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ORGANIC MATTER FRACTIONS AND QUALITY OF THE SURFACE LAYER OF A CONSTRUCTED AND VEGETATED SOIL AFTER COAL MINING. I - HUMIC SUBSTANCES AND CHEMICAL CHARACTERIZATION

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ABSTRACT

After open coal mining, soils are "constructed", which usually contain low levels and quality of organic matter (OM). Therefore, the use of plant species for revegetation and reclamation of degraded areas is essential. This study evaluated the distribution of carbon (C) in the chemical fractions as well as the chemical characteristics and humification degree of OM in a soil constructed after coal mining under cultivation of perennial grasses. The experiment was established in 2003 with the following treatments: *Hemarthria altissima* (T1), *Paspalum notatum* (T2), *Cynodon dactilon* (T3), *Urochloa brizantha* (T4), bare constructed soil (T5), and natural soil (T6). In 2009, soil samples were collected from the 0.00-0.03 m layer and the total organic carbon stock (TOC) and C stock in the chemical fractions: acid extract (C_{HCl}), fulvic acid (C_{FA}), humic acid (C_{HA}), and humin (C_{HU}) were determined. The humic acid (HA) fraction was characterized by infrared spectroscopy and the laser-induced fluorescence index (I_{LIF}) of OM was also calculated. After six years, differences were only observed in

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the C_{HA} stocks, which were highest in T1 (0.89 Mg ha^{-1}) and T4 (1.06 Mg ha^{-1}). The infrared spectra of HA in T1, T2 and T4 were similar to T6, with greater contribution of aliphatic organic compounds than in the other treatments. In this way, I_{LIF} decreased in the sequence T5>T3>T4>T1>T2>T6, indicating higher OM humification in T3 and T5 and more labile OM in the other treatments. Consequently, the potential of OM quality recovery in the constructed soil was greatest in treatments T1 and T4.

Keywords: humic fractions, infrared, laser-induced fluorescence, perennial grasses.

RESUMO: *FRAÇÕES E QUALIDADE DA MATÉRIA ORGÂNICA DA CAMADA SUPERFICIAL DE UM SOLO CONSTRUÍDO E VEGETADO, APÓS MINERAÇÃO DE CARVÃO. I - SUBSTÂNCIAS HÚMICAS E CARACTERIZAÇÃO QUÍMICA*

Após a mineração do carvão a céu aberto, os solos são construídos e normalmente apresentam baixos estoques e baixa qualidade de matéria orgânica (MO), sendo importante usar espécies para revegetação e recuperação da área degradada. Este trabalho objetivou avaliar a distribuição do carbono (C) em frações químicas, bem como as características químicas e o grau de humificação da MO em um solo construído após a mineração de carvão e sob cultivo de gramíneas perenes. O experimento foi instalado em 2003, com os seguintes tratamentos: Hemarthria altissima (T1), Paspalum notatum (T2), Cynodon dactilon (T3), Urochloa brizantha (T4), solo construído descoberto (T5) e solo natural (T6). Em 2009, amostras de solo foram coletadas na camada de 0,00-0,03 m e determinados os estoques de C orgânico total (COT) e de C nas frações químicas: extrato ácido (C_{HCl}), ácido fúlvico (C_{AF}), ácido húmico (C_{AH}) e humina (C_{HU}). A fração ácido húmico (AH) foi caracterizada por espectroscopia de infravermelho, e calculou-se o índice de fluorescência induzida a laser (I_{FIL}) da MO. Após seis anos, somente foram encontradas diferenças nos estoques de C da fração AH, sendo os maiores estoques observados em T1 (0,89 Mg ha^{-1}) e T4 (1,06 Mg ha^{-1}). Os espectros de infravermelho do AH de T1, T2 e T4 foram semelhantes ao do T6, com maior contribuição de compostos orgânicos alifáticos, em comparação ao AH dos demais tratamentos. Nesse sentido, o I_{FIL} decresceu na sequência T5>T3>T4>T1>T2>T6, o que indica maior humificação da MO em T3 e T5 e MO mais lábil nos demais tratamentos. Sendo assim, os tratamentos T1 e T4 evidenciaram maior potencial para recuperação da qualidade da MO do solo construído.

Palavras-chave: frações húmicas, infravermelho, fluorescência induzida a laser, gramíneas perenes.

