

Humic Substance Fractions and Attributes of Histosols and Related High-Organic-Matter Soils from Brazil

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Abstract: Knowledge of the distribution of soil organic matter (SOM) fractions is important in managing soils toward a sustainable agricultural system in a tropical environment. However, data on Histosols is limited. This study developed 19 profiles of Histosols and soils with high organic-matter content from different regions of Brazil. Soil organic matter was fractionated into fulvic acids (FAF), humic acids (HAF), and humin (HUM). The ratios HAF/FAF and AE (alkaline extract)/HUM were calculated. The objectives were to evaluate the method for SOM fractionating in Histosols and related soils and to correlate the distribution of organic fractions with other soil attributes. The humic fractions presented significant

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correlations with other soil attributes, the best being the correlation between FAF and nutrient level. The HAF and HUM presented high correlation with cationic exchange capacity, active acidity (H^+) and pH. Humin and the alkaline extract absorbance measured at 380 nm and 465 nm and presented good correlation with total organic carbon.

Keywords: Organic matter, peat soils, soil chemical properties, tropical soils

INTRODUCTION

The central concept of Histosols is that of soils forming from organic soil materials. Thus, the development of methods for organic matter characterization is more important than for mineral soils. The different humic fractions, which are higher in the Histosols soil order because of its predominantly organic nature, should be characterized to estimate the soil inherent tendency to mineralization and susceptibility to subsidence and loss of soluble organic matter. In tropical climates, the approach of fractionating humic substances in Histosols and relating them to soil attributes is even more relevant to sustainable agriculture.

The definition of humic substances (HS) is not simple and reflects the organic matter complexity. Humic substances may be defined as a series of yellow-brown and black polymers of relatively high molecular weight and formed by secondary, biotic, and abiotic synthesis reactions (Stevenson 1994). However, as explained by MacCarthy (2001), because of the uncertain aspect of this and other HS definitions, it is also usual to define these materials operationally in terms of laboratory procedures used to extract them from soils, sediments, and waters. The classic procedure to extract humic substances from soils results in three main fractions: humic acids (HAF), fulvic acids (FAF), and humin compounds (HUM). These fractions are defined in terms of their solubility in aqueous medium depending on the pH of the extracting solution (Schnitzer and Khan 1978; Tombácz and Meleg 1990). The alkaline solutions, most often 0.1 mol L^{-1} NaOH, extract HAF and FAF from soil, leaving the HUM associated to the mineral phase. The acidification of the black-colored alkaline extract results in the HAF coagulation (black or brownish precipitate), whereas the FAF remains soluble (yellow-brownish solution). Although this separation procedure seems artificial, some segregation degree of polymeric materials with different chemical properties is achieved (McBride 1994).

None of the soil organic matter fractions isolated represent separation of individual compounds but rather a mixture of heterogeneous compounds with similar chemical behavior. The humic substances play an important role in the flow of nutrients in ecological systems, in carbon (C) emission into the atmosphere, and in interactions with heavy metals and pesticides, where

each fraction plays a role in the mechanisms (Ferreira et al. 2002; Jones and Huang 2003; Lal 2004)

Because of the different functions performed by the humic fractions and the differentiated characteristics of Histosols and related soils with high organic-matter content, these attributes should be better studied in these soils. Knowledge about soil organic-matter fractions is important to manage the chemical and physical properties toward a sustainable agricultural system, especially in a tropical environment.

The objectives of this study were to evaluate organic-matter fractionation method in humic substances applied to Histosols and related soils with high organic-matter content, and to correlate the humic fraction distribution and ratios with some attributes of these soils.

MATERIAL AND METHODS

Nineteen soil profiles from different Brazilian edafoclimatic regions (Table 1) were collected, being 17 profiles of Histosols, one Inceptisol, and one Entisol profile, the last two having high-organic-matter content in the surface horizons. The soils were collected, described, and characterized according to procedures in the *Manual for Soil Description and Collecting* (Lemos and Santos 1996) and the *Soil Survey Manual* (Soil Survey Division Staff 1993). The profiles were classified according to the Brazilian soil classification system, SiBCS (Embrapa 1999) and the soil taxonomy system (Soil Survey Staff 1999) (Table 1).

