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# ORGANIC MATTER QUALITY AND DYNAMICS IN TROPICAL SOILS AMENDED WITH SUGAR INDUSTRY RESIDUE<sup>(1)</sup>

Jader Galba Busato<sup>(2)</sup>, Tairone Paiva Leão<sup>(2)</sup>, Marihus Altoé Baldotto<sup>(3)</sup> & Luciano Pasqualoto Canellas<sup>(4)</sup>

## SUMMARY

Soil organic matter depletion caused by agricultural management systems have been identified as a critical problem in most tropical soils. The application of organic residues from agro-industrial activities can ameliorate this problem by increasing soil organic matter quality and quantity. Humic substances play an important role in soil conservation but the dynamics of their transformations is still poorly understood. This study evaluated the effect of compost application to two contrasting tropical soils (Inceptisol and Oxisol) for two years. Soil samples were incubated with compost consisting of sugarcane filter cake, a residue from the sugar industry, at 0, 40, 80, and 120 Mg ha<sup>-1</sup>. Filter cake compost changed the humic matter dynamics in both content and quality, affecting the soil mineralogical composition. It was observed that carbon mineralization was faster in the illite-containing Inceptisol, whereas humic acids were preserved for a longer period in the Oxisol. In both soils, compost application increased fulvic acid contents, favoring the formation of small hydrophilic molecules. A decrease in fluorescence intensity according to the incubation time was observed in the humic acids extracted from amended soils, revealing important chemical changes in this otherwise stable C pool.

Index-terms: humic substances, soil electrical charges, stable carbon, filter cake.

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## RESUMO: QUALIDADE E DINÂMICA DA MATÉRIA ORGÂNICA EM SOLOS TROPICAIS SOB ADIÇÃO DE RESÍDUO DA INDÚSTRIA DO AÇÚCAR

*A depleção da matéria orgânica causada pelos sistemas de manejo de solos tem sido identificada como um problema crítico para a maior parte dos solos tropicais. A aplicação de resíduos orgânicos provenientes de atividades agroindustriais pode amenizar esse problema, devido à possibilidade de aumento da qualidade e quantidade da matéria orgânica. As substâncias húmicas têm papel importante na conservação do solo, mas a dinâmica das suas transformações é ainda pouco compreendida. Neste trabalho, foi avaliado o efeito da adição de composto orgânico sobre dois solos tropicais mineralogicamente distintos (Latossolo e Cambissolo) durante dois anos. O composto empregado foi preparado com torta de filtro, um resíduo proveniente da produção de açúcar, e as amostras dos solos foram incubadas com doses equivalentes a 0, 40, 80 e 120 Mg ha<sup>-1</sup>. A adição do composto de torta de filtro alterou quantitativa e qualitativamente a dinâmica das substâncias húmicas, e essa alteração foi relacionada com a composição mineralógica dos solos. Observou-se que a mineralização do carbono total foi mais rápida no Cambissolo, que apresentou mineral do tipo 2:1 em sua constituição (ilita), enquanto os ácidos húmicos foram preservados por maior período de tempo no solo sem argilominerais do tipo 2:1 (Latossolo). Em ambos os solos, a adição do composto aumentou o conteúdo de ácidos fúlvicos, sugerindo a formação de moléculas hidrofílicas de pequenas dimensões. Os ácidos húmicos extraídos dos solos apresentaram decréscimo na intensidade de fluorescência ao longo do tempo, revelando importantes modificações químicas nesse compartimento de carbono reconhecido como estável.*

*Termos de indexação: substâncias húmicas, cargas elétricas do solo, carbono estável, torta de filtro.*

## INTRODUCTION

Soil organic matter (SOM) depletion caused by agricultural management systems has been identified as a critical problem in most tropical soils. Organic matter plays a key role in agricultural sustainability, due its influence on soil properties such as the amount of electrical negative charges, water-holding capacity and nutrient status (Stevenson, 1994). The SOM content and quality are important for the maintenance of soil fertility and productivity. Therefore, strategies are required to restore SOM lost through oxidation in cultivated areas.

Industrial residues with high carbon (C) content and free of organic and inorganic pollutants can be applied to agricultural fields. In particular, filter cake (FC), a residue from the sugar industry, has great potential as soil amendment due to its high nutrient content (Busato et al., 2010). The use of FC as fertilizer is a traditional practice in many regions, although it can promote immobilization of soil nitrogen when incorporated directly into the soil, due to the stimulation of native microbial activity (Blagodatskaya & Kuzyakov, 2008). Composting the organic residues is attractive, as it converts them into environmentally safe products (Rivero et al., 2004). Many studies have shown increases in C and N soil contents after amendment with different composts but studies on the effects of FC on soil humus composition

are scarce. Humic substances (HS) are the most widespread natural products found on the Earth's surface but although their various important roles in environmental processes are recognized, the dynamics of their transformations remains one of the least understood aspects of soil chemistry.

