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Soil organic matter in podzol horizons of the Amazon region: Humification, recalcitrance, and dating

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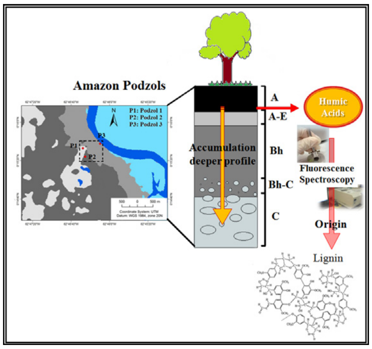
HIGHLIGHTS

- Structural variation in the humic acids for the depth profile.
- Humic acids originated from lignin-derived compounds.
- Lignin can accumulate in some Bh horizons.
- Amazonian podzols there are four kinds of the organic matter.
- Humification process has not direct association with the dating of organic matter.

GRAPHICAL ABSTRACT



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ABSTRACT

Characteristics of soil organic matter (SOM) are important, especially in the Amazon region, which represents one of the world's most relevant carbon reservoirs. In this work, the concentrations of carbon and differences in its composition (humification indexes) were evaluated and compared for several horizons (0 to 390 cm) of three typical Amazonian podzol profiles. Fluorescence spectroscopy was used to investigate the humic acid (HA) fractions of SOM isolated from the different samples. Simple and labile carbon structures appeared to be accumulated in surface horizons, while more complex humified compounds were leached and accumulated in intermediate and deeper Bh horizons. The results suggested that the humic acids originated from lignin and its derivatives, and that lignin could accumulate in some Bh horizons. The HA present in deeper Bh horizons appeared to originate from different formation pathways, since these horizons showed different compositions. There were significant compositional changes of HA with depth, with four types of organic matter: recalcitrant, humified, and old dating; labile and young dating; humified and young dating; and little humified and old dating. Therefore, the humification process had no direct relation with the age of the organic matter in the Amazonian podzols.

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1. Introduction

The Amazon forest provides important services to humanity, such as high biodiversity, climate regulation, carbon sequestration, and the regulation of water and nutrient cycles (Coe et al., 2013). Climate changes can directly affect the physical integrity of soils in the Amazon region, causing important alterations in their water balance, evapotranspiration, and carbon transport (Coe et al., 2013; Neill et al., 2013). In particular, any modification of the soil composition and water cycle due to anthropogenic and/or natural sources is expected to affect the amount and chemical nature of the soil organic matter (SOM) present in these natural ecosystems and, consequently, influence the CO_2 concentration in the atmosphere.

Understanding the dynamics of SOM and its chemically and biologically active fractions, including humic acids (HA), is fundamental for evaluating its vulnerability to changes in physical and chemical properties when subjected to different weather and water conditions (Stevenson, 1994; Senesi and Loffredo, 1999). Lignin is recognised as one of the main precursors of humic substances, including HA (Burgues et al., 1963; Flaig, 1972; Hatcher et al., 1981; Hedges and Ertel, 1984; Senesi and Loffredo, 1999; Lehmann and Kleber, 2015). The transformation of lignin into HA can proceed by small modifications of the constituent biopolymers that increase their solubility, such as by the degradation of lignin into simple phenols, which can subsequently re-polymerize (Hedges and Ertel, 1984; Schmidt et al., 2011; Jex et al., 2014; Lehmann and Kleber, 2015). Modified lignin is often present as a major HA component, especially in the SOM of flooded areas, such as peats, sediments, and hydromorphic soils, rather than in well-drained soils (Hedges and Ertel, 1984). Lignin is much more resistant to microbial degradation, compared to other HA precursors such as polysaccharides, amino acids, and other plant constituents. However, several physical, chemical, and biological factors can contribute to lignin degradation during its percolation through the soil, and can modify its structure (Jex et al., 2014).

The organic carbon stored in the surface layers (0 to 1.0 m) of hydromorphic podzols in the upper Rio Negro basin amounts to 87 ± 7 kg m^{-2}, which corresponds to a total of 14 ± 1 Pg of carbon in these soils (Cerri et al., 2000; Montes et al., 2011). Hence, the effects of soil textural and mineralogical characteristics on SOM dynamics are especially important in this ecosystem, which is one of the most relevant global carbon reservoirs (Cerri et al., 2000).