The soil chemical and physical properties were analyzed according to Embrapa (1997, 1999). The humic substances fractionating was performed in triplicates in 53 horizon samples from 19 soil profiles (Table 2), according to differential solubility techniques, using the humic fractions concept established by the Humic Substances International Society, as adapted by Benites, Madari and Machado (2003). Soil samples containing about 40 mg of C (in the Histosols, the values ranged from 0.1 to 0.5 g of soil sample) and 25 mL of 0.1 mol L⁻¹ NaOH were used in the extraction of HAF and FAF, with a contact time of 24 h. The separation between the alkaline extract and the residue was performed by centrifugation at 10,000 g (gravity) for 20 min. Two residue washings were carried out with 19 mL of the same solution by adding the extracts previously reserved that resulted in a final volume of approximately 45 mL. The residue was collected and reserved for the determination of carbon as humin compounds (HUM). The alkaline extract (AE) had the pH lowered to 2.0 ± 0.1 with 20% sulfuric acid (H₂SO₄) and decanted for 18 h. The H₂SO₄ solution was used instead of hydrochloric acid (HCl) to avoid interference from the chloride anion in the C-determination procedure by the titulometric method with dichromate. The precipitate, HAF, was separated from the soluble fraction by means of centrifugation at 3,000 g (gravity) for 5 min, rediluted in 0.1 mol L⁻¹

sodium hydroxide (NaOH) solution, and the volume was taken to 50 mL. The soluble portion in the acidified extract, fulvic acid fraction (FAF), had the volume also adjusted to 50 mL using distilled water.

The C determination in the HAF and FAF extract was performed according to the method of Yeomans and Bremner (1998) using 1 to 5 mL of extract, 1 mL of 0.2 mol_c L⁻¹ potassium dichromate (K₂Cr₂O₇), and 5 mL of concentrated H₂SO₄. The K₂Cr₂O₇ concentrations were adjusted so that 10 to 75% of the oxidizer was consumed in the reaction, thus maintaining the titration within the correlation linear range with C content (Nelson and Sommers 1982). Carbon content was computed by the following equation:

$$\text{g C kg}^{-1} \text{ soil} = \frac{(\text{mmol}_c \text{L}^{-1} \text{Cr}_2\text{O}_7^{2-} - \text{mmol}_c \text{Fe}^{2+}) 0.03.100}{\text{mass of sample (g)}}$$

The HAF/FAF ratio as the soluble fractions in the alkaline extract (AE = fulvic acid fraction + humic acid) and the humin compounds (AE/HUM) were then calculated. The total C (C_CHN) and total N were determined by dry combustion of soil samples with 5.0 mg (± 0.1 mg). A Perkin Elmer 2400 C-H-N-S elemental analyzer was used as the reference method.

To obtain optical absorbance values of the alkaline extracts, soil samples containing 100 mg of organic C were weighed and set in contact with 100 mL of 0.1 mol L⁻¹ NaOH solution for 24 h. After that, the soil suspension was filtered and the extract diluted in the proportion of 1:5 with distilled water. The color of the solution was read in a colorimeter at wavelengths of 380, 465, and 665 nm.

The bulk density was calculated from the weight of the oven-dry mass and volume of the soil core. For chemical analyses, samples of the fine earth (soil < 2 mm) were extracted with 1 mol L⁻¹ potassium chloride (KCl) for calcium (Ca²⁺), magnesium (Mg²⁺), and aluminum (Al³⁺), with 0.05 mol L⁻¹ HCl and 0.0125 mol L⁻¹ H₂SO₄ for potassium (K⁺) and sodium (Na⁺), and with pH 7 0.05 mol L⁻¹ calcium acetate [Ca(OAc)₂] for extractable acidity (H⁺ + Al³⁺). Extractable H⁺ was calculated by subtracting the tritiated Al from extractable acidity. The pH in water, 1 mol L⁻¹ KCl, and 0.01 mol L⁻¹ CaCl₂ were analyzed in a 1:2.5 soil/water solution. Cation exchange capacity (CEC) was calculated from the sum of base cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) plus extractable acidity. To determine mineral content, samples were ashed at 400°C (Embrapa 1999).

Statistical Analyses

The humic fraction C content and its percentile in relation to C_CHN were compared to each other and to the other forms of C using the Pearson correlation method. The relationship between the humic fractions and some soil attributes was evaluated by Pearson correlation and linear regression analyses.