The effects of compost on soil depend mainly on the nature of the composted matter, the composting period and soil mineralogy (Bernal et al., 1998; Schulthess & Huang, 1991). Saidy et al. (2012) showed that C mineralization is significantly influenced by clay mineralogy; higher rates were observed in the presence of kaolinitic than of illitic or smectitic clays. In oxidic and kaolinitic soils, humic acids (HA) are less sorbed than fulvic acids (FA). This difference can be attributed to the influence of carboxylic groups, which are more abundant in FA and contribute to the sorption of HS by oxides (Varadachari et al., 1995). There is a selective uptake of lower molecular weight material in 2:1 aluminosilicates (Feng et al., 2005), which results in lower HA sorption in highly weathered soils.

The objective of this study was to evaluate the effects of FC composting on the quality and quantity of SOM, specifically on the humus composition, in two contrasting tropical soils, during a 24-month incubation period. The SOM quality was assessed by the C-HA/C-FA ratio and fluorescence intensity of humic acids.

## MATERIAL AND METHODS

### Sugarcane filter cake compost

Filter cake is a pulp resulting from sugarcane milling. Briefly, the sugarcane syrup is treated with sulfur and calcium to clear it and to promote colloid flocculation, respectively. The resulting colorless and cleaned juice is evaporated and the broth is vacuum-filtrated. The remaining solid accumulated in the filter is called filter cake. The FC, provided by the Santa Cruz Sugarcane Co. located in Campos dos Goytacazes, Rio de Janeiro, Brazil, was composted in an outdoor pile for one year. This period was chosen to ensure the reduction of the C/N ratio in the FC compost before its incorporation, to avoid an excessive stimulation of microbial growth and consequently, the possibility of N immobilization by the priming effect, as pointed out by Blagodatskaya & Kuzyakov (2008). After this period, the material was sampled, air-dried and sieved for chemical characterization. Total organic carbon (TOC) in the FC was estimated using the modified dichromate oxidation method (Walkley & Black, 1934). Total N was determined after digesting the sample with concentrated  $\text{H}_2\text{SO}_4$  (1:20, w:v), followed by distillation (Bremner & Mulvaney, 1982). Total P was determined after mineralization by acidification ( $\text{H}_2\text{SO}_4$ ) of FC extracts and  $\text{PO}_4^{3-}$  formed was analyzed by the molybdenum-blue method (Murphy & Riley, 1962).

### Soils

Soil surface samples (0-0.20 m) were collected from a Eutradox (Oxisol) and a Eutrudept (Inceptisol) (Soil Survey Staff, 2010) from the northeastern region of the state of Rio de Janeiro, Brazil. The samples were air-dried, ground and sieved (2 mm mesh) and analyzed as described by Embrapa (1997). Mineral particle-size distribution was analyzed using the pipette method. The mineralogical compositions of the silt and clay soil fractions separated from the bulk soil by gravity settling was evaluated by powder X-ray diffraction analysis (XRD), in a Rigaku RU200B diffractometer with a copper rotating anode, nickel filter, graphite diffracted-beam monochromator and operated in a step-scan mode ( $0.02^\circ 2\theta$  by 5 s) between  $5$  and  $80^\circ 2\theta$ .

Permanent and variable negative surface charges were determined by the cesium sorption method proposed by Anderson & Sposito (1991), with a few modifications. In summary, a 2 g soil sample was repeatedly reacted with  $0.01 \text{ mol L}^{-1} \text{ CsCl}$  to prepare a Cs-saturated sorbent free of entrapped solution. Later, the samples were heated to  $65^\circ \text{C}$  for 48 h to enhance  $\text{Cs}^+$  sorption on the permanent negative charges by inner-sphere complexation. For the displacement of  $\text{Cs}^+$  from variable charge sites, 0.5 g of oven-dried Cs-saturated soil and 25 mL of  $0.01 \text{ mol L}^{-1} \text{ LiCl}$  were filled to 50 mL centrifuge tubes which were shaken and centrifuged, and the

supernatants saved for  $\text{Cs}^+$  measurement. The displacement of  $\text{Cs}^+$  from permanent charges was carried out through successive extractions with  $1.0 \text{ mol L}^{-1} \text{ NH}_4\text{OAc}$ .  $\text{LiCl}$  and  $\text{NH}_4\text{OAc}$  extracts were analyzed for cesium by flame atomic emission spectroscopy after addition of  $\text{K}^+$  (as  $\text{KCl}$ ) to suppress  $\text{Cs}^+$  ionization. Total organic C was determined by dichromate oxidation (Walkley & Black, 1934), pH was measured in water at 1:2.5 (w:v) and the total N content determined after digesting the sample with concentrated  $\text{H}_2\text{SO}_4$  (1:20, w:v), followed by distillation (Bremner & Mulvaney, 1982).