INTRODUCTION

Mineral coal is the main fuel for power generation on the planet, producing about 40 % of the world's electricity. According to the International Energy Agency, by 2030, 44 % of the electricity will be generated by coal as fuel. In the United States, half of all electricity is generated by coal and in China, two thirds. In Brazil, the main coal reserve is located in the State of Rio Grande do Sul (RS), which holds about 90 % of the country's stocks, approximately 28 billion ton. Half of the state's coal reserves lie in Candiota city (nearly, 12.3 billion ton) (Santucci, 2009), where coal is mined in open pits by the Companhia Riograndense de Mineração (CRM), due to the favorable geological conditions, with shallow reserves (to 50 m deep).

After mining, the soils are "constructed" with the upper soil layers and mine waste without economic value, which were previously removed and stored during coal mining. Due to the processes of removal and storage of the surface horizons and the subsequent re-arrangement on the tailings for soil "construction", such soils are often compacted and contain low levels of organic matter (OM), usually less than 1 % (Corrêa, 2009), making revegetation difficult. However, revegetation of the area is a mandatory and indispensable part of the recovery process of constructed soils to raise OM contents, in view of the beneficial effects on the chemical, physical and biological soil properties. Therefore, OM has been used as a key indicator of soil quality.

Recently, some authors stated greater sensitivity of OM fractions than of total soil OM to the effects of different agricultural cropping systems. This is mainly due to the different protection mechanisms acting in the different OM fractions, which directly reduce or increase the turnover rate of these fractions (Conceição et al., 2008).

In addition to the quantitative evaluation of OM fractions, qualitative analysis techniques such as Fourier transform infrared spectroscopy (FTIR) and Laser-induced Fluorescence (LIF) can be used to characterize OM chemically, identifying the presence of important functional groups and the degree of humification of OM fractions. Thus, the fractionation and chemical analysis of OM of constructed soils can indicate the most suitable managements and/or plant species for the recovery of soil quality in an early stage, accelerating revegetation. Similarly, Schiavo et al. (2007) used FTIR to characterize the humic acid (HA) fraction of a soil degraded by clay extraction and vegetated with different species. The authors observed changes in the composition of this fraction according to the species used for vegetation.

Laser-induced fluorescence consists in exciting the soil with a laser (ultraviolet region/blue), resulting in the preferential excitation of functional groups rich in unsaturated bonds, whose concentration increases throughout the OM humification process (Milori et al., 2006). The LIF index (I_{LIF}) of OM can be calculated by dividing the value of the fluorescence spectrum area by the organic carbon content (C) of the sample. Thus, the fluorescence values are corrected to equivalent values of C, considering the humification degree as single variable between samples (Milori et al., 2006). In the surface layer of an Oxisol under no-tillage (NT), conventional tillage and minimum tillage, Favoretto et al. (2008) reported a lower I_{LIF}, i.e., a lower humification degree of soil OM under NT, due to the different tillage intensities and greater input of fresh OM under NT.

Studies on quantification of C stocks and OM quality have frequently been conducted in soils under agricultural production to evaluate the effects of different management systems on soil OM (Rosa et al., 2008; Conceição et al., 2014; Reis et al., 2014). However, there is a lack of information on C distribution in OM fractions and its quality in constructed soils. Furthermore, the coal mining area in Candiota tends to expand, which will increase the area of degraded soil. Therefore, the objective of this study was to evaluate the total soil organic carbon stock (TOC), C distribution in the chemical fractions and the chemical characteristics of OM of a soil constructed after coal mining vegetated with grasses, to indicate the best species for recovery of soil quality.

MATERIAL AND METHODS

Study area, experimental design and soil sampling

The experimental area (31° 33’ 55.5” S and 53° 43’ 30.6” W), belongs to the coal mining area of CRM in the municipality of Candiota, RS. According to Wilhelm Köppen, the climate is classified as Cfa (humid subtropical), and the mean annual temperature and rainfall are 17 °C and 1,400 mm, respectively. The experiment was installed on the surface layer (“topsoil”) of a soil constructed after coal mining, about 30 to 40 cm thick. This soil has a clay texture (Table 1) and consists mainly of the B horizon of the natural soil. The natural soil (before mining) was classified as Alfisol (NRCS, 2010). Chemical properties of the soil of the experimental area are provided by Santos et al. (2008).

