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STRUCTURAL FEATURES OF HUMIC ACIDS EXTRACTED FROM INTEGRATED CROP-LIVESTOCK-FOREST SYSTEM

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ABSTRACT
Soil organic matter (SOM) and their humic fractions (e.g., Humic Acids, HA) are considered a relevant soil quality indicator, due to its direct relation with biological, chemical and physical soil properties, permitting to evaluate agricultural management impacts. Soils under Integrated Crop-Livestock-Forest Systems (CLFS) have the potential to capture and sequester carbon, in the form of increasing SOM content, contributing to the mitigation of greenhouse gas emissions from agriculture. In this study aimed was characterization the HA extracted from CLFS and Native Forest (NF) soils using elemental analysis (CHN), fluorescence spectroscopy and electronic paramagnetic resonance (EPR). For this, samples of a dystrophic Red-Yellow Latosol (Oxisol) were collected from the experimental site of a research station called Embrapa Pecuária Sudeste (located in the Southeast of Brazil), five years after the implementation of the agricultural integrated systems. Results showed positive correlation between HA humification index with semiquinone-type free radical present in these soils ($R = 0.69$). Therefore, these results showed that HA from these integrated systems have a more stable and humified soil organic matter than in native forest, contributing to soil carbon compounds with higher chemical stability and possibly with longer lifetime in the soil.
Key words: Humic Acid; Characterization; Humification

INTRODUCTION

Soils under Integrated Crop-Livestock-Forest Systems (CLFS) potentially can capture and store carbon (C) as soil organic matter (SOM), contributing to the reduction of greenhouse gases[1], but it necessary to increase number of field sites evaluation with long duration experiments as well as to promote deeper soil analysis to better understanding of soil C storage mechanisms and about C compounds lifetime estimate in the systems. In addition, CLFS benefit from the more efficient use of natural and artificial resources, such as: improving soil and water quality, using fertilizers and agrochemicals efficiently, providing greater global productivity of rural properties, diversifying production systems, and minimizing possible negative impacts of climate change[2,3]. According to Minasny and collaborators[4], in the first twenty years after the use of appropriate management systems, soil carbon rates increased compared to the initial C stock. These authors have demonstrated that this system there is a potential to increase soil organic carbon (SOC) on agricultural land. The challenge is to find agricultural technologies that will further improve soil condition and increase C content, enabling sequestration and lowering emissions.

SOM plays an important role in the sustainability of production systems, as it is related to C and nutrient cycling, water retention, among other factors and is, thus, acting directly on issues of global climate change and agronomic studies. The structural features of SOM and their chemical fractions (e.g. humic acids - HA) are essential to understand the cycling and the arrangement of nutrients in the soil, since this matrix accumulates three times more C than the amount in the atmosphere and in the terrestrial vegetation. In this study aimed was characterization the HA extracted from Integrated

Crop-Livestock-Forest Systems (CLFS) and Native Forest (NF) soils using elemental analysis (CHN), fluorescence spectroscopy and electronic paramagnetic resonance (EPR).

MATERIAL AND METHODS

Study area

The field experimental area of 30 ha was in the Research Center of "*Embrapa Pecuária Sudeste*", São Carlos, São Paulo State, Brazil (21° 57'S, 47° 50'W) at 860m altitude, and the soils were classified as Red-yellow Latosol (Haplorthox by Soil taxonomy). The description of the CLFS was implanted with pasture (Piatã grass, *Urochloa brizantha* sin. *Brachiaria brizantha*) with rotating crops (corn, Zea Mays L. var.) every three years, and 333 eucalyptus trees per ha (Eucaliptys urograndis clone GG100). The NF is a reserve area of semi-deciduous Forest (Atlantic Forest, in a transition zone to Savannah biome, called Cerrado, in Brazil). For the CLFS samples, the sampling occurred at distances of 0.0 m and 7.5 m from the tree lines.