Fluorescence spectroscopy is a technique widely used for differentiating and classifying SOM and HA according to their origin, genesis, and nature (Senesi et al., 1991). Emission and/or excitation fluorescence methods have been extensively applied to assess HA humification processes (Zsolnay et al., 1999; Kalbitz et al., 1999; Milori et al., 2002; Tadini et al., 2015). Among these, laser-induced fluorescence spectroscopy (LIFS) is a valuable tool for use in the structural and functional analysis of SOM. This technique is of interest due to its rapidity, simplicity, sensitivity, and performance under natural conditions (Milori et al., 2006, 2011; Martins et al., 2011; Tadini et al., 2015; Senesi et al., 2016). Milori et al. (2006) evaluated the humification index (H_{LIFS}) of SOM in whole soils using LIFS with fluorescence excitation in the blue region. The presence and conservation of structural units such as conjugated aromatic rings and substituted quinones were suggested to be directly related to humification processes.

Few studies (Bravard and Righi, 1991a, 1991b; Santos et al., 2015a, 2015b) have investigated HA isolated from Amazon podzols. Therefore, the main aim of this work was to perform a comparative evaluation of the characteristics of SOM and its HA in the different horizons of three podzols from the Amazon region, using elemental analysis (CHN) and fluorescence spectroscopy.

2. Materials and methods

2.1. Study area

The study site was located in the north of Barcelos City, near the Demeni River (0° 15′ 18″N; 62° 46′ 36″W) in the middle watershed of the Negro River region in the Amazon plains, Brazil (Fig. 1a). According to the Brazilian Institute of Geography and Statistics (IBGE, 2008), ferralsols, podzols, and gleysols are the most common soil types in this area. The climate is typically equatorial and is characterised by an average temperature of 25 °C and high rainfall (around 3000 mm) throughout the year, with no pronounced dry season.

2.2. Soil sampling and preparation for analysis

Soil samples were collected close to the Demeni River, from different horizons of three podzols developed on the Pleistocene sedimentary substrata of the Branco and Negro rivers (IBGE, 2008). The samples were from: (a) a permanently waterlogged podzol covered by herbaceous meadow of shrubs and grass, locally named “campina” (P1); (b) a seasonally waterlogged podzol covered by caatinga forest and rainforest (P2); and (c) a well-drained podzol under rainforest vegetation (P3) (Fig. 1b) (Pereira et al., 2015). Soil sample collection was carried out by hand auger drilling at different depths from 0 to about 390 cm, without replication. The vertical downward pedologic successions of layers sampled in the three podzol profiles were as follows:

- P1: A 0–15, A-E 15–30, Bh 40–50, BhC 240, Bh-C 260, and C 350;
- P2: A 0–15, Bh 165–175, Bh 180–183, Bh 210, Bh 280–310, and Bh 335–350;
- P3: A 0–20, A 20–30, A 30–40, Bh 110–120, Bh 170–180, Bh-C 270–280, Bh 370–380, and Bh 380–390.

In the above classification, P1, P2, and P3 represent the type of podzol; A, E, A-E, Bh, Bh-C, and C are the pedologic horizon types (Santos et al., 2015a, 2015b; Embrapa, 2006); and the numbers represent the upper and lower sampling depths (in cm).

The soil samples were oven-dried at 35 °C with air circulation and renovation, crushed, and sieved to <0.106 mm before analyses by laser-induced fluorescence spectroscopy (LIFS) and classical fluorescence spectroscopy.

2.3. Isolation of humic acids

The HA fractions were isolated from the soil samples using the procedure recommended by the International Humic Substances Society (Swift, 1996). Briefly, the HAs were extracted with 0.1 M NaOH (Synth) at a soil:extractant ratio of 1:200 (volume in L:mass in g). After centrifugation, the HA fraction was separated from the supernatant by precipitation at about pH 2.0 with 6 M HCl. The HAs were then suspended in a solution of 0.1 M HCl/0.3 M HF to remove dissolved mineral impurities. After centrifugation, the HAs were dialysed at pH 8 (cellulose membrane dialysis tubing, 43 mm, cut-off of 14,000 Da, Sigma-Aldrich) and finally lyophilised.

2.4. Soil analysis

The textures of the soils were analysed in a previous work (Pereira et al., 2013), using the Robinson pipette method (Santos et al., 2005).

The LIFS measurements were performed using soil pellets. The soil samples were first dried at room temperature and passed through a 5 mm sieve, followed by preparation of mixtures containing 70% soil and 30% boric acid. Pellets about 1 cm in diameter and 2 mm thick were obtained by applying 10 tons of pressure for 2 min. The LIFS analysis was carried out in duplicate for each sample. An additional LIFS analysis was performed for sample P3 Bh-C 270–280, with addition of 1, 5, and 10% of lignin standard (Sigma-Aldrich). In this procedure, mixtures were prepared using 360 mg of soil and 40 mg of lignin (10%), 380 mg of soil and 20 mg of lignin (5%), and 396 mg of soil and 4 mg of lignin (1%).