0.83	−0.01	0.32	−0.43	0.90	0.42	−0.03	0.10
C/N	0.52	0.75	−0.34	0.02	−0.08	−0.96	−0.27	−0.01
FA-C/N	0.20	0.10	−0.90	−0.10	0.53	−0.78	−0.24	0.22
AH-C/N	−0.09	0.51	−0.62	0.13	−0.79	0.27	−0.09	0.55
HUM-C/N	0.12	0.92	−0.29	0.13	0.68	−0.69	0.24	0.08
AHC/FAC	0.81	−0.04	0.26	0.01	0.96	0.24	−0.13	0.05
AEC/HUMC	−0.72	−0.19	−0.10	0.62	−0.87	−0.33	−0.25	0.26
AEC/TC	−0.80	0.34	0.20	−0.37	−0.41	0.70	−0.49	0.31
AHN/FAN	0.92	−0.28	−0.11	−0.17	0.91	−0.32	−0.24	−0.04
AEN/HUMN	−0.69	0.41	0.22	0.57	−0.83	−0.05	0.54	−0.14
AEN/TN	−0.52	0.71	0.35	−0.29	−0.71	0.69	−0.13	−0.03

Labile organic carbon (POXC), total carbon (TC), total nitrogen (TN), fulvic acid carbon (FAC), fulvic acid nitrogen (FAN), humic acid carbon (HAC), humic acid nitrogen (HAN), humin carbon (HUMC), humin nitrogen (HUMN), soil C/N ratio (C/N), fulvic acid C/N ratio (FA-C/N), humic acid C/N ratio (AH-C/N), humin C/N ratio (HUM-C/N), alkaline extract carbon (AEC) and alkaline stratum nitrogen (AEN).

The second cluster comprised a single soil profile classified as OXtipico. Clusters three and four were the most similar. The third cluster was composed of the profiles OXfitipico, OOylitico5, OOylitico6, OOstipico1, OOstipico2, OOstipico5, and OOscamb1, and the fourth cluster was composed of the profiles OOslitico2, OXytipico2, OOsfragmen, OOstipico6, and OOylitico2.

Horizons were subjected to the proposed classification for validation, and data from the chemical (P, Na^+, K^+, Ca^{2+}, Al^{3+}, H+Al, CEC, CECef, and BS) and physical (SD) attributes of the established classes were compared. Of note was the K^+ attribute, which showed significant positive correlations with the TC (0.71), TN (0.50), FAC (0.65), HAC (0.71), HAN (0.67), HUMC (0.68), HUMN (0.54), AEC/HUMC (0.50), C/N (0.54), FA-C/N (0.50) and HUM-CN (0.61) attributes (Table 7). This indicated the humification process of the high montane *Organossolos* classes is directly related to the dynamics of exchangeable potassium in these soils, which may partly originate from the rocks that constitute the substrate of these soils (Table 1). For the H+Al and CEC variables, there were significant positive correlations with the carbon content of FAC (0.53), HAC (0.63), and HUMC (0.44 and 0.50, respectively), and with the nitrogen content of HAN (0.55). As for soil density (SD), there was a negative correlation of less than −0.50 with the variables FAC (−0.67), FAN (−0.50), HUMC (−0.61), HUMN (−0.50), %HUMC (−0.53) HUM-C/N (−0.63). The DS showed a positive correlation above 0.50 only with the AEC/HUMC variable (0.56) (Table 7).

Variables selected as attributes in classifying *Organossolos* were based on two criteria. The first variable was the AEC/TC ratio obtained through analysis of the PCAs and the clusters, and the HUM-C/N values were obtained through correlation with the chemical and physical attributes of the studied soils. The limits for each variable were determined based on their averages, with a value of 0.28, adopted for AEC/TC (Table 3) and a value of 13 for the HUM-C/N variable (Table 4).

