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Pyrolytic appraisal of the lignin signature in soil humic acids: Assessment of its usefulness as carbon sequestration marker

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ABSTRACT

Lignin markers in humic acids (HA, the alkali-soluble, acid-insoluble soil organic matter fraction) molecular features are explored to assess the extent to which plant biomacromolecules are progressively transformed by humification processes leading to stable C-forms in soils. Humic acids extracted from a collection of mountain calcimorphic soils from Sierra María-Los Vélez Natural Park (Southeastern Spain) under different use and management practices were studied in detail by visible and infrared (FT-IR) spectroscopies and analytical pyrolysis (Py-GC/MS). The HAs display a more or less marked lignin pattern defined by characteristic methoxyphenol assemblages released after pyrolysis that are associated to a typical infrared pattern including absorption frequencies bands at 1510, 1460, 1420, 1270, 1230 and 1030 cm^{-1}. This variability in the HA spectroscopic and pyrolytic patterns was used as a source of molecular-level surrogates to establish the balance between complementary mechanisms of soil C sequestration i.e., a selective preservation of lignin associated to raw organic matter and other plant-inherited macromolecules, or alternative mechanisms involving microbial breakdown or plant precursors and its condensation with microbial metabolites.

We found that HAs in which the lignin signature was comparatively less marked also show high optical density values suggesting unsubstituted, condensed aromatic units and a chaotic organic structure, pointing to the presence of highly resilient carbon forms. Upon analytical pyrolysis, one group of HAs produced major yields of methoxyl-lacking aromatics (alkylbenzenes and alkylphenols), and poor yields of alkyl compounds, which suggest efficient cleavage of biomacromolecules and the occurrence of active microbial synthesis and condensation processes. In fact, these HAs also displayed broadband IR spectra, and visible spectra showing high optical density and polynuclear quinoid chromophors considered of fungal origin. Other group of HAs yielded upon pyrolysis conspicuous series of methoxyphenols and well-defined alkyl series (alkanes, alkenes and fatty acids). The IR spectra also displayed clear lignin and amide bands, as well as intense 2920 cm^{-1} band and a low optical density, indicative of a marked aliphatic character. This latter is interpreted as the result of recent diagenetic alteration processes of young organic matter and suggests that C sequestration mechanisms in these soils are mainly based on the stabilization of HAs from plant biomacromolecules and aliphatic structures.

These differential lignin alteration patterns indicate that HAs are responsive to soil C sequestration mechanisms, which in the studied soils seem to relay upon microtopographical features rather than to changes in soil use and management.

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1. Introduction

Despite the crucial global implications of carbon (C) stored in soils and sediments [1], the biogeochemical processes involved in C stabilization are not well understood [2]. The study of the molecular structure and variability in soil organic matter (SOM) may help in unravelling such stabilization processes as well as to infer resilience characteristics of different SOM fractions [3,4]. Although humification is an active process involving biological cleavage of plant and microbial biomass followed by secondary condensation of soluble products into humic substances [5], in some circumstances biodegradation is severely hampered by climatic, biotic or mineralogical soil-forming factors leading to accumulation of raw humus types [6]. In these cases the

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composition of the resulting humic substances could be described as a dynamic heterogeneous mixture of relatively low molecular size components associated via hydrophobic interactions and hydrogen bonds [7]. While at the early humification stages such a supramolecular conformation could be stabilized mainly by weak dispersive forces instead of covalent linkages [8], defining a conceptual model which accounts for their essential role in providing and maintaining soil physical and chemical quality [9], at advanced humification – maturation – stages the humic substances show an outstanding intrinsic resilience and this is crucial to define soil biogeochemical quality of soils temporarily behaving as active C sinks. In particular progressive organo-metallic interactions and additional free-radical condensation of the three-dimensionally bridged structure of humic substances in the course of progressive transformation – maturation – stages may end in comparatively rigid condensed domains. In this situation most of the humic structure could consists of a 'megamolecule' formed by a network of C—C and C—O links, where discrete structural units can no longer be recognizable due to the similar stability to chemical and biological degradation of all bonds involved in the whole structure [3]. Such SOM advanced transformation stage is often found in continental Mediterranean semiarid environments where abiotic factors i.e., contrasting temperature and moisture levels, sunlight exposure and the historical effect of wildfires, may lead to soils with low SOM content but highly stable and resistant to biodegradation (resilient).