Table 1. Location, classification,^a and altitude of soil profiles from Brazil

Profile code	Location	Classification		Altitude (m)
		SiBCS	Soil taxonomy	
AL1	Jequiá da Praia, AL	Organossolo Tiomórfico Fábrico térreo	Terric Sulfohemists	3
AL2	Coruripe, AL	Organossolo Tiomórfico Hêmico típico	Typic Sulfohemists	5
BA2	Ituberá, BA	Organossolo Tiomórfico Hêmico térreo	Typic Sulfohemists	5
BA3	Arraial D'Ajuda, BA	Organossolo Tiomórfico Hêmico típico	Typic Sulfohemists	7
DF1	Guará II, DF	Organossolo Méstico Sáprico típico	Typic Haplosaprists	800
ES1	Mimoso do Sul, ES	Organossolo Méstico Hêmico típico	Hydric Haplohemists	15
MG1	Juiz de Fora, MG	Organossolo Méstico Hêmico típico	Fluvaquentic Haplohemists	874
MG2	Coronel Pacheco, MG	Organossolo Méstico Hêmico térreo	Hydric Haplohemists	432
MS2	Porto Morumbi, MS	Organossolo Tiomórfico Sáprico térreo	Terric Haplosaprists	280
PR2	Tijucas do Sul, PR	Organossolo Méstico Sáprico típico	Typic Haplosaprists	850
PR3	Serra da Baitaca, PR	Neossolo Litólico Hístico típico	Lithic Udifolists	1330
RJ1	Parque Nacional de Itatiaia, RJ/MG	Cambissolo Húmico Distrófico típico	Humic Pachic Dystrudepts	1700
RJ3	São José da Boa Morte, RJ	Organossolo Háplico Hêmico térreo	Hydric Haplohemists	40
RJ4	Nova Friburgo, RJ	Organossolo Méstico Sáprico térreo	Humaqueptic Endoaquents	800
RS3	Cambará do Sul, RS	Organossolo Méstico Sáprico térreo	Terric Haplosaprists	890
RS4	Viamão, RS	Organossolo Tiomórfico Sáprico típico	Typic Sulfosaprists	20
RS5	Viamão, RS	Organossolo Tiomórfico Sáprico típico	Typic Sulfosaprists	20
SC2	Governador Celso Portela, SC	Organossolo Tiomórfico Hêmico típico	Typic Sulfohemists	10
SP1	Taubaté, SP	Organossolo Méstico Sáprico térreo	Terric Haplosaprists	500

^aSiBCS (Embrapa 1999); soil taxonomy (Soil Survey Staff 1999).

Table 2. Carbon content^a in the fraction fulvic acid (FAF), humic acid (HAF), humin (HUM), and sum of organic matter fractions, expressed as a function of soil weight and total^b organic carbon (C_CHN), and ratios of HAF/FAF and alkaline extract (AE = FAF + HAF)/HUM