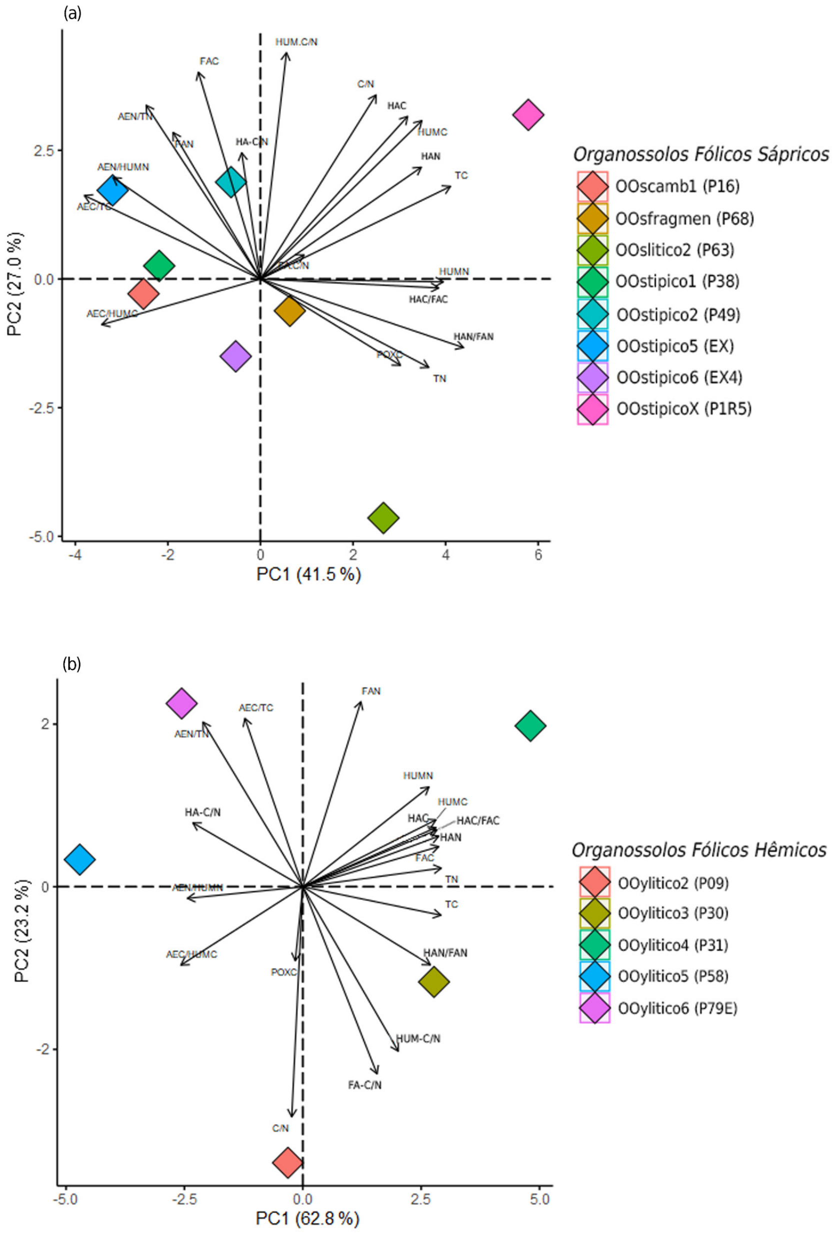

Figure 4. Principal component analysis of the variables labile carbon (POXC), total carbon (TC), total nitrogen (TN), fulvic acid carbon (FAC), fulvic acid nitrogen (FAN), humic acid carbon (HAC), humic acid nitrogen (HAN), humin carbon (HUMC), humin nitrogen (HUMN), soil C/N ratio (C/N), fulvic acid C/N ratio (FA-C/N), humic acid C/N ratio (HA-C/N), humin C/N ratio (HUM-C/N) and ratio between the HAC/FAC, AEC/HUMC, AEC/TC, HAN/FAN, AEN/HUMN, AEN/TN fractions of soil profiles classified as *Organossolos Fólicos Sápricos* (OOs) (a) and *Organossolos Fólicos Hêmicos* (OOy) (b), Itatiaia National Park in southeastern Brazil. OOscamb1: *Organossolos Fólicos Sápricos cambissólico*; OOsfragmen: *Organossolos Fólicos Sápricos fragmentários*; OOslitico: *Organossolos Fólicos Sápricos líticos*; OOstipico: Organossolos Fólicos Sápricos típicos; OOslitico: *Organossolos Fólicos Hêmicos líticos*; OXfitipico: *Organossolo Háplico Fíbrico típico*; OXstipico: *Organossolo Háplico Sáprico típico*; OXytipico: *Organossolo Háplico Hêmico típico*.

Only the chemical attributes associated with soil fertility pH, Mg, and SB were not selected for the validation process, as they did not show average correlation values ($-0.50 \geq r \geq 0.50$) with any of the variables associated with the chemical fractions of soil organic matter. Therefore, they were not used in the comparisons of soil attributes through the classes proposed by the AEC/TC ratio (obtained through PCA and cluster analysis) and the HUM-C/N values (obtained through the correlation analysis with the chemical and physical attributes of the studied *Organossolos*) (Table 8).