### Soil incubation

The soil samples were mixed with FC compost at doses equivalent to 0, 40, 80 and  $120 \text{ Mg ha}^{-1}$  on a dry weight basis and transferred to 10 L pots in a greenhouse. During incubation, soil moisture content was maintained at 60-70 % saturation by adding distilled water to the samples. Samples were collected 6, 12 and 24 months after compost incorporation for analyses. A sample of each soil was also evaluated at the beginning of the experiment, prior to the incorporation of FC compost, for comparison with incubated samples and for soil characterization.

### Total organic carbon and fractional humus composition

Total organic C in the soil samples was determined according to the modified Walkley & Black (1934) method. The carbon content in each humus fraction (FA, HA and humins) was evaluated after separation of soluble humic substances (HA and FA) from humins (HUM), using  $0.5 \text{ mol L}^{-1} \text{ NaOH}$  followed by HA isolation from FA by decreasing the pH to 1.5 with concentrated  $\text{H}_2\text{SO}_4$ . The C content in HUM was determined by wet chemical oxidation using  $0.167 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$  followed by titration of excess  $\text{Cr}_2\text{O}_7$  with  $0.2 \text{ mol L}^{-1} \text{ Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The C contents in HA and FA fractions were determined by the same procedure but using  $0.0833 \text{ mol L}^{-1} \text{ K}_2\text{Cr}_2\text{O}_7$ .

### Extraction of humic acids

Humic acids were extracted by shaking 50 g of soil with 1 L of  $0.1 \text{ mol L}^{-1} \text{ NaOH}$  for 16 h in a  $\text{N}_2$  atmosphere, centrifuging the suspensions at 5,000g and decreasing the pH to 1.5 with  $\text{H}_2\text{SO}_4$  to precipitate the HA, which was then resolubilized with  $0.1 \text{ mol L}^{-1} \text{ NaOH}$ . This cycle of solubilization-precipitation was repeated three times and then the HA was treated with 100 mL of a dilute HF-HCl solution [5 mL HCl (36 % m/v) + 5 mL HF (48 % m/v)] and agitated overnight. After centrifugation (5,000 g) for 15 min, the HA fraction was repeatedly washed with deionized water, dialyzed against deionized water using a 12 – 14 kDa-cutoff membrane (Thomas Scientific, Inc) and freeze-dried.

Elemental composition,  $E_4/E_6$  ratio and acidity of humic acids extracted from the compost

Elemental composition of the HA extracted from FC compost was determined using a CHN Perkin-Elmer 1420 autoanalyzer and the  $E_4/E_6$  ratio by dissolving 4 mg of each HA in 10 mL of 0.05 mol L<sup>-1</sup> NaHCO<sub>3</sub> followed by pH adjustment to 8.0 with dilute NaOH. Absorbances at 465 and 665 nm were measured in a Shimadzu spectrophotometer 8300 (Tokyo, Japan). Total acidity of HA was determined by the Ba(OH)<sub>2</sub> method with titration of the HCl excess, whereas the carboxylic acidity was assessed by adding Ca(OAc)<sub>2</sub> and determining OAc release by NaOH titration, according to Schnitzer & Gupta (1965). Phenolic acidity was obtained as the difference between total and carboxylic acidity.

### Fluorescence of humic acids

Fluorescence spectra of HA were obtained using a Hitachi F-4500 spectrometer (Tokyo, Japan) in aqueous solution (4 mg of each HA in 10 mL of 0.05 mol L<sup>-1</sup> NaHCO<sub>3</sub>). The pH of the solution was adjusted to 8.0 with NaOH 0.05 mol L<sup>-1</sup>. The excitation spectra were obtained by scanning the range of 270-500 nm with excitation in the blue region (465 nm), a 5nm slit and scan velocity of 120 nm min<sup>-1</sup>. Fluorescence intensity of the fluorophores in the spectra was obtained by automatic electronic integration of the spectrometer software.

### Data analysis

The treatments were arranged in a completely randomized design, organized in a factorial scheme, with three replicates. Statistical tests were performed using the SAEG 5.0 software; and treatment effects identified by one-way ANOVA. Least significant difference (LSD - Tukey test,  $p < 0.05$ ) was used to compare the treatment means at each incubation time.

## RESULTS AND DISCUSSION

Chemical, electrochemical and particle-size distribution analyses carried out for the two soils used in this study are presented in Table 1. The cesium-adsorption method indicated that the variable charges accounted for 71 and 39 % of the total negative surface charges of the Oxisol and Inceptisol, respectively. The presence of illite in both clay and silt fractions in the Inceptisol (Figure 1A) was responsible for the predominance of permanent negative surface charges, whereas for the Oxisol the measured permanent charges can be attributed to the presence of 2:1 aluminosilicates in these fractions, in undetectable amounts by powder XRD (Figure 1B). Furthermore, for both soils, small amounts of permanent negative charges can be attributed to the presence of kaolinite,

a silicate with permanent and variable negative surface charges that can also be measured by the cesium-adsorption method (Schroth & Sposito, 1997). The pH values of the two soils were similar (5.2 and 5.5, for the Oxisol and Inceptisol, respectively) and TOC was slightly higher in the Inceptisol.