In this line, several studies have pointed out the possibility to use the structural information provided by the molecular characterization of SOM to differentiate between (a) ecosystems where soil C sequestration relies upon microbial mediated processes with an intense reworking and abiotic condensation of precursors producing intrinsically resilient macromolecular humic substances of chaotic structure and (b) soils where the preservation of raw organic matter prevails and depends on extrinsic factors – mainly organo-mineral interactions – leading to a organic matter organization that is accessible to soil enzymes [10]. Adopting extreme positions about soil C sequestration mechanisms debate have frequently led to hermeneutic controversies in the search of a unified theory justifying SOM stabilization [11]. In particular, calcimorphic soils could be especially suitable to analyze qualitative and quantitative features relevant in the dynamics of SOM. This is due to the fact that these soils displays peculiar features associated both with e.g., microencapsulation processes of particulate plant-inherited materials [12,13] but also with active insolubilization mechanisms of the mineral matrix related to the release of low molecular weight compounds onto a Ca^{2+} saturated soil solution [14]. In fact, the prevailing limestone substrate in semiarid Southern Spain's soils has been considered to play a role in the low structural variability in the molecular structure of the HAs [12]. This situation demands the use of accurate analytical techniques (i.e., analytical pyrolysis) betraying environmental proxies (molecular markers) responsive of the different sources of environmental variability reflected in the composition of the SOM [15–17].

In the present study analytical pyrolysis (Py-GC/MS) together with visible and IR spectroscopies, are used to study HAs molecular structure and to find compositional descriptors informative about C stabilization processes in a variety of semiarid ecosystems developed on calcimorphic soils.

2. Materials and methods

2.1. Soil sampling

The area of study is located in the Natural Park Sierra María-Los Vélez (Almería, Southeastern Spain) which includes a wide variety of semiarid ecosystems both seminatural (forests and brushwood) and disturbed (almond-tree orchards and cereal fields) developed on calcimorphic soils. The natural vegetation consists of pine forests (>90 yr), oak forests, reforested pine forests, brushlands, almond-tree orchards and cereal crops (Table 1) [18]. The climate is Mediterranean-type, with typical continental features ranging from semiarid to subhumid. Temperatures are 11.9–16.9 °C with a dry summer season; rainfall events are intense and occasional. The geological substrate consists of sedimentary rocks (limestones, marls and dolomites) and soils are Rendzic and Lithic Leptosols, Calcic, Petrocalcic and Hypercalcic Chernozems, Kastanozems and Hypercalcic, Luvic and Petrocalcic Calcisols [19].

Soil samples (*ca.* 500 g) were collected with a spade from the uppermost horizon (0–10 cm) after litter removal. In the laboratory, composite samples (obtained by mixing three subsamples taken *c.* 20 m apart in the field) were air-dried and sieved to fine earth (<2 mm) before analysis.

2.2. Physical and chemical analyses

Soil pH was measured in a 1:1 soil:water suspension. Total carbonates were measured as $CaCO_3$ with the Bernard calcimeter [20]. The soil water holding capacity was estimated at −1.5 and −0.33 MPa in a pressure-membrane extractor [21]. Total nitrogen was determined by micro-Kjeldahl digestion and soil C by wet oxidation using dichromate in acid medium followed by redox titration [22]. Cation exchange capacity (CEC) and exchangeable ions Ca^{2+}, Mg^{2+}, K^+, and Na^+ were measured after extraction with ammonium acetate solutions (1 mol L^{-1} NH_4Ac at pH 7) [23].

2.3. Soil organic matter fractionation

The methods applied for the isolation and quantitative determination of the humus fractions were based on standard procedures [14,24]. The separation of the particulate, low density fraction (floating organic particles not yet transformed into humic substances, which in some cases may include some charcoal) was carried out by flotation using soil samples of 10 g suspended in 2 mol L^{-1} H_3PO_4. After rotary stirring for 1 min, the floating soil fraction or free organic matter was isolated by centrifuging the suspension and filtering, washed with distilled water and analyzed for total C. The soil pellet remaining after centrifugation was resuspended in 0.1 mol L^{-1} $Na_4P_2O_7$ (horizontal motion mechanical shaking for 3 h) and centrifuged. This treatment was repeated up to three times followed by two additional extractions with 0.1 mol L^{-1} NaOH; the dark brown extracts successively obtained (corresponding to the total humic extract: HA + fulvic acid) were aggregated. Two aliquots were taken from this extract, and precipitated with H_2SO_4 (1:1 by vol.) for further determination of the amounts of the acid-soluble fulvic acid and the precipitated HA fraction. The soil residue after the alkaline extraction was washed with distilled water and desiccated at 40 °C. The C concentration in this residue corresponded to the total humin.

2.4. Preparative isolation and purification of the HA fraction

Qualitative isolation and purification (de-ashing) of the HAs was performed by precipitating the total humic extract with 6 mol L^{-1} HCl to pH = 2, centrifuging, redissolving the acid insoluble HA in 0.5 mol L^{-1} NaOH and high-speed centrifuging at 43,500 × *g*. The centrifugation pellet (particulate organic matter and clay minerals) was discarded and the brown surnatant sodium humate was reprecipitated with HCl and centrifuged. Finally the HA in the gel state and acid pH was dialyzed in distilled water using cellophane bags (Visking® dialysis tubing, molecular weight cutoff 12,000–14,000 Da; pore diameter *ca.* 25 Å, Medicell) and desiccated at 40 °C.

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