Profile/ horizons	FAF (g C kg ⁻¹ soil)		HAF (g C kg ⁻¹ soil)		HUM (g C kg ⁻¹ soil)		SUM (g C kg ⁻¹ soil)		C_CHN (g C kg ⁻¹ soil)		HUM (%)		SUM (%)		HAF/ FAF		EA/ HUM	
AL1 Hip1	39.3 (6)		88.5 (17)		172.7 (11)		300.6		357.8		11	25	48	84	2.25	0.74		
AL1 Hip2	10.3 (10)		27.7 (6)		46.5 (9)		84.4		110.4		9	25	42	77	2.69	0.82		
AL2 Haij1	23.9 (3)		131.0 (1)		156.3 (16)		311.2		305.8		8	43	51	102	5.48	0.99		
AL2 Haij1	24.3 (29)		193.8 (11)		225.6 (14)		443.7		508.1		5	38	44	87	7.99	0.97		
AL2 Haij2	21.2 (15)		139.7 (4)		232.7 (15)		393.6		454.7		5	31	51	87	6.58	0.69		
AL2 Hij	9.2 (10)		22.0 (35)		79.2 (13)		110.4		120.7		8	18	66	91	2.41	0.39		
BA2 Haij1	23.2 (14)		185.7 (9)		252.8 (7)		461.7		525.3		4	35	48	88	8.01	0.83		
BA2 Haij1	23.8 (1)		188.8 (2)		267.2 (2)		479.8		528.5		5	36	51	91	7.93	0.80		
BA2 Haij2	16.7 (17)		189.5 (3)		175.8 (24)		381.9		369.9		5	51	48	103	11.37	1.17		
BA3 Haij1	36.5 (17)		159.5 (5)		184.3 (19)		380.3		387.6		9	41	48	98	4.37	1.06		
BA3 Haij2	16.2 (29)		198.9 (10)		281.1 (6)		496.2		555.4		3	36	51	89	12.31	0.77		
BA3 Haij	16.6 (23)		208.4 (13)		247.2 (6)		472.2		508.3		3	41	49	93	12.52	0.91		
DF1 Hap	11.8 (8)		37.8 (13)		38.6 (7)		88.2		101.7		12	37	38	87	3.21	1.29		
DF1 Ha1	16.3 (6)		67.3 (7)		43.5 (4)		127.1		132.4		12	51	33	96	4.14	1.92		
DF1 Ha2	17.8 (11)		119.4 (27)		35.1 (14)		172.3		196.6		9	61	18	88	6.69	3.91		
ES1 Hap1	19.1 (22)		47.0 (13)		88.0 (13)		154.0		179.8		11	26	49	86	2.46	0.75		
ES1 Hap2	20.1 (13)		53.0 (15)		97.7 (3)		170.7		157.7		13	34	62	108	2.63	0.75		
ES1 Hai	29.3 (12)		84.8 (5)		113.8 (9)		227.9		227.7		13	37	50	100	2.89	1.00		
MG1 Hai	40.0 (5)		65.9 (12)		147.4 (6)		253.4		279.0		14	24	53	91	1.65	0.72		
MG1 Ha	34.7 (4)		142.9 (0)		159.6 (4)		337.2		366.7		9	39	44	92	4.12	1.11		
MG2 Hai1	14.0 (1)		45.1 (21)		61.1 (3)		120.2		114.8		12	39	53	105	3.22	0.97		
MG2 Hai2	11.9 (18)		68.5 (10)		105.7 (6)		186.1		206.4		6	33	51	90	5.77	0.76		

MS2 Hao	20.2 (5)	52.3 (2)	41.4 (2)	114.0	121.1	17	43	34	94	2.58	1.75
MS2 2Ha	7.3 (28)	99.4 (4)	79.6 (4)	186.3	189.3	4	53	42	98	13.66	1.34
PR2 Hap1	13.1 (8)	89.5 (6)	36.5 (3)	139.2	144.1	9	62	25	97	6.81	2.81
PR2 Hap2	10.0 (8)	143.4 (10)	30.7 (8)	184.1	192.8	5	74	16	95	14.41	5.00
PR2 Hap3	21.0 (29)	153.7 (19)	39.6 (12)	214.3	270.0	8	57	15	79	7.31	4.42
PR3 Oi	57.3 (15)	84.2 (37)	235.2 (6)	376.7	418.9	14	20	56	90	1.47	0.60
RJ1 A1	9.9 (5)	21.4 (1)	27.5 (3)	58.9	63.5	16	34	43	93	2.16	1.14
RJ1 A2	6.4 (3)	12.8 (2)	53.6 (18)	72.9	38.0	17	34	141	192	1.99	0.36
RJ1 Bw	9.3 (3)	17.8 (3)	54.3 (11)	81.4	49.9	19	36	109	163	1.92	0.50
RJ12 Bw	10.5 (8)	28.2 (11)	30.9 (65)	69.7	55.3	19	51	56	126	2.69	1.25
RJ3 Hap	35.5 (13)	115.3 (8)	131.8 (6)	282.6	339.8	10	34	39	83	3.25	1.14
RJ3 Hai1	42.6 (14)	121.2 (1)	139.2 (16)	303.0	314.9	14	38	44	96	2.85	1.18
RJ3 Hai2	51.0 (10)	104.8 (4)	99.7 (21)	255.6	332.3	15	32	30	77	2.05	1.56
RJ3 Hi	24.0 (14)	95.2 (12)	184.4 (7)	303.6	288.5	8	33	64	105	3.97	0.65
RJ4 Hap1	15.6 (10)	30.5 (4)	20.9 (3)	67.1	91.7	17	33	23	73	1.95	2.21
RJ4 Hap2	17.2 (12)	34.2 (16)	8.9 (5)	60.2	99.5	17	34	9	61	1.99	5.79
RJ4 Cg1	12.7 (20)	22.4 (18)	3.5 (5)	38.6	69.8	18	32	5	55	1.76	9.94
RJ4 Cg2	11.0 (7)	22.1 (10)	6.0 (11)	39.1	44.8	25	49	13	87	2.00	5.56
RS3 Hai	22.3 (17)	60.9 (2)	70.4 (1)	153.6	158.3	14	38	44	97	2.73	1.18
RS3 Hai	11.0 (8)	52.8 (4)	45.2 (35)	109.0	110.3	10	48	41	99	4.81	1.41
RS3 Ha2	5.9 (10)	42.3 (9)	15.5 (8)	63.6	69.3	9	61	22	92	7.19	3.11
RS4 Hpj	19.4 (24)	160.7 (21)	199.4 (7)	379.6	425.7	5	38	47	89	8.27	0.90
RS4 Haj	16.6 (10)	153.7 (2)	240.1 (10)	410.4	482.2	3	32	50	85	9.29	0.71
RS4 Haij	12.1 (15)	138.4 (11)	256.3 (2)	406.8	490.0	2	28	52	83	11.49	0.59
RS5 Hapj	22.3 (5)	164.4 (9)	147.8 (4)	334.5	358.5	6	46	41	93	7.38	1.26
RS5 Haj	24.4 (4)	134.0 (7)	111.4 (2)	269.9	291.6	8	46	38	93	5.48	1.42
SC2 Haij1	30.9 (13)	143.1 (9)	235.6 (9)	409.6	460.0	7	31	51	89	4.63	0.74