The experiment was established in November/December 2003, in a complete randomized block design with four replications. The treatments were arranged in 20-m^2 plots and different grass species were implemented (in order to restore the Pampa Biome): [*Hemarthria altissima* (Poir.) Stapf and C. E. Hubbard] (T1); *Paspalum notatum* Flüggé (T2); [*Cynodon dactylon* (L.) Pers.] (T3); and [*Urochloa brizantha* (Hochst.) Stapf] (T4); T1 and T3 were planted from seedlings and the others sown, following technical recommendations.

In the beginning of the experiment, the soil was chiseled to 0.10-0.15 m. Subsequently, based on soil chemical analysis and on technical recommendations (Manual de adubação e de calagem para os estados do Rio Grande do Sul e Santa Catarina), liming was performed with 10.4 Mg ha^{-1} of lime with relative power of total neutralization 100 % and an application of 900 kg ha^{-1} of the blend 5-20-20 (NPK). Every year in October/November, ammonium sulfate (40 kg ha^{-1} N) was applied and weeds removed by hand hoeing.

Due to the high compaction degree of the constructed soil (B horizon of the Alfisol), the grass roots were mainly concentrated in the topsoil. Moreover, the soil analyses (layer 0.00-0.05 m) indicated no differences between treatments in OM contents until 2009. Since the duration of the experiment from the start until then was relatively short for a long-term experiment, soil samples were collected only in the 0.00-0.03 m layer, to detect the first effects of cover crops on soil OM fractions. With a cutting shovel, minimally disturbed soil samples were collected in each plot, preserving the aggregates. For comparative purposes, soil samples were also collected in two areas adjacent to the experiment: bare constructed soil (T5) and natural soil, with

Table 1. Particle-size fractions, texture class and bulk density (Bd) in the 0.00-0.03 m layer of a constructed soil under cover crops, a bare constructed soil and a natural soil in a coal mining area

Treatment	Clay	Sand	Silt	Texture class	Bd
	g kg^{-1}				kg dm^{-3}
T1 - Hemarthria	463.7	298.1	238.3	Clay	1.36
T2 - Paspalum	474.2	291.9	233.9	Clay	1.46
T3 - Cynodon	469.7	283.8	246.8	Clay	1.43
T4 - Brizantha	452.6	289.7	257.7	Clay	1.41
T5 - Bare soil	456.7	311.7	231.5	Clay	1.46
T6 - Natural soil	227.2	483.6	289.1	Loam	1.47

predominance of native vegetation of the Pampas Biome (T6). Due to the high degree of compaction and degradation of the constructed soil in the area adjacent to the experiment (T5), there was no spontaneous plant growth, and the area was maintained without vegetation throughout the experimental period. The air-dried samples were crumbled and sieved (<2.00 mm). Undisturbed soil samples were collected in steel cylinders (height 3.00 cm, diameter 4.85 cm) from the 0.00-0.03 m layer, to determine bulk density (Bd) and calculate C stocks.

Chemical fractionation of OM

Organic matter was fractionated based on solubility in acid and alkali, according to Dick et al. (1998). To 20 g of soil, 60 mL of HCl 0.5 mol L^{-1} was added and the suspension shaken for 2 h. After centrifugation at 2500 rpm for 15 min, the acid extract was separated. The procedure was repeated two more times and the final volume quantified. Thereafter, 60 mL of NaOH 0.5 mol L^{-1} was added to the residue from acid extraction and this suspension was shaken for 3 h followed by centrifugation at 2,500 rpm for 15 min. This procedure was repeated until the supernatant was colorless. In each extraction, the alkaline extract containing the humic substances (HS) was transferred to a collection bottle and the final volume measured. In this way, HS was separated from the humin fraction (HU) (precipitated material). The HS-containing alkaline solution was acidified with a HCl solution of 4 mol L^{-1} to pH 2.0 and left to stand for 24 h. This solution was centrifuged to separate the fulvic acid (FA, supernatant) from the humic acid (HA, precipitate). Aliquots of 20 mL of acid extract, HS and FA fractions were collected for C determination. The C content in the acid extract (C_{HCl}), in the HS (C_{HS}) and the FA fraction (C_{FA}) was spectroscopically quantified, by measuring the absorbance at 580 nm after reaction with acidic dichromate solution, with 1.25 mol L^{-1} K for 4 h at 60 °C, using a standard D-anhydroglucose curve of 0 to 250 mg L^{-1} C. The TOC content was determined by a TruSpec CHN Elemental Analyzer. The C content in the HA (C_{HA}) and HU fractions (C_{HU}) was estimated by the differences: $C_{HA} = C_{HS} - C_{FA}$; and $C_{HU} = TOC - (C_{HCl} + C_{HS})$, respectively. Based on Bd and C contents, C stocks in the chemical fractions of OM were calculated, as well as its distribution as percentage of the TOC stock.