Sampling and extraction of the humic acids from soils

Soil sampling was carried out between February and April 2016, after five years of field experiment implantations. Composite samples were prepared at depths of 0–20, 20–30, 30–40, 40–60 and 60–100 cm for isolation of chemical fractions (HA) using the procedure recommended by the International Humic Substances Society[5]. Detailed information regarding fractionation methodology can be found in Tadini and collaborators [6].

Elemental analysis

The elemental composition of the whole soils and HA samples were analyzed by a C, H and N elemental analyzer (Perkin Elmer model 2400).

Fluorescence Spectroscopy

Fluorescence measurements were performed with a luminescence spectrometer (Model LS50B, PerkinElmer), using aliquots of 12.5 mg L^{-1} (pH 8.0) solutions of HA dissolved in 0.05 mol L^{-1} $NaHCO_3$. The methodology proposed by Milori and collaborators[7] was employed for determined the humification index (A_{465nm}). Emission-Excitation model (EEM) was acquired in the scan range between 240-700 nm for emission and 220-510 nm for excitation, according the Tadini and collaborators[6].

Electronic Paramagnetic Resonance (EPR)

The Bruker EMX spectrometer operating in the X band (9 GHz) was used of determining the EPR spectra of the HA samples. The conditions and determination were following recommendation by Simões and collaborators[8].

RESULTS AND DISCUSSIONS

Figure 1 show the C content from whole soil (a) and HA (b) samples from integrated systems (CLFS) and native forest (NF). Figure 1a showed a higher amount of carbon in the CLFS than in the NF, demonstrating the potential for carbon sequestration in these integrated systems as supported and described by Bernardi and co-authors[9]. In Figure 1b observed C content of HA ranges from 45 to 55% of all systems and the distance from the tree line (0.0m and 7.5m for CLFS) did not influence the accumulation of C content in the whole soil (Figure 1a) and the humic fraction (Figure 1b).

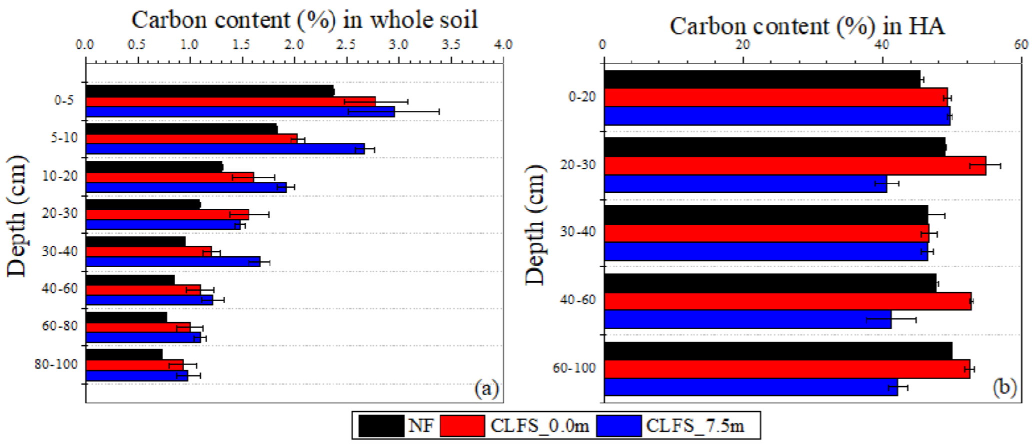

Figure 1. Carbon content (C%) of whole soil (a) and HA (b) samples from Native Forest (NF) and Integrated Crop-Livestock-Forest Systems (CLFS).

The results by EPR showed range from $8.8x10^{+17}$ to $4.8x10^{+18}$ g C^{-1} semiquinone-type free radical for all samples evaluated in this study, which the CLFS have more values than NF. In the literature, these values are higher range found in Gonzaléz-Pérez and collaborators[10] for soils of the Oxisol soil and other studies in the literature, which it shown semiquinone-type free radical values ranging from $0.3x10^{+16}$ to $2.4x10^{+18}$ g C^{-1} for soil HA[10-12]. Figure 2, showed the positive correlation (R=0.69) with Humification Index (A_{465nm}) vs. EPR (g C^{-1} spin) from CLFS and NF samples. Thus, this result conclude the HA there are more stable organic matter with complex structure (such as aromatic groups) and humified in the deeper layers.

