Effects on the composition and structural properties of the humified organic matter of soil in sugarcane strawburning: A chronosequence study in the Brazilian Cerrado of Goiás State

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ABSTRACT

The heating of soil organic matter after burning events can significantly change the composition and structure of humified organic matter. The impact of burning on the amount and quality of SOM depends on fire intensity, recurrence, the type of vegetation, soil texture and the local climate. The present study identified the composition and structural properties of humic acids (HA) extracted from a sandy loam textured *Latossolo Vermelho* (Oxisol) managed with the pre-harvest burning of sugarcane straw for chronosequences of 1, 5, 10 and 20 years in Rio Verde, Goiás (GO). Soil samples were collected at depths of 0–0.05, 0.05–0.10, 0.10–0.20 and 0.20–0.30 m. To obtain a reference of natural conditions, soil was also sampled in adjacent areas covered with native vegetation and Pasture grass. The HA samples from soil under different burning conditions and areas (Cerrado and Pasture grass) were analyzed using chemical-spectroscopic characterization and the chemiometric technique. The greatest modifications in HA composition after burning occurred in the most superficial soil layers. At a depth of 0.0–0.05 m, the main changes observed were a decrease in mean C and N levels and enrichment in O, irrespective of the length of time that burning practices had been adopted. Additionally, in the most superficial layer, the ultraviolet-visible spectroscopy assay showed that burning enhanced the aromatic properties ($<E_4/E_6$) of HA, and FTIR spectroscopy coupled with PCA confirmed that the top soil layer shows higher variations in the functional groups as a function of burning. The PCA analysis of ^{13}C NMR spectra also showed that stronger aromatic properties were found in the most superficial layer, and the PCA of FTIR spectra reinforced the result by grouping HAs in these layers and thereby indicated that the most intense changes occurred in the 0.0–0.05 m layer. The most intense disturbances produced by sugarcane burning on the composition and structure of humified organic matter occurred in the most superficial layer. The combined use of the methods adopted was efficient and, along with the chemiometric techniques, consisted of useful tools that can support the development of procedures to study phenomena such as burning.

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1. Introduction

The final products of biomass combustion are water, CO_2 and minerals contained in the ash. Total biomass oxidation depends on a number of conditions to ensure adequate oxygen supply during combustion. This is not observed in nature, where incomplete combustion yields a number of compounds, such as carbon monoxide, methane and a wide variety of pyrolysis products,

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including hydrocarbons and organic matter fractions. In addition to producing a substantial amount of different organic compounds, natural fire modifies other compounds through heating (González-Pérez et al., 2004).

The impact of fire on the amount and quality of soil organic matter (SOM) depends mainly on its intensity and recurrence, vegetation type, soil texture and local climate (González-Pérez et al., 2004; Knicker, 2007; Satín et al., 2008; Vergnoux et al., 2011; Granged et al., 2011). In general, SOM heating can considerably increase the aromaticity of the remaining organic matter to the detriment of carboxyl and aliphatic groups (Almendros et al., 1992). The structures formed are derived from carbon hydrates, lipids, alkylated macromolecules and peptides. As these structures are more recalcitrant, they are not readily humified and can be extracted as the humic fraction (Vergnoux et al., 2011).

Dry soil is an efficient insulator, and the effects of fire are usually restricted to the upper centimeters of the soil (Debano et al., 1998), which receives only a small fraction of the heat produced. The temperatures attained in the different soil layers, the heat exposure time and the soil stability determine the nature and intensity of the changes in the chemical and physical attributes of the soil.

In the short term, moderate fire becomes a mineralization agent because the ashes produced contain high levels of P, K and Ca, which increases the nutrient availability for plant growth, especially in layers up to 0.05 m (Coutinho, 1990; Kauffman et al., 1994; Rheinheimer et al., 2003; González-Pérez et al., 2004). In addition, vegetation fire can affect SOM stocks and quality (Roscoe et al., 2000; Knicker et al., 2005).

Pre-harvest sugarcane straw burning can compromise the maintenance of SOM levels by reducing the incorporation of crude organic matter and promoting mineralization of existing organic matter. Moreover, given that soil remains bare for a long period of time, erosion is accelerated and physicochemical attributes are affected (Molina, 1995; Mendoza, 1996).

The effect of burning suppression and maintenance of sugarcane straw on soil increases SOM levels as reported by Blair (2000) and Noble et al. (2003) in Australia, Dominy et al. (2002) in South Africa and Villegas et al. (1998) in Cuba. Studies conducted in Brazil found similar results in very clayey and medium-textured soil (Orlando Filho et al., 1998) but not in very sandy soil (Ball-Coelho et al., 1993).