The percentage of humic acid [$HP = (C_{HA}/C_{HS}) \times 100$] and the humification ratio ($HR = C_{HA}/C_{FA}$) were calculated as proposed by Chefetz et al. (1996).

FTIR of HA fraction and LIF of soil samples

Prior to FTIR analysis, HA was purified with a HCl + HF 5 %/5 % (v/v) solution to eliminate the inorganic fraction (Dick et al., 2003). The four replications per treatment were blended to form composite samples. The purified samples were oven-dried at 60 °C for 24 h. The FTIR analysis was performed on potassium bromide pellets in the range of 4,000-400 cm^{-1}, 4 cm^{-1} resolution, 21 scans/min (Shimadzu FTIR 830) in the ratio sample:KBr 1:100. The FTIR spectra were interpreted according to Tan (1998).

Composite soil samples were ground in a mortar and pressed into pellets (diameter 1 cm, thickness 2 cm) that were inserted into a home-made apparatus for LIF measurements. The LIF index (I_{LIF}) was calculated according to Milori et al. (2006), as the ratio of the area under the fluorescence emission spectrum curve (ACF) between 475 and 660 nm and the TOC content of the sample. The ACF and TOC data were published by Leal (2011).

Statistical analysis

The results of the treatments T1 through T4 were subjected to analysis of variance and the Duncan test at 5 %. The results of T5 and T6 were not included in the statistical analysis, for not being part of the experimental design. Therefore, they were only used for comparative purposes, to monitor the recovery process of vegetated constructed soil.

The Pearson correlation coefficient (r) was obtained by the correlation between C_{HA} stocks and the I_{LIF} of the soil OM.

RESULTS AND DISCUSSION

TOC stock and C distribution in OM chemical fractions

Considering the treatments with cover crops, the TOC stock ranged from 4.60 to 5.92 Mg ha^{-1}, and no differences were observed between treatments (Table 2), probably due to the short experimental period (six years) and the fact that the four species used for revegetation were grasses. Similar C contents (in % of TOC) were reported by Sever and Makineci (2009) in the 0.00-0.01 and 0.01-0.03 m layers of a soil constructed after coal mining and vegetated with pine 17 years earlier.

Compared to T6, the TOC stock in the bare constructed soil (T5) was reduced by 9.27 Mg ha^{-1}. However, the cover crops increased the TOC stocks by 2.32 Mg ha^{-1} (mean of the four treatments) over the control treatment T5. Despite the partial recovery of TOC stocks, these results are still far from the value of the natural soil (12.20 Mg ha^{-1}) (Table 2), as similarly reported by Chatterjee et al. (2009). In the 0.00-0.10 m layer of a natural soil, the authors found about 10 Mg ha^{-1} more C than in a constructed soil after coal mining vegetated with tree species 11

Table 2. Total organic carbon stock (TOC), carbon stocks in the acid extract (C_{HCl}), fulvic acid (C_{FA}), humic acid (C_{HA}) and humin (C_{HU}), humification ratio (HR), and percentage of humic acids (HP) in the 0.00-0.03 m layer of a constructed soil under cover crops, a bare constructed soil and a natural soil in a coal mining area

Treatment	TOC	C_{HCl}	C_{FA}	C_{HA}	C_{HU}	HR	HP
	Mg ha^{-1}						
T1 - Hemarthria	5.92 a	0.18 a	0.97 a	0.89 ab	3.87 a	0.91	47.34
T2 - Paspalum	5.10 a	0.16 a	0.90 a	0.62 bc	3.42 a	0.69	40.12
T3 - Cynodon	4.60 a	0.17 a	0.87 a	0.52 c	3.04 a	0.60	36.80
T4 - Brizantha	5.37 a	0.20 a	1.08 a	1.06 a	3.03 a	1.00	49.81
T5 - Bare soil	2.93	0.14	0.73	0.18	1.88	0.27	20.17
T6 - Fallow soil	12.20	0.42	2.55	1.97	7.26	0.77	43.38

