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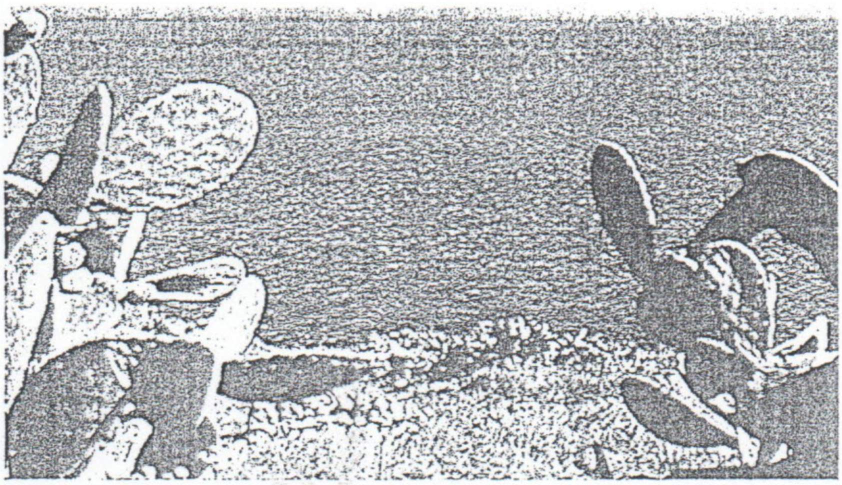

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Role of humic substances in sustainable agriculture and environment: field and molecular scale results

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1. INTRODUCTION

Questions associated to natural organic matter (NOM) and their main constituents, the humic substances, are of immense importance due to several functions of NOM in different terrestrial, aquatic and aerial environments. Nowadays, this importance has been extraordinarily intensified by association with C cycle that has a direct relationship with increase of greenhouse effect and climate changes in the Planet. Besides food and fiber productions from agriculture, the Brazil is engaged in biofuels program to substitute oil derivatives, as ethanol, from sugar-cane (last year Brazil produced 17 G liters of ethanol used mainly as car fuel, using just 3 M ha of a 100 M ha yet available to be cultivated), and started a biodiesel program with a huge potential of 300 G liters of biodiesel just in savanna region of country, without cut any tree in Amazonian rainforest. So agribusiness plays a very important role in the economy, society and environment. Specifically soil characteristics of Brazil gives to organic matter a fundamental role regarding questions associated to soil fertility (importance increased due to predominant kaolinite clay soil with low cation exchange capacity), aggregation of soil particles, reduction of erosion (generally very strong in tropical regions due to intense rainfall), and others naturally important aspects as interactions with pesticides and metallic ions, contribution to trihalomethane formation and water quality. Also due to some of these climate characteristics Brazil have increased strongly adoption of soil conservative practices, include no-till or direct drilling. Nowadays Brazil has around 22 M ha under no-till, more than 40% of total grains cultivated area. Besides contributions to soil fertility, local and regional environment, no-till have proven to be successful in promoting soil carbon sequestration in Brazil (Bayer et al., 2006). In this work will be described some important field studies on areas under soil carbon sequestration, including areas under no-till with grains and pastureland grass in Brazil, with an estimative of potential of these activities to mitigate greenhouse effects. To follow dynamic and reactivity of humic substances and SOM in these areas some spectroscopic tools, as Electron Spin Resonance (ESR), UV-Vis fluorescence and laser induced fluorescence, were applied helping to explain several reactions in the soil and environment.

2. MATERIALS AND METHODS

Experiments of tillage effects

The study was based on two long-term experiments, one established in 1992 near the town of Luziânia in the Brazilian state of Goiás, the second setup in 1994 near the town of Costa Rica in the Brazilian state of Mato Grosso do Sul, both at Central region of country. The experimental treatments were three tillage systems (conventional tillage (CT), reduced tillage (RT), and no-till (NT)) arranged in a complete randomized block design with three replicates. The soil was left fallow during the dry season and cultivated with soybean, maize, or cotton in the summer. No-till causes minimal soil disturbance, with crops being directly sown in summer on the residues of the weeds that grew up during the fallow period. Adjacent native Cerrado areas at each site were included in this study to represent the original soil conditions.