(continued)

Table 2. Continued

Profile/ horizons	FAF (g C kg ⁻¹ soil)	HAF (g C kg ⁻¹ soil)	HUM (g C kg ⁻¹ soil)	SUM (g C kg ⁻¹ soil)	C_CHN (g C kg ⁻¹ soil)	FAF (% C_CHN)	HAF (% C_CHN)	HUM (% C_CHN)	SUM (% C_CHN)	EA/ HUM
SC2 Haij2	24.5 (8)	188.4 (6)	260.3 (7)	473.2	528.1	5	36	49	90	7.68 0.82
SP1 Hp1	23.7 (12)	112.8 (13)	53.7 (8)	190.2	207.4	11	54	26	92	4.76 2.54
SP1 Hp2	13.2 (3)	95.1 (6)	17.7 (14)	126.0	144.4	9	66	12	87	7.19 6.12
Average	20.8	99.2	116.4	236.3	259.6	10	40	44	94	5.31 1.84
Standard deviation	11.2	57.8	85.6	140.2	158.4	5	12	22	20	3.42 1.81

^aAverage value of triplicates (variation coefficient, %, between brackets).

^bC_CHN method = total C, Perkin Elmer 2400 CHNS analyzer.

RESULTS AND DISCUSSION

Carbon Distribution in the Different Soil Humic Fractions

The humic substance fractionating resulted in good reproducibility and consistent data considering the complexity of the process. Twenty-six samples (49% of total) presented variation coefficients less than 10%, 45 samples (85%) had coefficient of variation less than 20%, and only 1 sample showed variation coefficients more than 30% (Table 2). For HAF, 31 samples (58% of total) presented variation coefficients less than 10%, 48 samples (90%) showed variation coefficients less than 20%, and only 2 samples had variation coefficients more than 30% (Table 2). In HUM, 34 samples (64% of the total) presented variation coefficients less than 10%, 49 samples (92%) with a variation coefficient less than 20%, and only 2 had variation coefficients more than 30% (Table 2). Variability of the humic fractions per sample did not show a relationship with the content of organic matter, because the variation coefficient was not correlated to the C content.

Considering the average values of the three organic-matter fractionating repetitions, the humin fraction presented the highest average and standard deviation ($116.4 \pm 85.5 \text{ g kg}^{-1}$). This fraction was predominant in most soil samples, with an average value of 43.8% of the total C determined by CHN (C_CHN). However, it showed a high variation coefficient (74%) and high amplitude, with minimum and maximum values of 3.5 and 281.1 g kg^{-1} , respectively. The method used tends to overestimate values of true humic substances, because it quantifies nonsoluble C forms in alkaline medium, which includes fibers and other forms of organic matter such as the light organic matter (Benites 1998).