Means followed by the same letter in the column do not differ by Duncan's test at 5 %.

years before. According to the authors, the low TOC stock of constructed soil can be attributed to intense OM mineralization, leaching and to soil erosion, due to the high degradation level. In the present study, the high mean annual rainfall in the region of the experimental area (1,400 mm), together with the presence of dissolved organic compounds, may have contributed to the leaching of organic material to subsurface layers. According to Guggenberger and Kaiser (2003), about 10 to 25 % of C applied to the soil is leached into deeper layers in the form of dissolved organic material.

The C_{HCl} stock in the cover crop treatments ranged from 0.16 to 0.20 Mg ha^{-1} (Table 2), representing 3-4 % of the TOC stock (Figure 1). These treatments did not differ from each other and contained C_{HCl} stocks that were lower than in natural and higher than in the bare soil (Table 2). The main C_{HCl} components are less complex organic compounds than the humic substances, i.e., hydrophilic and acid-soluble compounds, originated from root exudates or microbial activity. The weak association of these compounds with each other and with the mineral soil matrix explains their low representation (Santana et al., 2011). The higher input of biomass and roots in the natural soil under native vegetation in comparison to the low residue input in the constructed (vegetated and bare) soil may explain the differences in C_{HCl} stocks observed in this experiment.

The C_{FA} stocks ranged from 0.87 to 1.08 Mg ha^{-1} (Table 2) and the contribution of this fraction to the TOC stock ranged from 16 to 20 % (Figure 1), and no differences were observed between treatments with cover crops. These stocks were higher than in the bare soil and lower than in the natural soil (Table 2), indicating that after six years of grass cultivation, the C_{FA} stock was partially recovered.

Unlike for C_{FA}, the cover crop treatments differed with regard to C_{HA} stocks. The C_{HA} stocks in T4 (1.06 Mg ha^{-1}) and T1 (0.89 Mg ha^{-1}) did not differ from T2 (0.62 Mg ha^{-1}). Although the residue composition was not analyzed in this study, it can be inferred that the better adaptation of *Hemarthria* and *Brizantha* species to the adverse climate and soil conditions of the experimental area increased plant biomass production and enhanced protection against soil erosion, thus contributing to a greater C accumulation in humic fractions such as HA. According to Schiavo et al. (2009), in drastically degraded soils as in mined areas, a higher OM input can raise C stocks in the most humidified OM fractions.

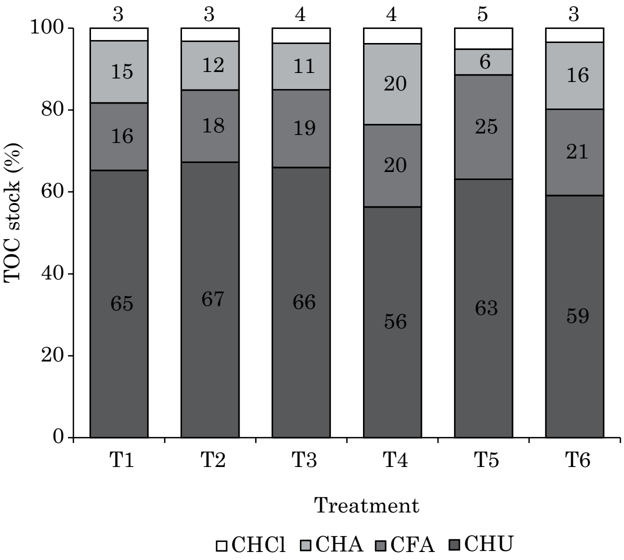

Figure 1. Proportion of chemical fractions in relation to the total soil organic carbon stock (TOC) in the 0.00-0.03 m layer of a constructed soil under cover crops, a bare constructed soil and a natural soil in a coal mining area. T1: Hemarthria, T2: Paspalum, T3: Cynodon, T4: Brizantha, T5: bare soil and T6: natural soil.