Table 1 shows that the FC had a higher total C and lower total N content than other residues used as organic fertilizers (Gigliotti et al., 2012). The maturing process involves several changes in chemical content and transformation in the structure of VC, which can be predicted by the C/N ratio. After one year of composting, a low C/N ratio (10.5, not shown) was observed in FC, suggesting a high stability level of the organic matter. The slightly acid pH of the FC (6.0) was probably due to the decomposition of organic matter, leading to the formation of HCO<sub>3</sub> and HA (Komilis & Ham, 2006). The first component contributes to a greater drop in pH at the initial stage of composting, and the presence of carboxylic and phenolic groups in HA probably caused further reduction of the pH in latter stages. The high level of available P found in the compost may have originated from the plant residues of the FC mineralized during the composting process (Galvez-Sola et al., 2010).

Table 2 summarizes the chemical and spectroscopic properties of HA determined in this study and those obtained in other studies. Low contents of C and N, as well as high O contents were comparable to those often found in HA derived from other composts (Adani et al., 2007; Brunetti et al., 2007; Senesi et al., 2007). This suggests that FC composting favored the formation of more oxidized HS, presenting larger oxygenated acidic functional groups as determined by the high value of total acidity. In addition, unlike other materials (Brunetti et al., 2007; Senesi et al., 2007), the compost obtained in this study had similar contents of carboxylic and phenolic-type groups, leading to the development of negative surface charges derived from the deprotonation of these groups, in a pH range of 3.5 - 6.0 for the carboxylic and > 7.0 for the phenolic groups (Plaza et al., 2005).

In general, the TOC contents remained constant in relation to untreated soils or increased at a rate proportional to the compost application rate in samples collected after 6 months of incubation (Figure 2). After this period, a decrease in TOC was observed until the end of the experiment, however, the rate of TOC depletion was greater in the Inceptisol samples. At the end of the incubation time, TOC contents returned to the levels of non-treated samples (15.8 and 20.3 g kg<sup>-1</sup>, in Oxisol and Inceptisol, respectively) in both soils, except for the samples treated with a compost dose of 120 Mg ha<sup>-1</sup>. Short-term incubation experiments showed that the proportion of substrate-derived C retained in the bulk soil is positively related to the soil clay content (Saggar et al., 1999). The content of fine particles/clay is therefore highly important for the preservation of organic C in soils. Clay contents were similar in both soils, however, the

silt fraction varied significantly (Table 1). It was expected that the increase in the C content, as well as the maintenance of this increase, would be more pronounced in the Inceptisol due to its higher silt content. Interactions of organic C with iron oxides may possibly be important in more weathered soils. The presence of Al and Fe oxides leads to the accumulations of organic carbon in comparison to other soil types (Oades, 1988). Several mechanisms including electrostatic interactions, specific adsorption by ligand exchange, hydrogen bonding and hydrophobic effects may be responsible for the sorption of HS on mineral

surfaces. Our experimental results confirmed this hypothesis and indicated that the sorptive phenomena of HS appeared to be more effective in the Oxisol.

Filter cake compost application also changed the amount and distribution of HS in both soils, and the transformations of humic fractions - HUM, HA and FA - differed between them (Figure 3). Although the HUM fraction is considered the most recalcitrant organic pool in the soil, representative increases in its contents in relation to the non-treated soil were observed in samples obtained after 6 months of incubation, in both soils. In the Oxisol, high humin

Table 1. Particle-size distribution, electrochemical and chemical properties of the soils and filter cake compost

Component	Oxisol	Inceptisol	Filter cake Compost
Total carbon (g dm <sup>-3</sup> )	15.9	20.5	64.0
Total nitrogen (g dm <sup>-3</sup> )	-	-	6.1
Total phosphorus (g dm <sup>-3</sup> )	-	-	4.3
pH (H <sub>2</sub> O)	5.2	5.5	6.0
Clay (g kg <sup>-1</sup> )	390.0	370.00	-
Silt (g kg <sup>-1</sup> )	30	310.00	-
Sand (g kg <sup>-1</sup> )	580.0	320.00	-
$\sigma_v^{(a)}$ (mmol <sub>c</sub> kg <sup>-1</sup> )	12.0	030.0	-
$\sigma_p^{(b)}$ (mmol <sub>c</sub> kg <sup>-1</sup> )	5.0	047.0	-

(a)  $\sigma_v$  = variable negative charges; (b)  $\sigma_p$  = permanent negative charges; (-) not determined or not reported.

