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Evaluation of the Humification Degree of Humic Acids Extracted from Soil Under Application of Wastewater by Fluorescence Spectroscopy and Laser-Induced Fluorescence (LIF)

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1. Introduction

Among activities developed by man, agriculture is undoubtedly one of the sectors that consume more water for irrigation. In Brazil, agriculture consumes about 61% of the total freshwater [1]. Different ways were tried by contemporary societies to solve or minimize the lack of this feature, however the use of wastewater from systems of sewage treatment by biological processes has been shown one of the most interesting solution. Another important point is that wastewater can be act as a soil conditioner providing nutrients in a sustainable way.

Despite these advantages, application of wastewater in soil requires careful monitoring because of the possibility of soil contamination and changes in organic matter that could cause serious implications for the crop where it is applied.

The UV-Visible fluorescence spectroscopy provides information about molecular structures, being sensitive to the presence of heavy metals and organic contaminants. For this reason, it can be an interesting tool to evaluate changes in soil organic matter (SOM) after long term application of wastewater.

The Laser-Induced Fluorescence (LIF) applied to soils is a new methodology that has proven effective in the analysis of SOM, providing results without the chemical fractionating process, allowing analysis of SOM near natural conditions [2].

The objective of this study was to evaluate changes in humification degree of organic matter (OM) in soils submitted to application of wastewater using fluorescence spectroscopy.

2. Matherial and Methods

Soil in this study is a Typic Hapludults, texture medium clay, cultivated with Tifton 85 Bermudagrass. Wastewaters were collected from the municipality of Lins in the State of Sao Paulo.

Effects of wastewater application were compared to reference treatments. The experiment was divided in six treatments: SI – without irrigation and without nitrogen as mineral fertilizer (NMF); E100 - irrigation with effluent and 100% (520 kg ha^{-1} $year^{-1}$) of the recommended dose of NMF for the Bermudagrass Tifton – 85; E66 - irrigation with effluent and 66% (343.2 kg ha^{-1} $year^{-1}$) of the NMF; E33 - irrigation with effluent and 33% (171.6 Kg ha^{-1} $year^{-1}$) of the NMF; E0 - irrigation with effluent and 0% (0 kg ha^{-1} $year^{-1}$) of the NMF; W100 - irrigation with water for consumption and 100% (520 Kg ha^{-1} $year^{-1}$) of the NMF.

In this study, it was evaluated humic acid and whole soil. To obtain the HA was performed extraction and fractionation of humic components of soil, using the standard procedure suggested by the International Humic Substances Society (IHSS). For whole soil analyses, the soil samples were air dried, ground and sieved through a mesh of 212 μm. After this, were prepared soil pellets using pressure 10 ton.

Fluorescence spectroscopy. Each HA sample was dissolved in a solution of sodium bicarbonate ($NaHCO_3$) 0,05 mol L^{-1} with a concentration of 20 mg L^{-1}. This concentration was used to minimize the effect of reabsorption of fluorescence and reduce interactions between molecules. The final pH of the solutions was around 8.0. After preparation of solutions, the spectra fluorescence were obtained in the modes of emission, excitation-emission (3D) and synchronous scan, according to the methodology proposed by [3, 4, 5].

Laser induced fluorescence (LIF) spectroscopy. The experimental setup of LIF system is shown in Milori et al. [2]. Humification degree (H_{LIF}) of SOM was estimated using the ratio of area under fluorescence emission spectra (excitation at 458 nm) and total organic carbon concentration (COT).

3. Results and Discussion

Humification degree of humic acid was assessed using three methodologies: Milori (A_{465}), Zsolnay (A_4/A_1) and Kalbitz (I_{468}/I_{374}). The correlation among the methodologies was higher than 95%. The results of humification degree obtained using methodology of Milori et al. [4] for different depths and treatments are shown in Figure 1.