The contribution of C_{HA} to the total TOC stock was similar to that of C_{FA} and ranged from 11 to 20 % (Figure 1). According to Santana et al. (2011), the greater C_{HA} stock (a fraction composed of humic micelles with high molecular weight and size) mainly in T1 and T4, indicates the likely presence of more stabilized OM in these treatments. According to the authors, this hypothesis is based on the OM structure proposed by Kleber et al. (2007), assuming a hydrophobic portion directed into the organic micelle, and a hydrophilic portion, oriented micelle-outwards. Thus, the larger the hydrophobic portion, the greater is the micelle size and, consequently, OM stability.

Compared to T5, the C_{HA} and C_{FA} stocks of the cover crops increased in the mean by 329 and 31 %, respectively. In this sense, Pinheiro et al. (2003) observed significantly higher C_{HA} and C_{FA} contents in the 0.00-0.05 m layer of a Latossol vegetated with *Panicum maximum* in comparison to an adjacent bare soil. This was attributed to the dense root system of these plants, which, in contact with the mineral particles of the soil, can increase OM quantity and quality, favoring the C increase in the most humidified fractions. These data corroborate findings of Filcheva et al. (2000), who observed higher C_{HA} and C_{FA} stocks in the 0.00-0.05 m layer of a 25-year-old soil constructed after coal mining and vegetated with tree species, compared to bare constructed soil.

The C_{HU} stocks ranged from 3.03 to 3.87 Mg ha^{-1} (Table 2) and did not differ between treatments with cover crops. The plants provided, in the mean, a 78 % higher C_{HU} stock than T5, but 117 % lower than T6, indicating a partial recovery of the C stock in this fraction. The C_{HU} was the greatest contributor to TOC stocks, accounting for 56-67 % in the treatments with cover crops (Figure 1). The higher chemical recalcitrance of this fraction, its interaction with the soil mineral matrix and its higher biodegradation resistance (Leal, 2011), probably led to the greatest C accumulation in this fraction. In addition, the selective preservation of the HU fraction and the considerable C_{HU} stock remaining in the constructed soil even without cover crops (1.88 Mg ha^{-1}) (Table 2) may have contributed to the higher representation of this fraction in comparison to the others.

Despite the changes resulting from coal mining activities, in all treatments, including T5 and T6, the contribution of chemical fractions to the TOC stocks declined in the following sequence $C_{HU}>C_{FA}>C_{HA}>C_{HCl}$, except for T4, $C_{HU}>C_{FA} = C_{HA}>C_{HCl}$. In chemically poor soils with lower microbial activity, as in the case of constructed soils, the C_{HA} content is usually low, due to the lower intensity of OM humification (Cunha et al., 2009). However, despite the low representation of C_{HA} in this study, this fraction plays an important role as indicator of OM quality and also in the C accumulation process in the soil, essential for recovery of constructed soils.

The HR values (C_{HA}/C_{FA}) ranged from 0.27 to 1.00 (Table 2) and decreased in the sequence T4>T1>T2>T3. The highest HR in T4 occurred mainly due to the greatest C_{HA} stock in this treatment, since the C_{FA} stocks were similar between treatments. These data are in line with findings of Filcheva et al. (2000), who obtained HR values of 0.45 and 0.81, in the 0.00-0.05 m layer of constructed soils after coal mining and vegetated with tree species. According to Canellas et al. (2002), in soils with a lower intensity of humification, due to edaphic constraints and low exchangeable cation content, as is often the case in constructed soils, the HR values are usually lower than 1.

The HP values [(C_{HA}/C_{HS}).100)] ranged from 20.17 to 49.81 (Table 2) and the cover crops that induced highest HP rates were Hemarthria and Brizantha (Table 2), suggesting the formation of more humified OM. Since HP indicates the percentage of HS formed by C_{HA} and since C_{FA} stocks in the treatments did not differ, the changes in HP are mostly explained by changes in C_{HA} stocks. The HR and HP were lowest in T5, which was ascribed to the low C_{HA} stock, four times lower than the C_{FA} stock, while this ratio was approximately 1 in T1 and T4.

Spectral behavior of HA fraction and I_{LIF} of OM

The FTIR spectra of HA in the treatments T1, T2, T4, and T6 were similar, while the HA spectra in T3 and T5 differed from the others. Thus, the FTIR spectra were divided in two groups GA = T1, T2, T4, and T6; and GB = T3 and T5 (Figure 2).