The FAF fraction consists of true fulvic acids as well as other low-molecular-weight organic compounds, co-extracted in the extraction progress (Benites 1998). The FAF presented the lowest values of average and standard deviation ($20.8 \pm 11.2 \text{ g kg}^{-1}$), representing 10% of the total C on average (Table 2), and also the lowest variability, with variation coefficient of 54% [with a minimum HUM value (5.9 g kg^{-1}) and maximum (57.3 g kg^{-1}) content]. The (HAF) exhibited average value and standard deviation of $99.2 \pm 57.9 \text{ g kg}^{-1}$, with variation coefficient of 58%, and represents 40% of the total C on average. The minimum value was also above the HUM minimum value (12.5 g kg^{-1}) and maximum value of 208.4 g kg^{-1} (Table 2).

From a total of 53 samples collected in this study, 3 showed FAF values compared to HUM. This occurred in horizons with relatively low organic C content, near the minimum limit to be identified as organic horizon and with low fiber content or from mineral horizons, corresponding to horizons Ha2, Cg1, and Cg2 of a hydromorphic soil from Nova Friburgo region, Rio de Janeiro State, profile RJ4. In 20 samples, C content in HAF was higher than that found in HUM fraction, and most of these horizons contained low fiber.

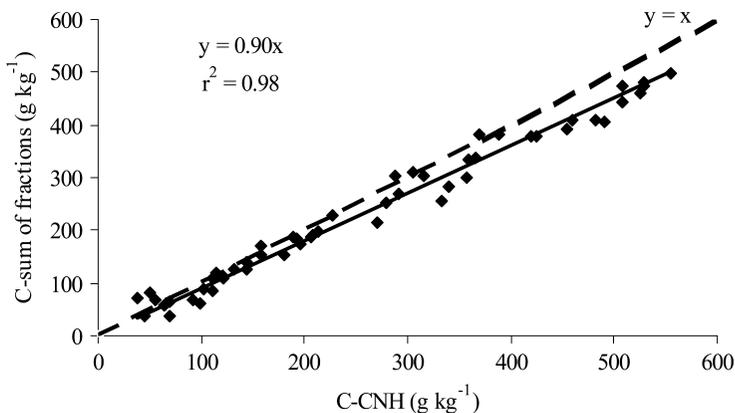


Figure 1. Relationship between the sum of humic fractions and total carbon measured by the CHN reference method. Coefficient significant at 0.001.

The sum of the humic fractions averaged 93.9% of the total C determined by CHN, dry combustion as a reference (Table 2). These variables were also highly correlated (Figure 1).

The recovery percentile showed a large variation, ranging from 55.3 to 191.8%. However, the recovery factor had a non uniform distribution (Figure 2), and there was a higher recovery variability in relatively low total C content samples, below 120 g kg^{-1} , where the variation coefficient is of 39% and the maximum and minimum values are within this range. The samples with high organic C presented low variability, with variation coefficient equal to 7% and minimum and maximum values of 76.9 and

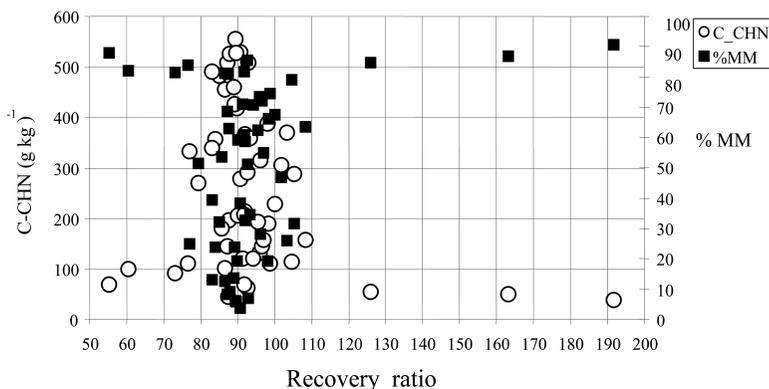


Figure 2. Relationship between carbon recovery ratio, soil mineral material (MM) percentage, and total C measured by the CHN reference method.

108.3%, respectively. The highest variability in both recovery forms was verified for low organic C values and higher mineral material content, profiles RJ1 and RJ4 (Figure 2).

