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The importance of humin in soil characterisation: A study on Amazonian soils using different fluorescence techniques

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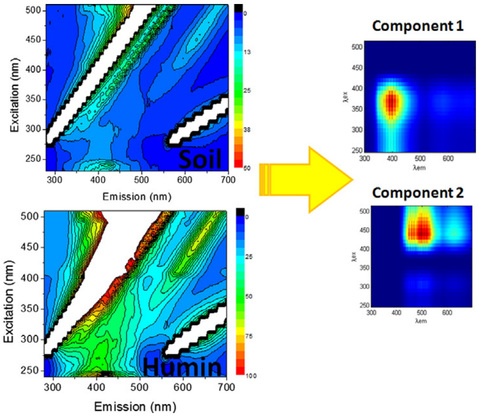
HIGHLIGHTS

- Two fluorophores were observed in the structures of humin and the whole soil.
- The fluorescence of the soil is strongly related to the fluorescence of the humin.
- Humin fraction can represent 80-93% of fraction of the Amazonian SOM.

GRAPHICAL ABSTRACT



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ABSTRACT

Soil organic matter (SOM) is a complex mixture of molecules with different physicochemical properties, with humic substances (HS) being the main component as it represents around 20–50% of SOM structure. Soil of the Amazon region is considered one of the larger carbon pools of the world; thus, studies of the humic fractions are important for understanding the dynamics of organic matter (OM) in these soils. The aim of this study was to use laser-induced fluorescence spectroscopy (LIFS) and a combination of excitation–emission matrix (EEM) fluorescence with Parallel Factor Analysis (CP/PARAFAC) to assess the characteristics of humin (HU) extracted from Amazonian soils. The results obtained using LIFS showed that there was an increasing gradient of humification degree with depth, the deeper horizon presenting a higher amount of aromatic groups in the structure of HU. From the EEM, the contribution of two fluorophores with similar behaviour in the structures of HU and whole soil was assessed. Additionally, the results showed that the HU fraction might represent a larger fraction of SOM than previously thought: about 80–93% of some Amazon soils. Therefore, HU is an important humic fraction, thus indicating its role in environmental analysis, mainly in soil analysis.

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1. Introduction

Soil organic matter (SOM) plays an important role in environmental sustainability, particularly in the carbon cycle in soil, which has been attracting considerable interest due to carbon accumulation/sequestration in soils. The main components of SOM are the humic substances (HS), which have defined physical and chemical characteristics, and are fractionated into humic acids (HA), fulvic acids (FA) and humin (HU) according to their solubility (Stevenson, 1994).

Currently, there is scarce information available in the literature on the structure of HU compared to the other two fractions, even though the HU fraction makes up between 20% and 50% of the HS present in soil (Rice and MacCarthy, 1989; Stevenson, 1994; Rice, 2001; Yang et al., 2004; Nichols and Wright, 2006). HU is defined as the extracted portion that remains insoluble in aqueous solutions at all pH levels, and is operationally treated as the remaining SOM residue (Stevenson, 1994; Rice, 2001). This humic fraction is also known to strongly bind to hydrophobic organic compounds, and to present unchanged biopolymers, such as lignin and polysaccharides, in its structure (Nearpass, 1976; Chiou et al., 2002).

Rice and MacCarthy (1989) demonstrated that HU had the characteristics of a lipid mixture of humic structures and mineral compounds (insoluble residue). Rice (2001) demonstrated the importance of a deeper knowledge of HU structures and their interactions with soil, allowing a better understanding of the role of SOM in carbon sequestration. Recent studies showed that the stability of HU in soil is not due to low humic reactivity, but to the agglomeration of humic materials responsible for particle aggregation mechanisms in the soil, which may represent the majority of the carbon present in the humified soil (Benites et al., 2003; Lombardi et al., 2006).

According to Stevenson (1994), HU consists of a variety of materials, such as HA bound to mineral materials (clay) that were not separated in the extraction process. It is humic materials with high carbon content (more than 60%) that are insoluble in a basic medium, fungal melanins and/or paraffinic substances. According to this author, the soil HU can be divided into two fractions based on the separation of their microaggregates, which consists of a modified lignin polymer and other subcellular particles of plants retained as microaggregates.