In GA, the main absorption bands and their respective assignments were identified as follows: band at 3,440 cm^{-1}, attributed to the stretching of OH bonds; 2,920-2,849 cm^{-1} due to aliphatic CH stretching (CH_3 and CH_2); band at 1,690 cm^{-1} assigned to COOH vibrations and COO^- stretching; 1,630 cm^{-1} due to stretching of aromatic C=C; band at 1,510 cm^{-1} ascribed to aromatic C=C bonds; band in the region of 1,425 cm^{-1} attributed to aliphatic CH bonds; the band at 1,285 cm^{-1} due to CO stretching and OH deformation of the carboxylic group; and 1,125 cm^{-1} attributed to the presence of polysaccharides, resulting from the decomposition of organic residues and microbial metabolism (Schiavo et al., 2007).

In GB, similar absorption bands were observed. However, the intensities at 3,440 cm^{-1} in GA were higher, indicating a more rigid configuration of the OH bonds due to the slower formation of inter- and intramolecular H^+ bonds, ascribed to the higher complexity of the HA fraction (Schiavo et al.,

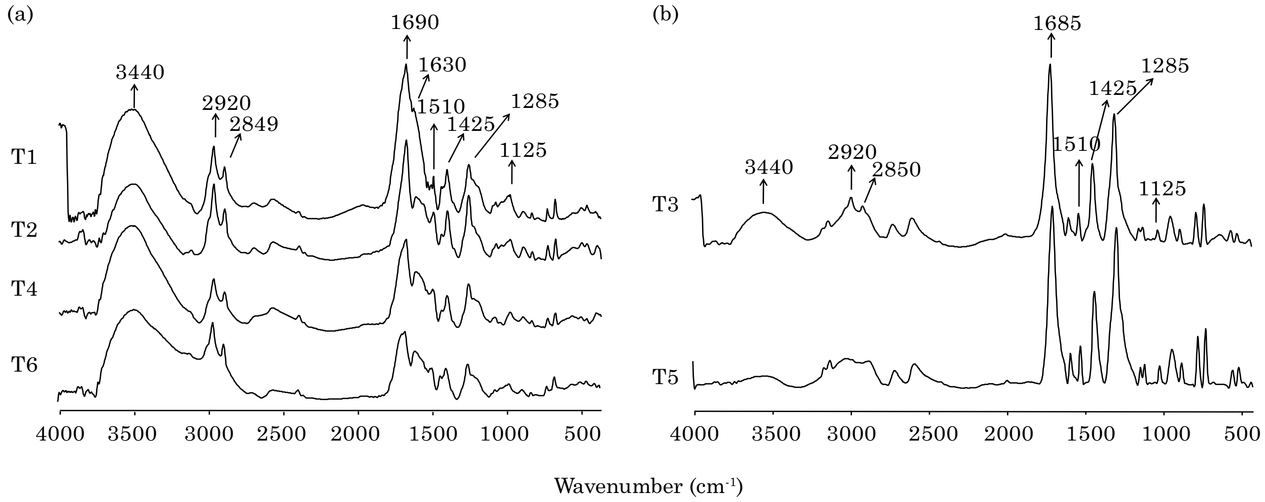

Figure 2. FTIR spectra of the humic acid fraction of the organic matter in the 0.00-0.03 m layer of a constructed soil under cover crops, a bare constructed soil and a natural soil in a coal mining area. (a) GA: Hemarthria (T1), Paspalum (T2), Brizantha (T4) and natural soil (T6). (b) GB: Cynodon (T3) and bare soil (T5).

2007). In GB, the intensities were lowest in the 2,920-2,850 cm^{-1} and highest in the 1,685, 1,425 and 1,285 cm^{-1} regions, suggesting a greater contribution of aromatic compounds than of aliphatic structures to OM composition. Low plant residue input in the soil in T3 and T5, along with the high degradation degree and high clay content of the constructed soil (in the mean 463 g kg^{-1} in the 0.00-0.05 m layer) may have caused a greater proportional contribution of aromatic groups associated with the mineral soil matrix.

