



Analytical pyrolysis of humic substances from a Latosol (Typic Hapludox) under different land uses in Minas Gerais, Brazil

Cristiane Pereira de Assis^a, José A. González-Pérez^{b,*}, José María de la Rosa^b, Ivo Jucksch^c, Eduardo de Sá Mendonça^{c,d}, Francisco J. González-Vila^b

^a UNIVASF – Universidade Federal do Vale do São Francisco, Ceagro, Rod. BR 401, km 12, 56300-000 Petrolina, PE, Brazil

^b IRNAS-CSIC – Inst. Recursos Naturales y Agrobiología de Sevilla, PO Box 1052, 41080 Sevilla, Spain

^c UFV – Universidade Federal do Viçosa, Depto. de Ciência do Solo, Av. P.H. Rolfs, s/n, 36570-000 Viçosa, MG, Brazil

^d DPV/UFES – Depto. de Produção Vegetal, 29500-000 Alegre, ES, Brazil

ARTICLE INFO

Article history:

Received 28 June 2011

Accepted 13 October 2011

Available online 20 October 2011

Keywords:

Py-GC/MS

Oxisols

Typic hapludox

Organic matter

SOM

Humic substances

Brazil

ABSTRACT

Humic acid (HA) and fulvic acid (FA) fractions isolated from a humic red-yellow Latosol (Typic Hapludox) under different land uses (forest, pasture, coffee) were studied by pyrolysis–gas chromatography–mass spectrometry (Py-GC/MS). Humic substances were extracted from Soxhlet lipid free soil samples and the pyrolysis experiments consisted of a thermal desorption at sub-pyrolysis temperature (280 °C) followed by a flash pyrolysis (600 °C) on the same sample.

Thermal desorption of HA and FA released mainly carbohydrate-derived compounds, N-compounds and series of alkanes. In surface samples most lignin- and carbohydrate-derived compounds are found weakly bounded to the HA structure indicating recent lignocellulosic contribution. In deeper dark soil layers the release of carbohydrate-derived moieties and N-compounds could indicate active biosynthesis by soil biota producing secondary biopolymers like chitin. Major compounds released after pyrolysis of HA were phenol and other benzene derivatives, whereas for FA aromatic and polyaromatic, N-containing and furan derivatives prevailed.

In terms of land use the soils under pasture, FA became more aromatic and enriched in carbohydrate-derived compounds and the presence of *p*-vinylguaicol in the HA could indicate the contribution of lignin from grasses. In contrast, the coffee culture seems to favor the formation of FA with a more polyaromatic and phenolic structure. Most N-bearing compounds in HA and FA extracted from forest soil samples were released by desorption, indicating comparatively weaker bonds in their structure. This could be explained as a more recent contribution and/or comparatively rapid cycling of these organic substances in natural environments.

With respect to the general dynamic of organic matter (OM) in the studied Oxisol, our results are compatible with the occurrence of a high biological activity associated with fast humification processes and the migration of oxidized OM, probably with soil cations as vectors.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Soil contains the largest near-surface reservoir of terrestrial C [1]. Research for a better knowledge of the chemical structure and dynamics of soil organic matter (SOM) is necessary for understanding key environmental processes intimately related with the maintenance of ecosystem services like global climate change mitigation through C sequestration. Nevertheless, soil organic C is in dynamic balance of gains and losses being sensitive to environmental changes and, in fact, land uses may alter C dynamics leading to major C shifts at a global scale. It is known that land uses affect SOM

quantity and composition. In particular progressive loss of SOM by conversion of natural vegetation to cultivated use is well known. Much of this loss can be attributed to reduce inputs of organic matter, tillage effects that cause breakdown of soil aggregates where particulate SOM were stabilized through physical protection [2], or accelerated decomposition of crop residues before its complete incorporation to soil [3,4].

In the tropics, soil organic matter largely influences soil fertility and productivity, especially in highly weathered soils managed without external inputs of organic or inorganic fertilizer [5,6]. Several studies have focused on organic matter dynamics in tropical soils of South America [7,8 and references therein] and specific research on the processes leading to SOM depletion and nutrient turnover has generally shown greater mineralization rates in tropical soils than those observed in temperate zones [9,10]. Therefore,

* Corresponding author. Tel.: +34 9546247111; fax: +34 954624002.

E-mail address: jag@irnase.csic.es (J.A. González-Pérez).

the influence of soil management systems on SOM content and quality, and consequently on soil properties, as well as the ability to promote C stabilization (sequestration), is a research subject of major interest for subtropical Brazilian soils.

The general pattern of land use in Mata Mineira zone in Minas Gerais, Brazil, is coffee (*Coffea arabica*) crops and pastures of molasses grass (*Melinis minutiflora*) [11]. Due to favorable permeability, water retention capacity and friability, most of the cultivated areas are supported by humic Latosols [12]. These clay reddish-orange soils (up to 200 cm deep), are highly weathered, well-drained, dystrophic, with thick A horizons encompassing large SOM stocks (up to 30.2 kg m⁻²) and where humic substances (HS) accumulation is apparent at first sight as a darker layer at 60 cm depth or more [12,13].

Within the SOM pool, the humified fractions contain chemical markers, biogeochemical indicators informing about soil history and the effects of management on soil quality [14,15]. The analysis of HS allows diagnosing the progressive changes in the biogeochemical cycle of ecosystems as well as in ecosystem productivity, since they act in the compartmentalization of nutrients and soil microstructure [16].