For samples with mineral material (%MM) of more than 80% (Figure 2), a similar effect on variability was observed. These data demonstrate lower result reproducibility in samples with total C contents less than 120 g kg^{-1} or %MM more than 80%. When observed with the simple linear regression analysis, with a confidence interval of 95%, total carbon as the X axis and the sum of humic fractions as Y axis, the linear coefficient may be considered as 0 (zero) and the angular coefficient has as minimum, average, and maximum values 0.88, 0.90, and 0.92, respectively, indicating that the sum of humic fractions represents from 88 to 92% of total C obtained from CHN reference method (Figure 1).

The values of the ratio HAF/FAF ranged from 1.47 to 14.41, with a predominance of HAF in all soil samples. According to INCORA (1974), a higher value for HAF/FAF indicates higher polymerization degree of organic matter. The increase in this ratio is observed in most profiles without regard to soil depth, which is the inverse of what occurs in mineral soils (Benites, Ker and Mendonga 2000). These values result from the fact that Histosol upper horizons periodically are placed under oxidizing conditions, due to water-table seasonal oscillation. This furthers the formation of soluble organic compounds as a result of an increase in the microbiological activity. Zech, Guggemberger, and Schulten (1994) observed highest formation of lower-molecular-weight humic substances in soils during hotter periods and with higher microbiological activity.

The ratio AE/HUM, where AE is the sum of the FAF and HAF fractions, also showed a large variation, with values between 0.36 and 9.94. However, 79% of samples gave values lower than 2. According to Benites, Ker, and Mendonga (2000), this ratio provides information on the soil genesis, identifying movement zones or C accumulation and identifying peaks of the AE/HUM ratio in spodic horizons.

The profile RJ4, which is classified as a Humaqueptic Endoaquents, formed under hydromorphic conditions with high mineral material contents and under coverage of pasture, presents a behavior similar to that observed in Spodosols (Benites et al. 2001). In this profile, a peak of the relation AE/HUM occurred in the third horizon (Cg1), which coincides with the increase in the mineral material percentage, thus demonstrating high interaction of the soluble alkaline humic fractions with the soil mineral matrix. The profile PR3, formed by a single O horizon directly overlying rock, located in a mountainous topography and well drained, presented a low AE/HUM ratio, indicating the loss of more soluble humic fractions and maintenance of insoluble fractions. The other profiles vary in behavior with soil local environment, independent of soil depth. Thus, the AE/HUM variations in Histosols indicate that the dynamics of humic substances is different from mineral soils.

Humic Fractions and Carbon and Nitrogen

The total C values determined through C_CHN showed significant correlation at 0.1% probability with fractions FAH ($r = 0.90$) and HUM ($r = 0.95$), although there was no significant correlation at this level with FAF. According to Schnitzer (1986), the humic acids in association with colloids form insoluble complexes at pH lower than 6.5, thus enabling the immobilization and accumulation of this fraction in acid soils. The humin fraction, as determined, includes undecomposed fibers present in the soil organic matter, which should be responsible for the high correlation observed between this fraction and the total C. The lower correlation of FAF with the total organic C reflects the higher FAF solubility and mobility in the soil (Stevenson 1994).

The amount of total N measured by the CHN method showed a high correlation with the FAF fraction ($r = 0.86$, $P = 0.001$) (Figure 3), indicating that this fraction is closely related to the soil N content. The FAH ($r = 0.53$), HUM ($r = 0.66$), and the sum of humic fractions ($r = 0.69$) also correlated with the N level and the coefficients are significant at $P = 0.01$.

The values obtained in the alkaline extract readings at 380 nm showed high correlation with C_CHN contents, indicating the potential of the method to estimate the total C content in Histosols and related soils with high organic-matter content. Similarly, the alkaline extract readings at 465 nm were correlated with FAH (Table 3). The readings at 665 nm did not have significant correlations with other properties.