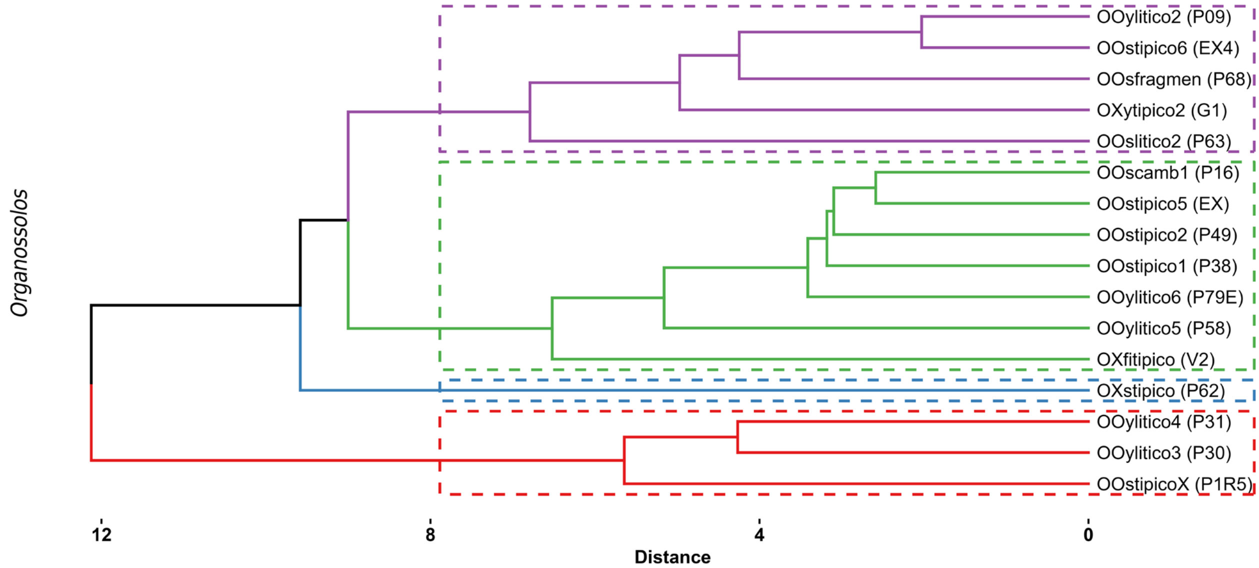

Figure 5. Cluster analysis of the *Organossolos* profiles observed in Itatiaia National Park according to the variables labile carbon (POXC), total carbon (TC), total nitrogen (TN), fulvic acid carbon (FAC), fulvic acid nitrogen (FAN), humic acid carbon (HAC), humic acid nitrogen (HAN), humin carbon (HUMC), humin nitrogen (HUMN), soil C/N ratio (C/N), fulvic acid C/N ratio (FA-C/N), humic acid C/N ratio (HA-C/N) and humin C/N ratio (HUM-C/N). OOscamb1: *Organossolos* Fólicos *Sápricos cambissólico*; OOsfragmen: *Organossolos Fólicos Sápricos fragmentários*; OOslitico: *Organossolos Fólicos Sápricos líticos*; OOstipico: *Organossolos Fólicos Sápricos típicos*; OOslitico: *Organossolos Fólicos Hêmicos líticos*; OXfitipico: *Organossolo Háplico Fíbrico típico*; OXstipico: *Organossolo Háplico Sáprico típico*; OXytipico: *Organossolo Háplico Hêmico típico*.

A significant difference was observed only for Ca^{2+}, with the highest levels observed in the alkaline-soluble and hypoalkaline-soluble class (Table 8). Between the proposed Mineralizable Humin and Mineralizable Hypo-Humin classes, there was a significant difference in the chemical attributes Na^+ and K^+, with higher levels in the Mineralizable Humin class and the physical attribute SD, with higher values in the Mineralizable Hypo-Humin class (Table 8).