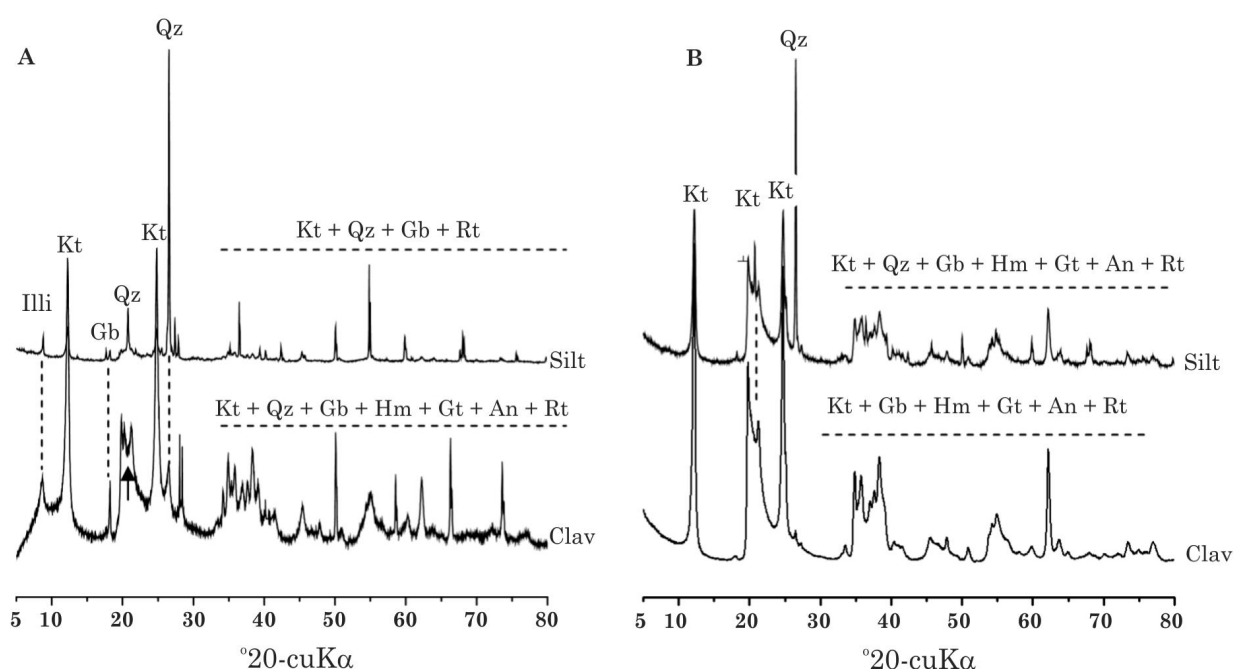


Figure 1. X-ray diffraction patterns of the silt and clay fractions of the Inceptisol (A) and Oxisol (B). Illi = Illite; Kt = Kaolinite; Gb = Gibbsite; Qz = Quartz; Hm = Hematite; Gt = Goethite; An = Anatase; Rt = Rutile0.

Table 2. Elemental composition, C/N, E<sub>4</sub>/E<sub>6</sub> ratio and acidic functional group content of humic acids extracted from different composts

	This work	Senesi et al. (2007)	Adani et al. (2007)	Brunetti et al. (2007)
	Filter cake compost	Plant residue compost	Food waste and wood chips	Compost of sewage sludge
C (g kg <sup>-1</sup> )	465.0	560.0	546.0	535.0
N (g kg <sup>-1</sup> )	30.0	63.0	76.0	100.0
H (g kg <sup>-1</sup> )	57.0	85.0	51.0	63.0
S (g kg <sup>-1</sup> )	-	7.0	9.0	19.0
O (g kg <sup>-1</sup> )	452.0	285.0	316.0	283.0
(C/N) ratio	18.0	7.7	8.0	6.2
(H/C) ratio	0.1	0.1	0.1	0.1
E <sub>4</sub> /E <sub>6</sub> ratio <sup>(a)</sup> (HA)	3.5	6.9	-	6.3
TA <sup>(b)</sup> (mmol g <sup>-1</sup> )	7.4	4.2	-	5.8
COOH <sup>(c)</sup> (mmol g <sup>-1</sup> )	3.5	1.4	-	2.5
PhOH <sup>(d)</sup> (mmol g <sup>-1</sup> )	3.9	3.8	-	3.3

<sup>(a)</sup> E<sub>4</sub>/E<sub>6</sub> ratio = Absorbances of HA at 465 and 665 nm; <sup>(b)</sup> TA = Total acidity; <sup>(c)</sup> COOH = carboxylic acidity; <sup>(d)</sup> PhOH = Phenolic acidity; (-) not measured or not reported.