In spite of the environmental importance of SOM, its molecular structure and dynamics continues to be largely unknown. This in part derives from the high complexity and heterogeneous nature of this material. Pyrolysis in association with gas chromatography and mass spectrometry (Py-GC/MS) has been largely used for the molecular characterization of complex macromolecular material and presents several advantages in the structural analysis of recalcitrant SOM over other degradation methods; good reproducibility, and require small amount of sample [17–22]. Contributions have been made in detailing the chemical structure of HS, mainly in the elucidation of the origin of structural components [23–25], and in the identification of changes in its structural composition resulting from soil use and management [26–28]. In addition, recently double shot Py-GC/MS has been used to acquire information on the structural composition of complex organic macromolecular matrices [29,30]. Double shot Py-GC/MS, include a previous thermal desorption stage at sub-pyrolysis temperature before the real pyrolysis performed in the same sample. This allow to a more accurate identification of the origin of the volatile compounds released. The products released in the first desorption step should correspond to structures probably with a recent origin, in general weakly condensed and peripherally bound to the more thermostable humified structures [29,31].

The aim of this work was to evaluate the impact of contrasted land uses (forest, pasture, coffee culture) on the structure of HAs and FAs extracted from a humic red-yellow Latosol in Atlantic Forest Zone in Minas Gerais State Brazil and to assess the impact in soil C sequestration mechanisms using a two-step (double shot) analytical pyrolysis technique.

2. Materials and methods

2.1. Agroecological description

This study area was the Atlantic Forest Biome region at “Mata Mineira” zone, Southeast Brazil, located at 20°28'26" S and 42°28'55" W, at an average altitude of 712 m.a.s.l. The typical climate of the region is Cwb (Köppen classification) i.e., temperate climate with rainy summers and dry winters. The mean annual rainfall and temperature are 1300 mm and 18 °C, respectively. The vegetation in the area can be classified as a mountain semi-deciduous mesophytic forest (semi-deciduous tropical forest) with emergent canopy [32]. The soil was a red yellow humic Latosol (Typic Hapludox), clayey, dystrophic and acid, with a high

content of exchangeable aluminium and organic matter. These soils are derived from migmatite volcanic rocks and are typical in the higher altitude areas.

The area selected follows the typical pattern of land use at Mata Mineira. The standard farming exploration when established at the beginning of the settlements has led to continuous deforestation; the native tropical forest was substituted by cultures that would come to be traditional in the region (mainly coffee plantations and pastures). For this study three sites with the typical pattern of land use (coffee, pasture and forest) under the same taxonomic soil units and slope were sampled. The soil under coffee has been cultivated for the last 12 years and the fertilization management consisted of addition of NPK (25–10–20) fertilizer twice a year and limed every two years. The pasture site was established in the 1940s after slashing and burning the forest (“tumba y quema”), but after a livestock crisis with low inputs in the 60s, large part of this area was converted into coffee cultures. In the region the major area early used as pastures is nowadays degraded and farmers keep only the clean areas for cattle grazing, without much expenditure for maintenance and molasses grass (*M. minutiflora*) is the predominant species in the pasture. The widespread occurrence of this grass is indicative of low productive acid soils. For comparative purposes, soil samples under the native forest ecosystem were also sampled and studied.

2.2. Sampling, extraction and purification of HA and FA

Composite soil samples were taken with a spade at two depths in the A horizon at 0–10 and 60–100 cm. Up to ten sub-samples were collected in an area of ca. 100 m² and mixed to form one composite sample. The samples were air-dried, homogenised and sieved to fine earth (<2 mm). Sub-samples were collected for chemical and physical analysis. The main physico-chemical characteristics of the soils are shown in Table 1.

Sieved soil samples were previously Soxhlet-extracted at 70 °C for 16 h using 200 mL of a dichloromethane–methanol mixture (3:1 v/v) [33]. This pre-treatment removed the free lipid fraction and avoided further co-extraction as acid- and alkali-soluble emulsified forms. Humic acids and FAs were then extracted and purified as proposed by Swift in 1996 [34]. Briefly, soil samples were extracted with a 1:10 cold solution of 0.1 M NaOH under N₂. The alkaline extract with the HSs was re-dissolved by adding 100 mL of 0.1 M KOH under N₂. Solid KCl was added to attain a final concentration of 0.3 M [K⁺]. After the complete dissolution, the material was centrifuged at 14,000 × g to remove solids in suspension (clays). The HS extract was then stirred for 2 h at 25 °C with a 10% HF and 5% HCl. This acid treatment, which causes precipitation of acid-insoluble HA, was repeated seven times, in order to reduce the ash content to <1%. The HA fraction was dialyzed in cellulose tubes D-0405 (Sigma Aldrich) and lyophilized. The FA-containing solution was eluted in a column filled with DAX-8 at 10 mL min⁻¹. The adsorbed fraction was eluted at 2 mL min⁻¹ with 0.1 mol L⁻¹ NaOH and collected in a flask with ion exchange resin Dowex 50.

2.3. Double-shot pyrolysis-gas chromatography–mass spectrometry

A double-shot pyrolyzer PY2020iD (Frontier Lab Ltd., Fukushima, Japan) attached to a GC/MS system Agilent 6890 was used. In a first step, a thermal desorption was carried out by increasing the initial temperature of 100 °C at a rate of 20 °C min⁻¹ to a final temperature of 280 °C for 3 min. In a second step, the sample was heated at pyrolysis temperature, 600 °C for 1 min. The GC/MS conditions were the same for both desorption and pyrolysis experiments: the GC was equipped with a fused silica capillary column DB5 MS (J&W Scientific) (30 m × 250 μm × 0.25 μm film thickness), oven temperature was held at 50 °C for 1 min, then

Download English Version:

<https://daneshyari.com/en/article/1197675>

Download Persian Version:

<https://daneshyari.com/article/1197675>

[Daneshyari.com](https://daneshyari.com)