DISCUSSION

Humic fractions and C/N ratios in *Organossolos*

Comparing the carbon contents quantified in the humic fractions in this study with those obtained by Valladares et al. (2016) for a profile classified as an *Organossolo Fólico Fíbrico típico* located in the southern region of the country in a pasture area, the authors quantified C contents in the humic fractions of 57.3 g kg^{-1} for FAF, 84.2 g kg^{-1} for FAH and 235.2 g kg^{-1} for HUM. In another study, when analyzing *Organossolos Mésicos* and *Háplicos* from different pedoenvironments in the South, Southeast, and Central-West regions of Brazil, Valladares et al. (2008a) found FA carbon values varying between 13 and 38 g kg^{-1} (average values of 17.8 g kg^{-1}); HA between 27 and 129 g kg^{-1} (average values of 68.8 g kg^{-1}); and HUM between 10 and 139 g kg^{-1} (average value of 64 g kg^{-1}). Carbon contents of all the *Organossolos* fractions in this study were lower than those found by Valladares et al. (2008a), but the average values of the profiles evaluated by the authors are similar to those observed for the humic fractions in this study (HUMC = 68.63 g kg^{-1}; followed by HAC = 26.92 g kg^{-1} and FAC = 17.88 g kg^{-1}) (Table 2). Carbon content of the fractions decreased in the following order (HUMC > HAC > FAC). This variation is due to the humification process in these soils, resulting in the HUM fraction being more resistant to transformation owing to its specific chemical characteristics (Piccolo et al., 2018).

Table 7. Pearson's correlation matrix between the organic fractions (quantitative and qualitative values) and the chemical and physical properties of *Organossolos* profiles in Itatiaia National Park

ATRI	POXC	TC	TN	FAC	FAN	AHC	AHN	HUMC	HUMN
pH(H_2O)	−0.10	0,3	0.10	0,12	0.16	0.10	0.17	0.30	0.24
P	−0.51*	−0.02	0.33	0.03	−0.25	0.14	0.20	0.14	0.44**
Na^+	0.05	0.59*	0.16	0.12	−0.03	0.50**	0.38	0.51*	0.33
K^+	−0.11	0.71*	0.50**	0.65*	0.20	0.71*	0.67*	0.68*	0.54*
Ca^{2+}	−0.07	0.50**	0.05	0.00	−0.23	0.21	0.14	0.21	0.02
Mg^{2+}	0.30	0.24	0.03	0.01	−0.16	−0.07	−0.10	0.07	0.02
Al^{3+}	0.35	0.64*	0.42	0.34	0.12	0.59*	0.51*	0.43**	0.25
H+Al	0.22	0.65*	0.61*	0.53*	0.07	0.63*	0.55*	0.44**	0.31
SB	0.13	0.59*	0.19	0.19	−0.14	0.28	0.22	0.37	0.20
CEC	0.22	0.68*	0.60*	0.53*	0.05	0.63*	0.55*	0.50**	0.31
CEC ef	0.33	0.66*	0.40	0.35	0.08	0.57*	0.50**	0.44**	0.25
BS	−0.12	0.11	−0.10	−0.25	−0.26	−0.19	−0.14	0.03	0.10
SD	−0.33	−0.43**	−0.34	−0.67*	−0.50**	−0.43**	−0.36	−0.61*	−0.50**

ATRI	AHC/ FAC	AEC/ HUMC	AEC/ TC	AHN/ FAN	AEN/ HUMN	AEN/ TN	C/N	FA-C/N	AH-C/N	HUM-C/N
pH(H_2O)	0.09	−0.29	−0.26	0.15	−0.02	0.08	0.37	0.08	−0.22	0.16
P	0.06	−0.20	0.00	0.38	−0.52*	−0.36	−0.50**	0.14	−0.22	−0.42
Na^+	0.27	−0.41	−0.15	0.43**	−0.20	0.04	0.73*	0.12	0.14	0.50**
K^+	−0.16	−0.50**	0.06	0.34	−0.14	0.04	0.54*	0.50**	−0.08	0.61*
Ca^{2+}	0.05	−0.16	−0.31	0.32	−0.17	−0.16	0.61*	0.26	0.21	0.35
Mg^{2+}	−0.05	−0.20	−0.21	0.22	−0.17	−0.11	0.35	0.19	0.09	0.15
Al^{3+}	0.07	−0.14	−0.06	0.26	0.05	−0.01	0.51*	0.15	0.14	0.53*
H+Al	−0.08	−0.13	−0.01	0.31	−0.02	−0.19	0.27	0.36	0.02	0.50*
SB	−0.02	−0.36	−0.25	0.41	−0.23	−0.11	0.69*	0.35	0.13	0.50**
CEC	−0.08	−0.15	−0.03	0.34	−0.04	−0.19	0.32	0.38	0.03	0.52*
CEC ef	0.04	−0.18	−0.09	0.29	0.00	−0.03	0.56*	0.21	0.15	0.54*
BS	0.09	−0.31	−0.31	0.33	−0.35	−0.12	0.29	0.07	−0.03	−0.12
SD	0.27	0.56*	−0.18	0.06	−0.01	−0.24	−0.29	−0.30	−0.03	−0.63*