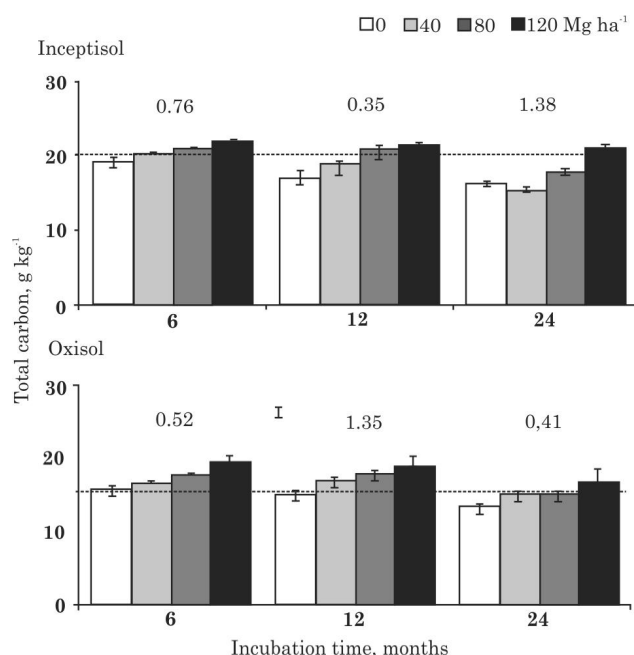


Figure 2. Carbon content in Inceptisol and Oxisol samples with time for different doses of filter cake application. Error bars represent the standard error of the mean. Horizontal dashed line represents values for untreated soil at the beginning of the experiment. Numbers refer to least significant difference (Tukey test,  $p < 0.05$ ).

contents were observed even after 12 months of incubation for the higher compost doses (equivalent to 80 and 120 Mg ha<sup>-1</sup>). At the end of the experiment, HUM contents dropped to the initial non-treated

sample values in the Oxisol (around 4.6 g kg<sup>-1</sup>). On the other hand, high values were observed in the Inceptisol samples treated with FC compost even after 24 months of incubation (Figure 3). For both soils, changes in the HA pools were quite similar to those observed for TOC. Similar to that of HUM, the application of FC compost resulted in an increase in HA content in the Oxisol after 6 months of incubation. This effect was also observed in the samples after 12 months of incubation, but at the end of the experiment all values had decreased to levels close to that of non-treated soil with the exception of samples treated with the highest dose of compost application (120 Mg ha<sup>-1</sup>). In the Inceptisol samples, HA contents at the end of the incubation period were lower than the initial values for all compost doses.

Fulvic acids contents increased at a slower pace during the first 12 months and later the increments were more pronounced (Figure 3). In general, contents of both HUM and HA increased after 6 months and decreased after 12 months of incubation. Wang & Xing (2005), using solid and liquid-state nuclear magnetic resonance (<sup>13</sup>C NMR), observed that the aliphatic fractions of the HS were preferentially sorbed on 2:1 aluminosilicates and kaolinite, while aromatic fractions remained in solution. It is possible that the presence of both illite in the Inceptisol and kaolinite in the Oxisol contributed to the maintenance of FA. Fractions characterized as aromatic were preferentially degraded over time, as shown by the reduction of participation of HA in both soils.

Although HS are normally considered a stable pool of OM (Galantini & Rosell, 2006), our data showed that the humus composition varied significantly, not only according to the rate of organic compost, but also