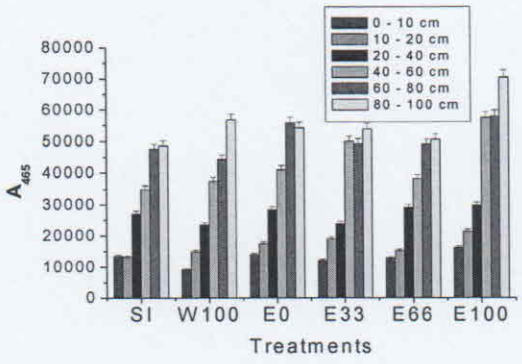

Figure 1: Values of humification index (A_{465}) obtained for the HA in solution using the methodology of Milori et al. [4]

Irrigation with wastewater caused a slight increase in the humification degree of HA for all depths in all treatments when compared with W100 treatment.

Three-dimensional excitation-emission matrix (EEM) fluorescence spectra of the HA are shown in Figure 2.

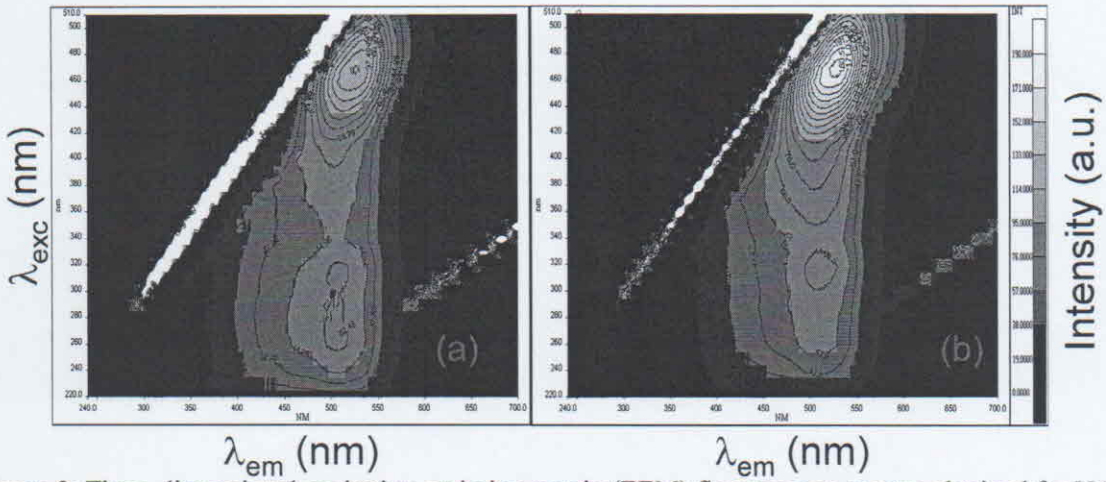

Figure 2: Three-dimensional excitation-emission matrix (EEM) fluorescence spectra obtained for HA in the layer of 0-10 cm of: (a) W100 - irrigation with water for consumption and 100% of the NMF; and (b) E100 - irrigation with effluent and 100% of NFM

Comparing the treatments W100 and E100, the application of wastewater leads to a significant increase in the intensity of fluorescence emission, caused by an increase in the concentration of structures bigger and more complexes related with increasing of humification degree.

The results of humification degree of SOM obtained using LIF for different depths and treatments are shown in Figure 3.

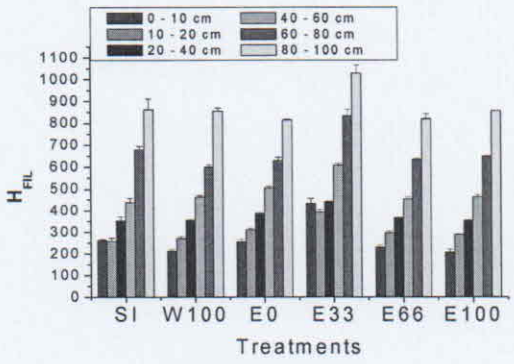

Figure 3: H_{LIF} values obtained for all soil samples whole Typic Hapludults in the profile of the sampling

For LIF spectroscopy using whole soil, irrigation with wastewater during four years also increased the humification degree of soil organic matter. Similar what was observed for HA in solution.

4. Conclusions

The application of wastewater seems to lead an increase of humification degree of soil organic matter, even when compared to irrigation using fresh water. Probably, fresh organic matter from wastewater is increasing microbiological activity and, this high activity is taking to a decreasing of soil carbon by degradation of stable fractions [6].

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