ATRI	%FAC	%AHC	%HUMC	%HC	%HNC	%FAN	%AHN	%HUMN	%SN	%HNN
pH(H_2O)	−0.21	−0.25	0.10	−0.02	0.02	0.02	0.16	0.19	0.17	−0.17
P	−0.05	0.08	0.13	0.09	−0.09	−0.36	−0.21	0.20	0.06	−0.06
Na^+	−0.26	0.04	0.16	0.06	−0.06	−0.12	0.39	0.25	0.22	−0.22
K^+	−0.01	0.12	0.26	0.20	−0.20	−0.11	0.42**	0.19	0.17	−0.17
Ca^{2+}	−0.22	−0.32	−0.14	−0.21	0.21	−0.22	0.01	0.00	−0.05	0.05
Mg^{2+}	−0.09	−0.36	−0.07	−0.13	0.13	−0.11	−0.07	0.02	−0.02	0.02
Al^{3+}	−0.13	0.02	0.01	−0.02	0.02	−0.12	0.24	−0.05	−0.04	0.04
H+Al	−0.11	0.09	0.00	−0.01	0.01	−0.29	0.15	−0.17	−0.20	0.20
SB	−0.17	−0.31	−0.01	−0.10	0.10	−0.19	0.12	0.10	0.05	−0.05
CEC	−0.12	0.06	0.00	−0.02	0.02	−0.30	0.16	−0.16	−0.19	0.19
CEC ef	−0.13	−0.04	0.01	−0.03	0.03	−0.14	0.22	−0.03	−0.04	0.04
BS	−0.17	−0.42	−0.04	−0.14	0.14	−0.11	−0.12	0.22	0.14	−0.14
SD	−0.13	−0.19	−0.53*	−0.43**	0.43**	−0.18	−0.31	−0.34	−0.35	0.35

Values in bold: mean correlation (−0.50≥ r ≥0.50). (*) Significant at 5 %. (**) Significant at 10. pH, active acidity; P, available phosphorus; Na^+, exchangeable sodium; K^+, exchangeable potassium; Ca^{2+}, exchangeable calcium; Mg^{2+}, exchangeable magnesium; Al^{3+}, exchangeable aluminum; H+Al, potential acidity; SB, base sum; CEC, cation exchange capacity at pH 7.0; CECef, effective cation exchange capacity; BS, Base saturation; and SD, soil density, HAC: humic acid carbon; FAC: fulvic acid carbon; AEC: alkaline extract carbon (HAC+AFC); HUMC: humin carbon; TC: total carbon; HAN: humic acid nitrogen; FAN: fulvic acid nitrogen; AEN: alkaline extract nitrogen (HAN+FAN); HUMN: humin nitrogen; TN: total nitrogen; C/N: soil carbon and nitrogen ratio; FA-C/N: ratio of carbon to nitrogen in the fulvic acid fraction; HA-C/N: ratio of carbon to nitrogen in the humic acid fraction; HUM-C/N: ratio of carbon to nitrogen in the humin fraction; %NHC: percentage of non-humified carbon; %FAC: percentage of carbon in the fulvic acid fraction; %HAC: percentage of carbon in the humic acid fraction; %HUMC: percentage of humin carbon; %NHN: percentage of non-humified nitrogen; %FAN: percentage of fulvic acid fraction nitrogen; %HAN: percentage of humic acid fraction nitrogen; and %HUMN: percentage of humin fraction nitrogen.

Table 8. Comparisons of soil attributes based on the classification proposed by the AEC/TC ratio and HUM-C/N values for the *Organossolos* of Itatiaia National Park