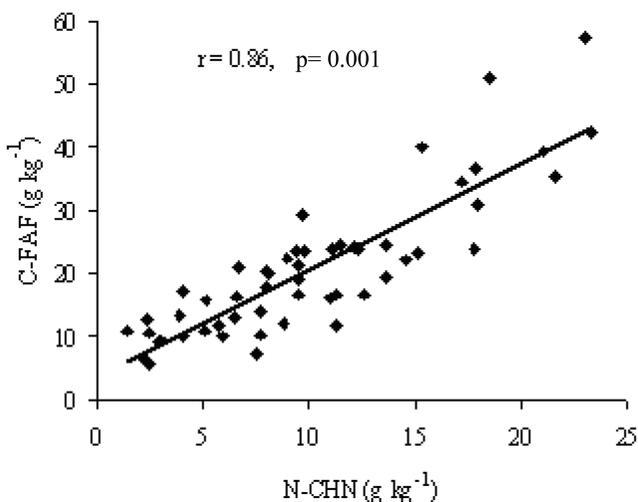


Figure 3. Relationship between content of N measured by the CHN reference method with fulvic acid fraction (FAF).

Table 3. Matrix with correlation coefficients for organic fractions FAF, HAF, HUM, and total C_CHN, as related to CEC, sum of bases, phosphorus, exchangeable acidity, extractable Al; pH in water, KCl, and CaCl₂; and bulk density and alkaline extract measured at 380, 465 and 665 nm

Property	FAF	HAF	HUM	C_CHN
CEC	0.01ns	0.60***	0.44**	0.50***
Sum of bases	0.42**	0.28*	0.28*	0.33*
P	0.49***	-0.08ns	0.15ns	0.09ns
H ⁺	-0.11ns	0.66***	0.42**	0.50***
Al ³⁺	-0.13ns	-0.05ns	0.05ns	-0.01ns
pH KCl	-0.18ns	-0.73***	-0.65***	-0.71***
pH water	-0.03ns	-0.58***	-0.60***	-0.58***
pH CaCl ₂	-0.02ns	-0.50***	-0.63***	-0.56***
Abs. at 380 nm	0.41**	0.89***	0.87***	0.92***
Abs. at 465 nm	0.28*	0.92***	0.77***	0.86***
Abs. at 665 nm	-0.09ns	0.50***	0.12ns	0.29*
Ds	-0.55***	-0.63***	-0.71***	-0.75***

***Significant at 0.1%; **significant at 1%; *significant at 5%; ns: non significant.

Notes: FAF = fulvic acid fraction; HAF = humic acid fraction; HUM = humin; CEC = cation exchange capacity; sum of bases = (Ca + Mg + Na + K); Ds = soil bulk density. C_CHN method = total C, Perkin Elmer 2400 CHNS analyzer.

Humic Fractions and Soil Attributes

The CEC presented positive significant correlation with HAF, HUM, and total C_CHN. Related to soil acidity, the strongest correlation was obtained for HAF, H⁺, and pH in KCl (Table 3). This result indicates the important role of the humic acid fraction in the generation of negative charges in soil, thus contributing to CEC. Similar results were obtained by other authors on different tropical soil classes (Benites 1998; Benites, Ker, and Mendonga 2000; Souza et al. 2003). The sum of bases and phosphorous (P) content presented a significant correlation with FAF, indicating FAF is more related to the level of nutrients available in soil. FAF presented no correlation with acidity indicators H⁺, Al³⁺, and pH. These results suggest that in Histosols with higher natural fertility, the transformation of the organic matter favors the FAF production. The highest correlation coefficients in absolute value for pH were found with pH in KCl and variables HAF, HUM, and C_CHN (Table 3).

The C/N ratio did not show a significant correlation with any of the humic fractions. However, it is possible to define an equation with a determination coefficient r² of 0.594 (P < 0.001) with the use of the multiple regression analysis, where the C/N ratio may be determined as a function of the FAF

content and the sum of humic fractions (SUM), where all coefficients are significant at $P = 0.001$:

$$\frac{C}{N} = 23.454 - 0.593 (\text{FAF}) + 0.065 (\text{SUM}).$$

The soil bulk density (Ds) showed negative significant correlation with C_CHN and with all humic fractions. That is, the higher organic-matter content resulted in lower Ds, therefore a higher subsidence potential.

CONCLUSIONS

The method employed for humic substance fractionation was shown to be suitable, giving good reproducibility and easy technical execution, which indicates it may be included in routine laboratory characterization of Histosols and related soils with high organic-matter content.

The FAF was better correlated with level of nutrients than with soil acidity variables and thus may be an indicator of nutrient availability on Histosols. The humic acid and humin fractions presented high correlation with CEC, active acidity (H^+), and pH. The humin fraction and the alkaline extract absorbance level measured at 380 nm and 465 nm showed a high correlation with the total soil organic C content.

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