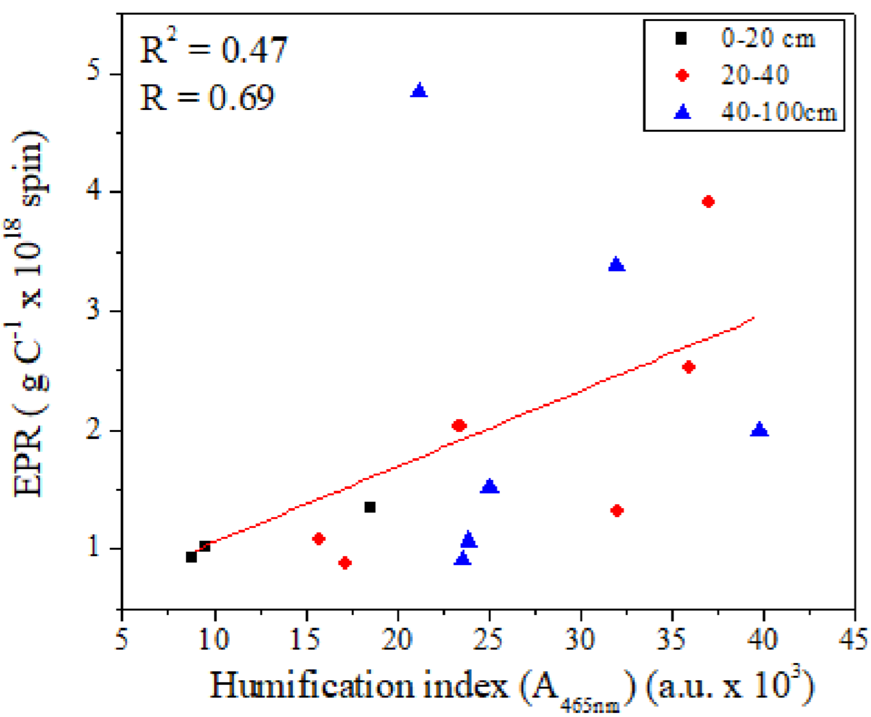

Figure 2. Correlation graph with Humification Index (A_{465nm}) *vs.* EPR (g C^{-1} spin) from HA samples of the NF and CLFS systems evaluated in this study (highlighted square black, red point and blue triangle represent the 0–20, 20–40 and 40–100cm layers, respectively).

CONCLUSIONS

The integrated Crop-Livestock-Forest systems (CLFS) showed positive correlation between HA humification index with semiquinone-type free radical present in these soils (R = 0.69). Therefore, the HA of these integrated systems have a more stable and humified soil organic matter than in native forest, contributing to soil carbon compounds with higher chemical stability and possibly with longer lifetime in the soil.

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REFERENCES

BERNARDI, A. C. C.; ESTEVES, S. N.; PEZZOPANE, J. R. M.; ALVES, T. C.; BERNDT, A.; PEDROSO, A. F.; RODRIGUES, P. H. M.; OLIVEIRA, P. P. A. Soil carbon stocks under integrated crop-livestock-forest system in the Brazilian Atlantic Forest region. In: WORLD CONGRESS OF SOIL SCIENCE, 21. **Proceedings…** Rio de Janeiro, Brazil: SBCS, v. II, p.483, 2018.

CONCEIÇÃO, M. C. G.; MATOS, E. S.; BIDONE, E. D.; RODRIGUES, R. A. R.; CORDEIRO, R. C. CHANGES in Soil Carbon Stocks under Integrated Crop-Livesctok-Forest System in the Brazilian Amazon Region. **Journal Agricultural Science**, v.8, p.904-913, Sep. 2017.

GONZÁLEZ PÉREZ, M.; MARTIN-NETO, L.; SAAB, S. C.; NOVOTNY, E. H.; MILORI, D. M. B. P.; BAGNATO, V. S.; COLNAGO, L. A.; MELO, W. J.; KNICKER, H. Characterization of humic acids from a Brazilian Oxisol under different tillage systems by EPR, 13C NMR, FTIR and fluorescence spectroscopy. **Geoderma**, v.118, p.181–190, 2004.