Experiments on pastureland

This study refes to a long-term experiment located in São Carlos city, state of São Paulo, Brazil, at experimental farm of Brazilian Corporation for Agricultural Research (Embrapa), at Southeast Cattle Center, on a Brachiaria decumbens pastureland, established 27 years ago, following a corn field. Soil was a low fertility, acid Oxisok, with 25% clay content. Treatmente were: T00 – 27 years under Brachiari decumbens pasture, without lime and fertilizer additions; t0- without surface liming, but with 400 kg y^{-1} N- ammonium sulfate and K_2O; t2m- 2 t ha^{-1} surface limestone with same t0 NK fertilizer use and 1 t ha^{-1} reinforcement of limestone; t4sa- 4 t ha^{-1} of surface limestone without NK fertilizer use; CV- dense cerrado vegetation in transition to a native mesophyle semideciduous tropical forest and tilled soil- pasture area changed to crop, with 0-20 cm depth till.

Organic Carbon and Elemental Analysis Measurements

Total carbon analysis were performer in soil and humic acids (HA) samples using a total carbon analyzer (LECO model CR 412) and CHN (Perkin Elmer model), respectively, and also using the Walkley-Black wet combustion method. Soil bulk density was assessed and used to calculate the soil C stocks

Humic Acids Extraction and Purification

HA samples were extracted from soil samples and purified according to the International Humic Substances Society (IHSS) method. HA samples analyzed were extracted from two depths: 0-10 cm and 10-20 cm, in all treatments reported before.

Spectroscopic Analyses

Electron Spin Resonance (ESR). The ESR measurements of HA were performed in a Bruker EMX spectrometer operating at 9 GHz (X- band) at room temperature. The relative concentrations for semiquinone-type free radicals were obtained using Singer's method (Martin-Neto et al., 2001) using as a secondary standard a ruby crystal calibrated with strong pitch reference of know free radical content, provided by Bruker.

Ultraviolet-Visible light fluorescence. Fluorescence spectra in the emission and synchronous-scan excitation modes were acquired in a Perkin Elmer LS-50B luminescence spectrometer. Each HA sample was dissolved in 0.05 mol L^{-1} NaHCO3 with 20 mg L^{-1} concentration, and pH 8 (Milori et al., 2002).

Laser Induced Fluorescence (LIF). Soil samples of approximately 0.5 g as pellet of 1 cm diameter and 2 mm thickness, were prepared and inserted ito a home assembled apparatus to run LIF measurements (Milori et al., 2006). Samples were excited with 458 nm radiation emitted by an argon laser equipment (Coherent Innnova 90-6), with 300 mW exit power.

3. RESULTS AND DISCUSSION

In Figure 1 is possible to observe variations in total carbon content in areas under different tillage practices. As can be seen there is an increase in carbon content in area managed under no-till in comparison to native Cerrado or under conventional tillage area. Based in these two experimental areas and several other data from literature it was estimated that savanna region of Brazil has a potential to accumulate 0.35 Mg C/ha/year (Bayer et al., 2006). Considering the large potential area to cultivation in savanna region (Cerrado) of Brazil a 100 M ha under no-till could remove from atmosphere a 0.126 Pg CO2/year, around 10% of total Planet emission due to deforesting and land use (Lal et al., 2004).

Analysis of fluorescence induced by laser (LIF) of whole soil samples from these areas under different tillage practices demonstred a clear possibility of identify humification degree of soil organic matter, confirming potential of these new tool to work on samples without any chemical or physical extraction procedures of SOM (Milori et al., 2006). In soil samples from areas under no-till in 0-5 cm it was identified a decrease in humification degree compared with conventional tillage practice (data not shown), in agreement with previous observations made using humic acids (Milori et al., 2002).

The work with pastureland was undertaken to measure the carbon storage potential of a 25% clay content Oxisol under well managed tropical grass pasture, *Brachiaria decumbens*, established 27 years ago after corn crop, in comparison to native dense Cerrado vegetation, in São Carlos, SP, Brazil.. Greatest SOM content occurred under pastureland in the 10 cm surface soil layer (data not shown). Compared to native Cerrado, the C stocks in pasture increased from 1.7 to 3.5 Mg C ha^{-1} y^{-1} for the 0-100 cm layer, depending on nitrogen availability. Changing the soil management from Cerrado vegetation to good managed grass pasture will result in an annual sequestration rate ranging from 6.1 to 12.8 Mg CO_2 ha^{-1} y^{-1}, which corresponds to 8.3 to 17.3% of the total emissions from deforestation and land use change worldwide.

ESR studies (Figure 2) demonstrated that HA from pasture soil had higher semiquinone-type free radicals than from Cerrado soil under native vegetation and tilled soil. Higher semiquinone-type free radical content occurred in t2m and t4sa treatments, more probably due to lime presence. Lime use is known to increase soil pH, stimulating soil microbial activity and generating more humified humic acids. Alternatively or simultaneously the Ca-HS bond could also contribute to generate more humified humic acids. These ESR data agreed with Fluorescence Spectroscopy of dissolved HA (data not shown).