The chemical and spectroscopic techniques applied to soil organic matter, particularly humic substances, permit acquisition of important information on the structural characteristics and properties of these compounds in addition to monitoring these features throughout events and phenomena of soil (Cunha, 2005). Recent studies on soil organic carbon are based on the spectrophotometric analysis of soil humic substances, particularly humic acid, which allows the most detailed investigations because it is easier to extract, exhibits a close relationship with soil identity and especially because of its capacity to express soil trans-formations including changes caused by degrading management practices (Fontana et al., 2006).

The present study aimed to identify the composition and chemical properties of humified SOM through spectrophotometry and chemometric determination of humic acids extracted from *Latossolo Vermelho* (Oxisol) and under a sugarcane crop chronose-quence, a Pasture area and a natural Cerrado in Goiás.

2. Material and methods

2.1. Study area description

The study was performed using *Latossolo Vermelho* (Oxisol) (Embrapa, 2006) with a sandy loam texture in Rio Verde, Goiás

state, and managed with the pre-harvest burning of sugarcane straw for chronosequences of 1, 5, 10 and 20 years (areas 1Y, 5Y, 10Y and 20Y, respectively). The soil samples were collected at depths of 0–0.05, 0.05–0.10, 0.10–0.20 and 0.20–0.30 m. The adjacent areas, which were covered by native Cerrado vegetation and Pasture grass, were also sampled to serve as a reference of the natural soil conditions. The history of soil use in the last 40 years is described in Fig. 1.

Areas cropped with sugarcane received 500 kg ha^{-1} of 5–30–20 NPK at the initiation of planting and 500 kg ha^{-1} of 18–00–27 NPK at ratoon. Area 10Y was first renewed in 2010, and area 20Y was renewed on February 2, 2000 and after the 2010 crop season. In the 2009/2010 season, the sugarcane yield was 113 Mg ha^{-1} in Y1, 111 in 5Y, 85 in Y10 and 96 in Y20. Area Y20 received annual inputs of 60 m^3 ha^{-1} of vinasse (N = 0.03, P = 29, K = 225, Ca = 70, Mg = 87, in mg L^{-1}; pH (H$_2$O) = 3.5).

The humic acids (HA) were isolated and purified as recommended by the International Humic Substance Society- IHSS (Swift, 1996). The soil samples were pretreated with 0.1 mol L^{-1} HCl and extracted in 0.1 mol L^{-1} NaOH at 1:10 (v/v) soil:solvent ratio. The humic acids were precipitated using decreasing pH (1.0–1.5) with 6 mol L^{-1} HCl. This procedure was performed twice. The humic acids were then treated with 0.1 mol L^{-1} HCl and 0.3 mol L^{-1} HF and then dialyzed with deionized water until a negative test against AgNO$_3$ was obtained, followed by freeze-drying. The total organic carbon (TOC) was determined in samples with 200–400 g of total carbon and using a Carlo Erba automatic C—N analyzer (EA 1108, Milan, Italy) coupled to a Delta Plus continuous-flow isotope ratio-mass spectrometer (Finnigan Mat, Bremen, Germany).

2.2. Elemental composition of humic acids

Determination of C, H, N and S in the humic acid samples was conducted using a Flash EA1112 Elemental Analyzer (ThermoFinnigan) at the University of Coruña. The samples were weighed in 9 × 5 mm tin capsules using an MX5 Microbalance (Mettler Toledo, 1 μg resolution) and analyzed by spontaneous combustion in a quartz tube containing Cu/WO$_3$ and maintained at 1020 °C. Sulfanilamide and BBot were used as standards for C, H, N and S quantification. The C, H and N levels (in percentage) were corrected to a dry ash-free base using data from thermogravimetric analysis and according to the equation: %corrected = %original × 100/(100 − %humidity − %ash). The oxygen level was obtained by subtracting the corrected level of the other elements: % O = (100 − %C − %H − %N). The atomic ratios were calculated using the formulas: H/C = (%H/1)/(%C/12); O/C = (%O/16)/(%C/12); O/H = (%O/16)/(%H/1) and C/N = (%C/12)/(%N/14).
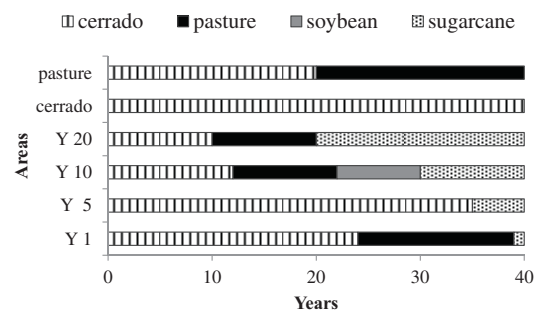

Fig. 1. Land use history in the study area. Areas cropped with sugarcane were managed with pre-harvesting burning for 1 (Y1), 5 (Y5), 10 (Y10) and 20 (Y20) years.