GONZÁLEZ PÉREZ, M.; MARTIN-NETO, L.; COLNAGO, L.A.; MILORI, D. M. B. P.; CAMARGO, O. A.; BERTON, R.; BETTIOL, W. Characterization of humic acids extracted from sewage sludge-amended oxisols by electron paramagnetic resonance. **Soil and Tillage Research**, v.91, n.1–2, p.95-100, 2006.

MILORI, D. M. B. P.; MARTIN-NETO, L.; BAYER, C.; MIELNICZUK, J.; BAGNATO, V. S. Humification degree of soil humic acids determined by fluorescence spectroscopy. **Soil Science**, v.167, p.739-749, 2002.

MINASNY, B.; MALONE, B. P.; MCBRATNEY, A. B.; ANGERS, D. A.; ARROUAYS, D.; CHAMBERS, A.; CHAPLOT, V.; CHEN, Z.; CHENG, K.; DAS, B. S.; FIELD, D. J.; GIMONA, A.; HEDLEY, C. B.; HONG, S. Y.; MANDAL, B.; MARCHANT, B. P.; MARTIN, M.; MCCONKEY, B. G.; MULDER, V. L.; O'ROURKE, S.; RICHER-DE-FORGES, A. C.; ODEH, I.; PADARIAN, J.; PAUSTIAN, K.; PAN, G.; POGGIO, L.; SAVIN, I.; STOLBOVOY, V.; STOCKMANN, U.; SULAEMAN, Y.; TSUI, C.; VÅGEN, T.; WESEMAEL, B.; WINOWIECKI, L. Soil carbon 4 per mille. **Geoderma**, v. 292, p. 59-86, 2017.

SÁ, J. C. M.; LAL, R.; CERRI, C. C.; LORENZ, K.; HUNGRIA, M.; FACCIO CARVALHO, P. C. Low-carbon agriculture in South America to mitigate global climate change and advance food security. **Environment International**, v.98, p.102-112, 2017.

SIMÕES, M. L.; SILVA, W. T. L.; SAAB, S. C.; SANTOS, L. M.; MARTIN-NETO, L. Caracterização de adubos orgânicos por espectroscopia de ressonância paragmagnética eletrônica. **Revista Brasileira da Ciência do Solo**, v.31, p.1319-1327, 2007.

SOARES, M. B.; FREDD, O. S.; MATOS, E. S.; TAVANTI, F. R.; WRUCKE, F.; LIMA, J. P.; MARCHIORO, V.; FRANCHINI, J. C. Integrated production systems: An alternative to soil chemical quality restoration in the Cerrado-Amazon ecotone. **Catena**, v.185, 104279, 2020.

SWIFT, R. S. Organic matter characterization. In: SPARKS, D. L.; PAGE, A. L.; HELMKE, P. A.; LOEPPERT, R. H.; SOLTANPOUR, P. N.; TABATABAI, M. A.; JOHNSTON, C. T.; SUMMER, M. E. (Eds). **Methods of soil analysis:** Chemical methods. Madison: Soil Science Society of America, 2009. Cap.35, p.1018-1020.

TADINI, A. M.; NICOLODELLI, G.; SENESI, G. S.; ISHIDA, D. A.; MONTES, C. R.; LUCAS, Y.; MOUNIER, S.; GUIMARAES, F. G. E.; MILORI, D. M. B. P. Soil organic matter in podzol horizons of the Amazon region: Humification, recalcitrance, and dating. **Science of the Total Environment**, v.613/614, p.160-167, 2018.

WATANABE, A.; MCPHAIL, D. B. M.; MAIE, N.; KAWASAKI, S.; ANDERSON, H. A.; CHESHIRE, M. V. Electron spin resonance characteristics of humic acids from a wide range of soil types. **Organic Geochemistry**, v.36, n.7, p.981-990, 2005.