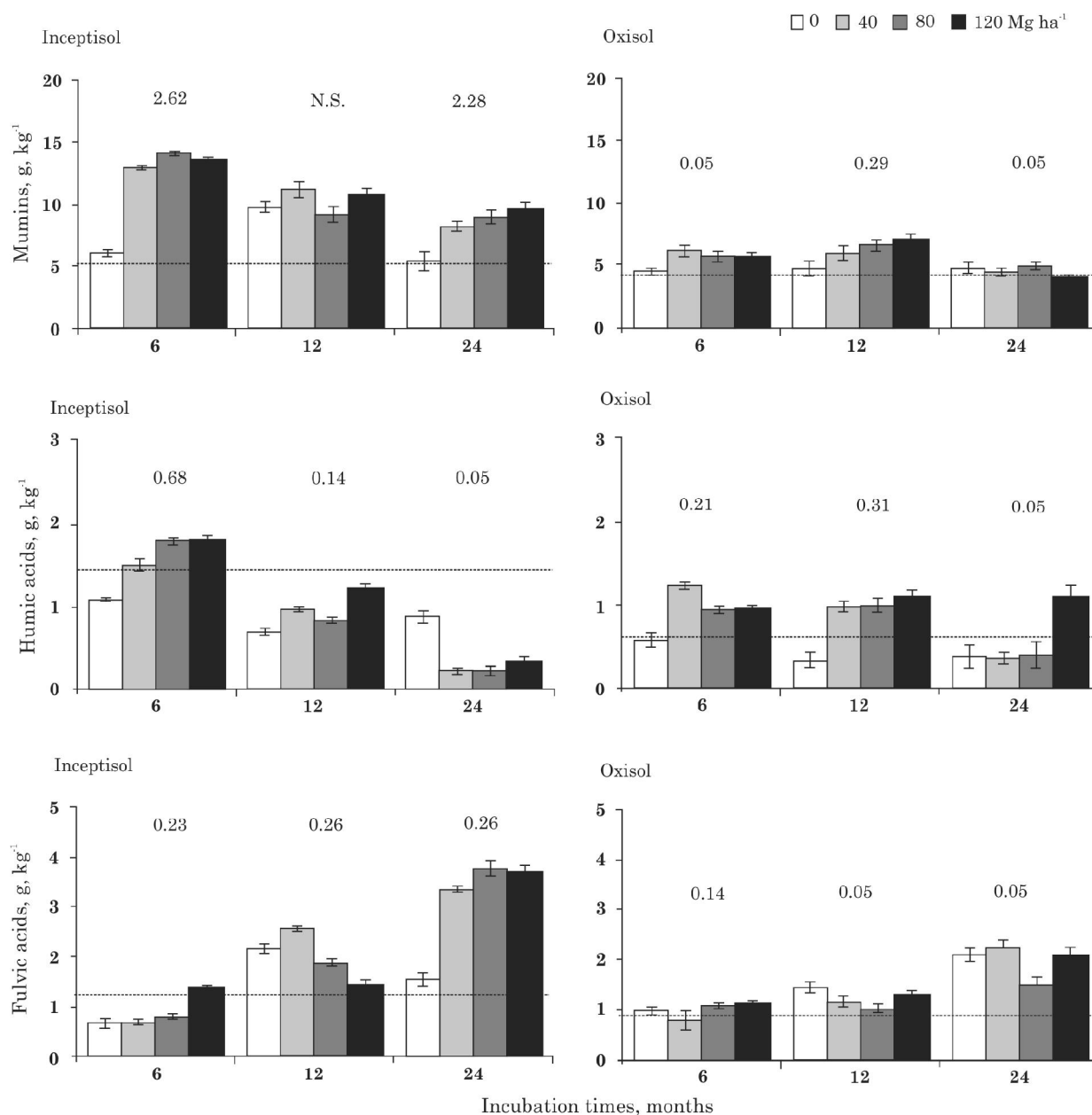


Figure 3. Humic fractions content in Inceptisol and Oxisol samples with time for different doses of filter cake application. Error bars represent the standard error of the mean. Horizontal dashed line represents values for untreated soil at the beginning of the experiment. Numbers refer to least significant difference (Tukey test,  $p < 0.05$ ).

to soil mineralogy. The balance among the humic matter fractions was reflected in changes in the C-HA/C-FA ratio (Figure 4). As expected, the application of FC compost to Oxisol increased the C-HA/C-FA ratio in the first year, mainly due to the significant increase in HA content. After this period, there was a progressive reduction with higher compost doses. Furthermore, it was observed that after the 1-year incubation period there was an increasing trend in FAs. On the other hand, FC compost induced a decrease in the C-HA/C-FA ratio in the Inceptisol

samples after 6 months of incubation. For the Inceptisol, the values of this ratio at the end of the incubation period was lower than of non-treated soil.

In general, the application of organic composts increases TOC, N content, cation exchange capacity, and the levels of some plant nutrients, where these changes are associated to higher HA contents (Adani & Tambone, 2006; Adani et al., 2007). In this work, an increase in soil HA contents was observed only in short incubation periods (less than 12 months for the Inceptisol), while the FA contents increased after 6



months in both soils. Aluminosilicates can affect soil carbon pools differently, as shown by Feng et al. (2005), who observed that kaolinite is able to retain greater amounts of HA than montmorillonite. Zhou et al. (1994) also reported a higher sorption of HA on kaolinite than on 2:1 aluminosilicates, despite the higher surface charge density of montmorillonite than of 1:1 aluminosilicate. Some humic fractions are sorbed through ligand exchange on iron and aluminum oxides and via cation bridges on aluminosilicates (Zhou et al., 1994; Chorover & Amistadi, 2001). The rapid increase of the HA content in highly weathered soils, mainly Oxisols, may be due to the aggregation effect of metal interaction with organic compounds. Nebbioso & Piccolo (2009) found that unsaturated long-chain alkanolic acids in HA interact preferentially with Al and Ca, with consequent increase of conformational rigidity and molecular size of humic hydrophobic domains.

The fluorescence intensity (FI) at 465 nm in HA samples was analyzed to detect possible changes in chemical characteristics during the incubation time (Figure 5). The FI was 100 % higher in HA of Inceptisol than of Oxisol and decreases were observed in FI for both soils after 6 months of incubation, independent of the FC compost rate. Fluorescence intensity was proposed by Senesi (1990) as a fundamental property to discriminate HS according to their origin. The modifications in FI during the incubation period were

less intense in soils without incorporation of FC compost than in treated soils (Figure 5).