Attributes	Alkaline-soluble (n = 09)	Hypoalkaline-soluble (n = 07)
P (mg dm^{-3}) (1)	8.03 a	9.57 a
Na^+ ($cmol_c$ dm^{-3}) (2)	0.07 a	0.09 a
K^+ ($cmol_c$ dm^{-3}) (2)	0.24 a	0.28 a
Ca^{2+} ($cmol_c$ dm^{-3}) (1)	0.15 b	0.34 a
Al^{3+} ($cmol_c$ dm^{-3}) (1)	3.44 a	4.22 a
H+Al ($cmol_c$ dm^{-3}) (1)	19.66 a	22.58 a
SB ($cmol_c$ dm^{-3}) (1)	1.04 a	1.48 a
CEC ($cmol_c$ dm^{-3}) (1)	20.71 a	24.06 a
CEC ef ($cmol_c$ dm^{-3}) (1)	4.49 a	5.62 a
SD (Mg m^{-3}) (1)	0.42 a	0.47 a
Attributes	**Mineralizable Humin (n = 08)**	**Mineralizable Hypo-Humin (n = 08)**
P (mg dm^{-3}) (1)	8.38 a	9.03 a
Na^+ ($cmol_c$ dm^{-3}) (2)	0.09 a	0.05 b
K^+ ($cmol_c$ dm^{-3}) (1)	0.34 a	0.17 b
Ca^{2+} ($cmol_c$ dm^{-3}) (2)	0.24 a	0.23 a
Al^{3+} ($cmol_c$ dm^{-3}) (1)	4.32 a	3.25 a
H+Al ($cmol_c$ dm^{-3}) (1)	22.38 a	19.49 a
SB ($cmol_c$ dm^{-3}) (2)	1.37 a	1.12 a
CEC ($cmol_c$ dm^{-3}) (1)	23.74 a	20.61 a
CECef ($cmol_c$ dm^{-3}) (1)	5.60 a	4.37 a
SD (Mg m^{-3}) (1)	0.36 b	0.53 a

Means with the same lowercase letter do not differ between the soil classes proposed for the fifth categorical level. (1) ANOVA without data transformations at 10 % probability; and (2) ANOVA with data transformations at 10% probability. (3) Kruskal-Wallis test + Fisher's least significant difference (LSD) with Bonferroni correction. P: available phosphorus; Na^+: exchangeable sodium; K^+: exchangeable potassium; Ca^{2+}: exchangeable calcium; Al^{3+}: exchangeable aluminum; H+Al: potential acidity; SB: base sum; CEC: cation exchange capacity at pH 7.0; CECef: effective cation exchange capacity; and SD: soil density.

In general, the percentages of carbon and nitrogen in the humic fractions demonstrated the importance of these fractions for total soil carbon and reducing CO_2 emissions. Soil labile carbon (POXC) is a soil carbon component with the greatest oxidation potential and can therefore be converted into CO_2. The *Organossolos* in this study indicated that, on average, 1.49 g kg^{-1} of these soils can be transformed into CO_2 owing to rapid oxidation (Table 5). The quantified levels of POXC indicated that these soils require greater attention in terms of environmental preservation, as this fraction of SOM can be oxidized and lost in the form of CO_2 because of its high solubility. POXC is a good predictor of SOM stabilization compared with other soil carbon fractions (Hurisso et al., 2016). Culman et al. (2012) suggested that POXC reflects a more processed and stabilized compartment of labile carbon in the soil.

In a study conducted by Silva et al. (2009), the C/N ratio was obtained for the first 0.20 m of three soil profiles under different drainage conditions (P1, moderate drainage; P2 and P4, poor drainage) in peatland areas in southern Brazil. The C/N ratios were 35 for P1, 25 for P2 and 13 for P3. The C/N ratio of P2 was similar to that obtained for the OOstipicoX profile, which was the highest value observed among the profiles evaluated; however, unlike the profiles studied by Silva et al. (2009), this profile had good drainage. The profiles found in the poor drainage situation (OX) in this study had a soil C/N ratio similar to that observed in P3 by Silva et al. (2009).

Evaluating the morphological, physical, and chemical attributes of Organossolos and soils with high MOS content, Valladares et al. (2008b) found these soils had an average C/N ratio of 19.9. The authors found a negative correlation between the C/N ratio of the soil and the pH of the water. These values are similar to those found in the present study (Table 4).

Humic indexes and the classification of *Organossolos*

Humic fractions of SOM and the humic indices obtained can be used to assess the degree of transformation. The ratio of the C content of humic acids to that of fulvic acids (HAC/FAC) indicated the mobility of carbon in the soil (Benites et al., 2003). The higher the ratio, the greater the selective loss of the FA fraction, which is the most soluble fraction. The ratio between the alkaline extract (EA = FAC + HAC), which is composed of FAC and HAC, and humin (EA/HUM) represents the illumination of SOM or stable SOM (Benites et al., 2003). For surface soil horizons, the values of this ratio are usually not higher than 1. Values equal to 0.5 indicate high SOM stability, possibly due to interaction with the mineral fraction of the soil (Benites et al., 2003). High ratio values (close to 2.0) indicated the movement of more labile fractions within the profile.