The determination of the optical properties of organic matter (OM) is an important method for the structural understanding of its fractions. Spectroscopic techniques, such as EPR, FTIR and ^{13}C NMR spectroscopies, require the extraction and fractionation of the HS, making the soil analysis a limited, laborious process. However, the laser-induced fluorescence spectroscopy (LIFS) technique applied to soils is a new technique that has been shown to be effective in the analysis of SOM. It provides fast and sensitive results and it can be applied to samples without pre-treatment (Milori et al., 2006; Martins et al., 2011). Using LIFS, it is possible to determine the humification index of a sample, which is related to the concentration of rigid structures within, like quinone groups and aromatic rings.

The three-dimensional fluorescence spectroscopy or emission–excitation matrix (EEM) is a selective and sensitive spectroscopic technique, whose spectra allow the composition and configuration of OM and HS of various origins to be determined (Coble, 1996; Filella et al., 2005; Ziegelgruber et al., 2013). The intensity, shift and position of the fluorescence peaks can be related to the presence of electron donor and/or acceptor groups, polycondensation, aromaticity, heterogeneity and chemical properties (Chen et al., 2002; Peuravuori et al., 2002; Sierra et al., 2005). Thus, the use of this technique on environmental samples, especially humic fractions, provides important data concerning the chemical structure of the present fractions. The EEM is a more complete technique of fluorescence analysis, and it allows a simple set or a mixture of fluorescent components present in humic fractions to be evaluated, thus providing a fingerprint of the sample (Chen et al., 2002; Sierra et al., 2005; Rodríguez et al., 2014; Zhu et al., 2014). Moreover, the EEM spectrum can be used for the qualitative and quantitative characterisation of OM when combined with advanced multivariate statistical techniques, such as Parallel Factor Analysis (CP/PARAFAC), which can decompose the complex signal of the fluorescence spectra onto the combination of simple components. EEM-CP/PARAFAC is a potentially useful technique for the evaluation of complex samples, such as HS. This technique allows for the evaluation of the decomposition of the fluorescent-independent components of the complex EEM, which represent groups such as fluorophores (Luciani et al., 2008; Santín et al., 2009; Ziegelgruber et al., 2013; Zhu et al., 2014). Although this technique has not yet been applied to the characterisation of the HU fraction, it can provide further information on the optical characterisation of HU and its dynamics in the environment.

To the best of our knowledge, there are no published studies using LIFS and EEM-CP/PARAFAC techniques with the objective to discover the structural analysis of HU fraction. The few studies found in the literature report on HU behaviour in adsorption and absorption processes with organic compounds and/or metals using chromatographic analysis, infrared spectroscopy and thermogravimetry (Ferri et al., 2005; Mecozzia et al., 2005; Jerzykiewicz, 2013; Zhang et al., 2015).

LIFS and EEM-CP/PARAFAC techniques will make access to the structural analysis of HU fraction feasible, since it can be used on solid-state samples. Therefore, the main objectives of this study were: (1) to assess the characteristics of HU and the whole soil using LIFS; and (2) to evaluate the main components in this fluorescent HU fraction and compare them to the fluorescent components present in the soil using EEM associated with CP/PARAFAC.

2. Materials and methods

2.1. Study area

The study area located north of Barcelos city, Amazon State, Brazil, at the coordinates 0°15′33.1″N and 62°46′27.6″W. The sedimentary cover of the rivers Branco and Negro with some younger depositional areas surrounding the Demeni river (Holocene alluvium of Demeni river) is the geological substratum (Pereira et al., 2015). The climate is typically equatorial and is characterised by an average temperature of 25 °C with high rainfall (around 3000 mm) throughout the year and a light dry season. Three soil types developed in the area according to IBGE (2008), oxisols, entisols and spodosol.

Seven spodosol profiles with different soil drainage conditions were studied for characterisation of the area. For this study one soil profile of an overflood Humiluvic Spodosol was selected. The soil profile (0 to 350 cm of depth) presents sandy-loam texture and quartz is the prevalent mineral with kaolinite and gibbsite as accessory.

The samples were collected by hand auger pits and due to the collapse of the sand of overlying spodic horizons, it was necessary reinforce the wall holes with PVC tubes.

2.2. Soil and humin sample preparation for analysis

Sampling procedures, preservation and preparation of the samples followed the recommendations of official methods. The extraction and purification of HU followed the recommendations described by the International Humic Substances Society (IHSS), Rice and MacCarthy (1989) and Swift (1996). The pellets of whole soil and HU containing 30% boric acid were prepared for the analysis of LIFS and EEM, as observed in Fig. 1.

2.3. Elemental analysis

For the chemical analysis of the elemental composition, the samples of the whole soil and HU were homogenised and grinded into particles