The humification process increases the concentration of semiquinone free radicals (SFRC) in humus and high FI is correlated with the electron spin resonance spectroscopy (Millori et al., 2002). According to these authors, the FI decrease in HA represents a lower degree of humification of soil humus after FC compost application. Decreases in FI after compost incorporation suggest the presence of simple structural components with wide molecular heterogeneity and low content of conjugated chromophores in HA, and similar FI to that of FA (Senesi, 1990). The increase in FA content during incubation is possibly due to the conversion of the HA fraction into more hydrophilic components.

The long resistance to mineralization reported for humic matter consisting of the HUM, FA and HA fractions should be revised, since a rapid transformation of these fractions was observed, consistent according to soil mineralogy. Doane et al. (2003) found a relevant carbon turnover in all HS fractions, supporting the idea that individual humic fractions may play different roles in C cycling depending on inputs and seasonal conditions. This study shows that soil mineralogy influences fractional humus composition in soils amended with compost. The mineralization of carbon pools was intense and

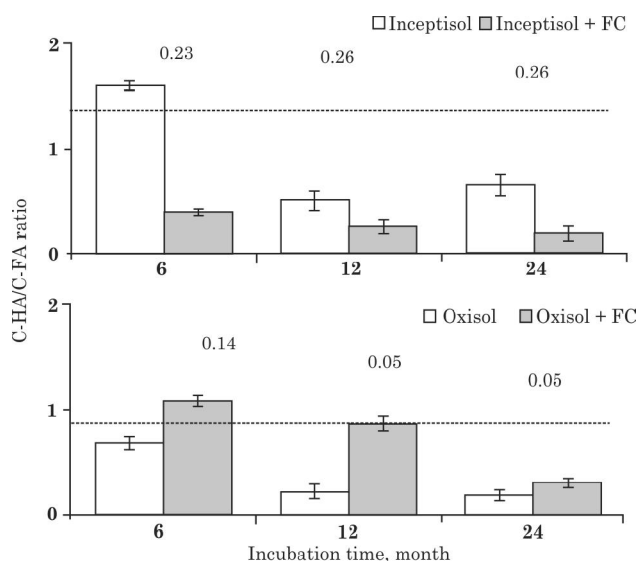


Figure 4. Effect of filter cake compost on C-HA/C-FA ratio. Error bars represent the standard error of the mean. White bars represent soil without compost application and gray bars represent the average of all three doses of FC compost application. Horizontal dashed line represents values for untreated soil evaluated at the beginning of the experiment. Numbers refer to least significant difference (Tukey test,  $p < 0.05$ ).

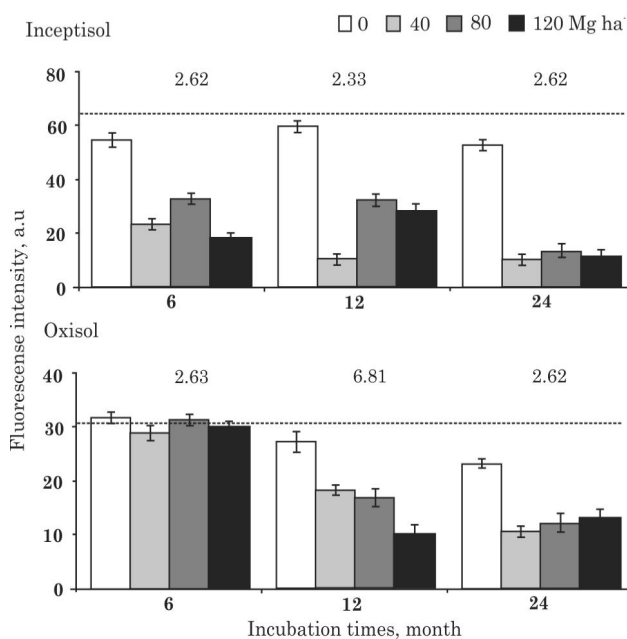


Figure 5. Fluorescence intensity of humic acids isolated from Inceptisol and Oxisol samples for different doses of filter cake application. Error bars represent the standard error of the mean. Horizontal dashed lines represent values for untreated soil at the beginning of the experiment. Numbers refer to least significant difference (Tukey test,  $p < 0.05$ ).

resulted in a decrease of TOC contents to levels below the initial values with the application of 40 and 80 Mg ha<sup>-1</sup> of FC compost to the Inceptisol after 24 months. The chemical characteristics of the stable soluble humic fraction represented by HA were significantly altered as indicated by a marked decrease in FI during the incubation period.

## CONCLUSIONS

1. Total organic carbon and humic fractions distribution in soils were significantly modified with the FC compost application, but the dynamics of this transformation differed according to the soil mineralogy.

2. Total organic carbon depletion was more accentuated in Inceptisol than Oxisol.

3. Humic acid and humin fractions were preserved for a longer time in the Oxisol.

4. The filter cake compost application increased the fulvic acid fraction in both soils.

5. A reduction of fluorescence intensity in humic acids suggests a reconversion of humic fractions during the incubation period.

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