4. CONCLUSIONS

Compared to conventional tillage, no-till management and pastureland areas increased the C stock in Cerrado Oxisols. Considering the large Cerrado land area which is, and could be, used for cropland and pasture (about 200 million hectares), the adoption of no-till management and well managed pastureland has the potential to turn Cerrado soils into a significant atmospheric C sink and

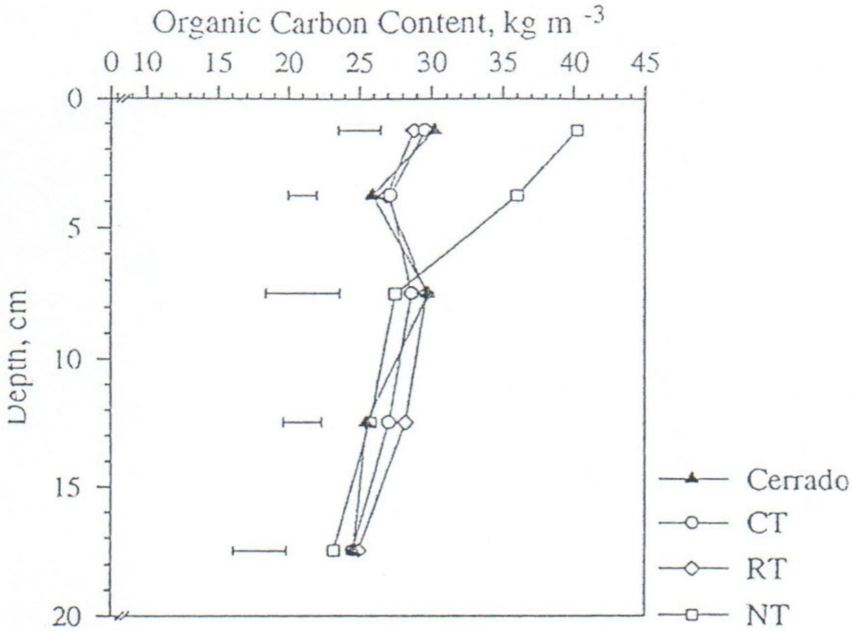

Figure 1- Organic C concentration as affected by tillage systems in the Costa Rica clayey Oxisol. Horizontal bars refer to the LSD obtained by Tukey's test ($P \leq 0.05$). Cerrado- is native savanna soil; CT- conventional tillage; RT- reduced tillage and NT- no-till. (Adapted from Bayer et al., 2006).

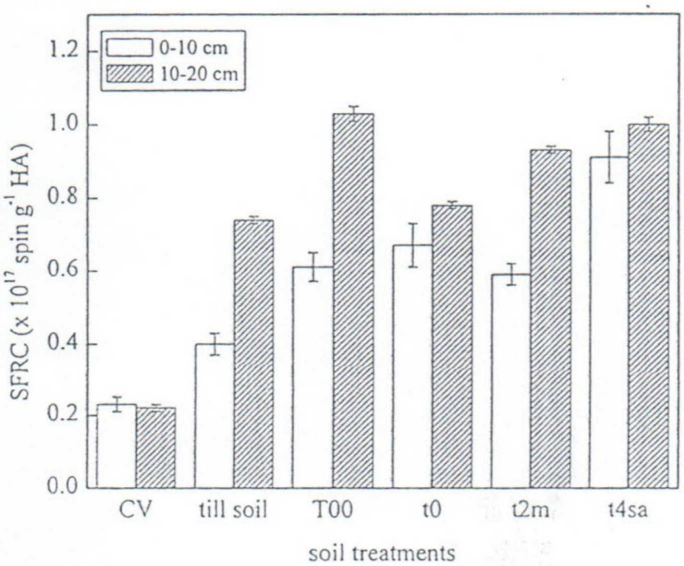

Figure 2 - Level of semiqüinone-type free radical [spins g^{-1} ($x10^{17}$)] of soil humic acids determined by Electron Spin Resonance (ESR) under different soil treatments in the pastureland Brachiaria Decumbens areas.

contribute to mitigating global climate changes in addition to increased food and biofuel productions.

The spectroscopic analysis permitted identify changes in humic substances due to tillage effects, including use of no-till, in areas with grains, and liming and fertilization of pastureland, generated new insights about structure and reactivity of humic acids. The combination of long-term field experiments, extractions and fractionation of humic substances and spectroscopic analysis was very fruitful permitting generation of agronomic and environmental interest results and molecular scale humic acids data.

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