The classification suggestions for the 4th categorical level proposed by Fontana et al. (2008b) and Valladares et al. (2003) adopt the C content of the FA fractions (= 20.0 g kg^{-1}: *hipofúlvico*; > 20.0 g kg^{-1}: *fúlvico*) and HA (= 90.0 g kg^{-1}: *hipohúmico*; > 90.0 g kg^{-1}: *húmico*) and the index obtained from the AEC/HUM ratio (= 1.0: *hipoalcalino-solúvel*; > 1.0 *alcalino-solúvel*). Fontana et al. (2011) suggested using the HAC/FAC ratio for both the O and H horizons to classify soil profiles into lower hierarchical levels.

The ratio between the alkaline extract carbon (FAC + HAC) and total soil carbon indicated the amount of carbon in the most functionalized form in the soil. According to the cluster analysis, the value of the index obtained between the alkaline extract and total carbon (AEC/TC) was one of the variables that allowed distinct groups to be separated. A value below 0.28 indicates that less than 28 % of soil carbon is in the form of AH and AF. Based on the classification proposals suggested by Fontana et al. (2008b) and Valladares et al. (2003), the terms hipoalcalino-solúvel (< 0.28) and alcalino-solúvel (≥ 0.28) can be used to classify the *Organossolos* studied. Humic substances were separated by adding an alkaline solution (sodium hydroxide or sodium pyrophosphate) to the sample, resulting in an insoluble residue called humin and an alkaline solution containing FA and HA. Quantification of the carbon in this alkaline solution and the carbon in the soil is sufficient to determine this attribute for characterizing humic substances in the soil.

The use of the C/N ratio of the humin fraction (HUM-C/N) proved to be efficient in classifying *Organossolos* profiles found in the upper part of the INP. Humin is a highly decomposed stable soil organic matter (SOM) fraction. In general, many nitrogenous compounds are mineralized during the decomposition process, which can result in a higher carbon-to-nitrogen ratio in humin. It should be noted that the values for the ratio between C and N in humin obtained in this study were low, which may be associated with the conditions in which these soils were found. The studied *Organossolos* were found in altomontane environments influenced by low temperatures and covered by high-altitude grasslands. This vegetation provides a constant influx of fresh material into the system, and the low temperatures inhibit decomposition by microorganisms.

The HUM-C/N variable correlated significantly with most of the chemical and physical attributes evaluated. The use of variables related to the use and management of soil is encouraged to classify lower hierarchical levels in the SiBCS. As mentioned, these soils are under natural conditions and have, therefore, never been managed, but the influence of Na^+, K^+, Al^{3+}, H+Al, SB, CEC, CECef, and SD on the ratio between carbon and nitrogen in the humin fraction can be observed.

When comparing the soil attributes based on the proposed classifications (Table 7) for the AEC/CT variable, the Ca^{2+} attribute was the only one that allowed differentiation between the soil classes proposed for this variable. When comparing the soil attributes with the HUM-C/N variable, Na^{+} and K^{+} showed significant differences, allowing for differentiation between the proposed classes. Humic substances contain functional groups, such as carboxylic and phenolic acids, which can bind to metal ions, such as the elements mentioned (Yang et al., 2021). Calcium forms more stable complexes with humic substances due to its high electrostatic charge, whereas sodium and potassium form fewer stable bonds. In addition, humic substances can represent a large reservoir of these nutrients for plants, which is why the natural system in which the studied *Organossolos* are found has been maintained over time (Crawford, 2021).

Moreover, for the HUM-C/N variable, soil density could be a physical attribute allowing differentiation between the proposed classes. The relationships between humin, carbon, nitrogen, and soil density are associated with the quantities of SOM observed and the conditions under which this organic material is found. As mentioned above, the highest amount of carbon was observed in the humin fraction, which may directly affect soil density and the importance of this variable for soil classification.

Therefore, a new classification proposal for the fifth categorical level of the studied *Organossolos* is presented in table 9. The adoption of these indices can indicate the functionality and quantity of humic substances present in *Organossolos* and simplify practical methods of quantification. In addition, the use of total soil carbon in relation to the C content of the alkaline extract can be useful in classifying organic soils that have material with the presence of carbon in their mineral matrix.