The I_{LIF} varied from 3,845 to 8,905 (Figure 3) and decreased in the sequence T5>T3>T4>T1>T2>T6, indicating the highest concentration of recalcitrant compounds in the bare soil. On the other hand, the lower I_{LIF} in natural soil suggested the presence of labile organic compounds in the OM composition, derived from the constant input of organic residues into the soil. Probably due to the recent revegetation, the I_{LIF} values in the cover crop treatments were intermediate, suggesting the presence of recalcitrant compounds, rich in unsaturated bonds and also the input of labile compounds due to biomass addition to the soil.

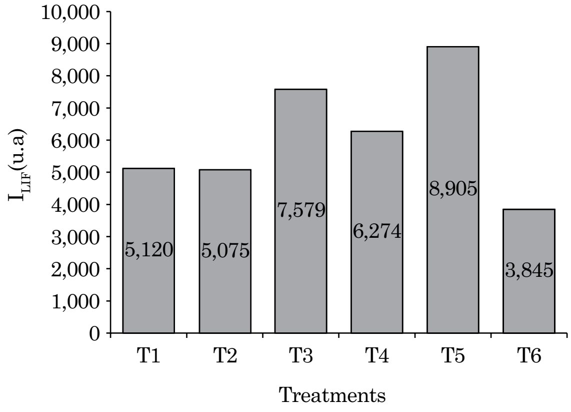

Figure 3. Laser-induced fluorescence index (I_{LIF}) of organic matter in the 0.00-0.03 m layer of a constructed soil under cover crops, a bare constructed soil and a natural soil in a coal mining area. T1: Hemarthria, T2: Paspalum, T3: Cynodon, T4: Brizantha, T5: bare soil and T6: natural soil.

These results are in agreement with those of Milori et al. (2006), who analyzed the I_{LIF} under different management systems and observed lower OM humification under NT than conventional tillage (CT), probably due to the lower contribution of labile OM and to the greater soil disturbance under CT, exposing OM to decomposition. Thus, the OM that remains in the soil is associated with minerals, more humified and stable, similarly to HU. This may have occurred in T5, where OM is more resistant to decomposition, reminiscent of the natural soil, where the HA fraction contributes with only 6 % to OM composition, while the contribution of the HU fraction is considerably higher, 63 % (Figure 1). Accordingly, the negative correlation between I_{LIF} and C_{HA} stocks (Figure 4) shows the process of decrease in the OM decomposition degree in the constructed soil after planting cover crops, which promote the input of labile organic material and C accumulation in more functionalized and less recalcitrant OM fractions, such as HA compared to the HU fraction.

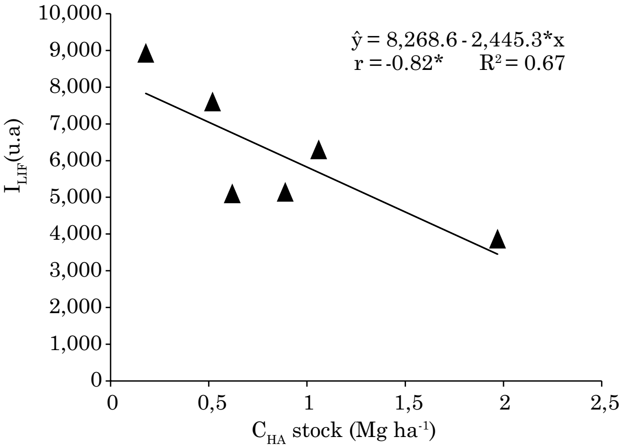

Figure 4. Relationship between the humic acid stock (C_{HA}) and laser-induced fluorescence index (I_{LIF}) of organic matter in the 0.00-0.03 m layer of a constructed soil under cover crops, a bare constructed soil and a natural soil in a coal mining area. * significant at 5 %.

CONCLUSIONS

After six years of cover crop cultivation, the total organic carbon content and carbon content in the fulvic acid, humic acid and humin fractions were partially recovered.

The species Hemarthria and Brizantha were most efficient in increasing humic acid stocks in the constructed soil. The humic acids of these species and of Paspalum have a more aliphatic and reactive character, similarly to humic acid of the natural soil.

The introduction of plants in the constructed soil decreased the humification degree of organic matter, and Cynodon is the species with lowest potential to increase organic compounds with higher reactivity. The species with greatest potential and therefore the most suitable for quality recovery of constructed soils are Hemarthria and Brizantha.

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