Table 9. Proposed classification for the fifth categorical level of *Organossolos* according to the Brazilian Soil Classification System, based on the groups obtained from the Cluster analysis and the relationship between the alkaline extract of humic substances and total soil carbon

SiBCS	HUM-C/N	AEC/ TC	Suggested classification
			Group 1
OOylitico2	15	0.25	*Organossolo Fólico Hêmico lítico hipoalcalino-solúvel humina-mineralizável*
OOstipico6	13	0.22	*Organossolo Fólico Sáprico típico hipoalcalino-solúvel hipohumina-mineralizável*
OOsfragmen	13	0.23	*Organossolo Fólico Sáprico fragmentário hipoalcalino-solúvel hipohumina-mineralizável*
OXytipico2	15	0.31	*Organossolo Háplico Hêmico típico alcalino-solúvel humina-mineralizável*
OOslitico2	8	0.21	*Organossolo Fólico Sáprico lítico hipoalcalino-solúvel hipohumina-mineralizável*
			Group 2
OOscamb1	11	0.28	*Organossolo Fólico Sáprico cambissólico alcalino-solúvel hipohumina-mineralizável*
OOstipico5	14	0.36	*Organossolo Fólico Sáprico típico alcalino-solúvel humina-mineralizável*
OOstipico2	14	0.30	*Organossolo Fólico Sáprico típico alcalino-solúvel humina-mineralizável*
OOstipico1	13	0.35	*Organossolo Fólico Sáprico típico alcalino-solúvel hipohumina-mineralizável*
OOylitico5	12	0.38	*Organossolo Fólico Hêmico lítico alcalino-solúvel hipohumina-mineralizável*
OOylitico6	12	0.32	*Organossolo Fólico Hêmico lítico alcalino-solúvel hipohumina-mineralizável*
OXfitipico	14	0.30	*Organossolo Háplico Fíbrico típico alcalino-solúvel humina-mineralizável*
			Group 3
OXstipico	8	0.15	*Organossolo Háplico Sáprico típico hipoalcalino-solúvel hipohumina-mineralizável*
			Group 4
OOylitico4	14	0.34	*Organossolo Fólico Hêmico lítico alcalino-solúvel humina-mineralizável*
OOylitico3	14	0.26	*Organossolo Fólico Hêmico lítico hipoalcalino-solúvel humina-mineralizável*
OOstipicoX	15	0.20	*Organossolo Fólico Sáprico típico hipoalcalino-solúvel humina-mineralizável*

OOscamb1: *Organossolos Fólicos Sápricos cambissólico*; OOsfragmen: *Organossolos Fólicos Sápricos fragmentários*; OOslitico: *Organossolos Fólicos Sápricos líticos*; OOstipico: *Organossolos Fólicos Sápricos típicos*; OOslitico: *Organossolos Fólicos Hêmicos líticos*; OXfitipico: *Organossolo Háplico Fíbrico típico*; OXstipico : *Organossolo Háplico Sáprico típico*; OXytipico: *Organossolo Háplico Hêmico típico*.

CONCLUSIONS

Labile organic carbon contents showed a small range of variation between the profiles, with the low levels of oxidizable carbon in *Organossolo Fólico Hêmico lítico* 3 (0.87 g kg^{-1}) and the highest values in *Organossolo Háplico Hêmico típico* 2 (2.22 g kg^{-1}) standing out. Total carbon and total nitrogen contents of the soil and humic fractions varied widely variation in values, especially in the *Organossolo Fólico Hêmico lítico* profile. The highest C and N contents in the humic fractions were also quantified in the *Organossolo Fólico Hêmico* lítico profile and the lowest in the *Organossolo Háplico Sáprico típico* profile.

The indexes of the ratios between the carbon and nitrogen of humic acids and fulvic acids (averages of HAC/FAC = 1.61 and HAN/FAN = 1.05), carbon and nitrogen of the alkaline extract and humin (averages of AEC/HUMC = 0.71 and AEN/HUMN = 0.38), carbon and nitrogen of the alkaline extract and total carbon and total nitrogen (averages of AEC/TC = 0.28 and AEN/TN = 0.19) obtained from the fractionation of soil organic matter were efficient in assessing the degree of humification of the *Organossolos* profiles.

There was a decreasing pattern for the values of the stoichiometric ratios of carbon and nitrogen in the soil and humic fractions: HA-C/N > FA-C/N > C/N ≥ HUM-C/N. Except for the profiles of *Organossolo Háplico Fíbrico típico* and *Organossolo Háplico Sáprico típico*.

A differential characteristic in the fifth categorical level for the *Organossolos* order is the use of the ratio between alkaline extract carbon and total soil carbon: hipoalcalino-solúvel (AEC/TC < 0.28) and alcalino-solúvel (AEC/TC ≥ 0.28), as well as the ratio between carbon and nitrogen in the humin fraction: hipohumina-mineralizável (HUM-C/N ≤ 13) and humina-mineralizável (HUM-C/N > 13).

DATA AVAILABILITY

The data will be provided upon request.

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