



# Response of humic acid structure to soil tillage management as revealed by analytical pyrolysis

J. Dorado<sup>a</sup>, G. Almendros<sup>b,\*</sup>, F.J. González-Vila<sup>c</sup>

<sup>a</sup> Institute of Agricultural Sciences, CSIC, Serrano 115B, 28006 Madrid, Spain

<sup>b</sup> MNCN, CSIC, Serrano 115B, 28006 Madrid, Spain

<sup>c</sup> Instituto de Recursos Naturales y Agrobiología (IRNAS), CSIC, Reina Mercedes 10, 41012 Seville, Spain

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## ABSTRACT

The effects on the structural features of humic acids (HA) from dryland farming soils under long term management practices have been approached by analytical pyrolysis (Curie-point pyrolysis-gas chromatography/mass spectrometry, Py-GC/MS). The field experiments (started in 1987) include conventional, minimum and no-tillage plots, as well as non cultivated plots. The HAs isolated from the various plots showed significant differences in their pyrolytic behavior, in particular regarding the total abundances of alkyl pyrolysis compounds (fatty acids, alkenes and alkanes). The occurrence of very short-chain fatty acids (C<sub>5</sub>–C<sub>11</sub>) in uncultivated plots could be indicative of constitutional alkyl structures in the relictual HA from undisturbed soil. The effect of soil tillage managements substantially increased total abundances of fatty acids in plots under conservation practices (mainly no-tillage).

The HAs from uncultivated soils showed the greatest percentages of alkanes and alkenes. This was associated to the increased proportions of even C-numbered alkene homologues from C<sub>12</sub> to C<sub>18</sub>, possibly related to the incorporation of microbial compounds during the humification process. High percentage of alkylbenzenes and catechols were also characteristic of the uncultivated plots. The increased proportions of methoxyphenols, in special of the syringyl (dimethoxyphenyl) type, in HAs from plots subjected to conventional tillage pointed out to humification processes based on progressive alteration of plant lignins. From the viewpoint of soil quality, the results suggest comparatively advanced transformation stages of the HA from uncultivated plots, which means that conservation tillage practices seems to lead to increasing soil C levels, at expenses of the accumulation of comparatively recent organic matter derived either from altered lignins and/or microbial biomass.

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## 1. Introduction

Current agroecological research is paying increasing attention to the assessment of soil quality descriptors useful in forecasting sustainability of productive fields [1–4]. Among such descriptors total soil C has been considered a key parameter to assess soil, since it is generally accepted that soil organic matter (SOM) influences many soil properties related to its productivity, including water holding capacity, bulk density, aggregate stability, cation exchange and biological activity [5,6]. However, at this respect, a new trend deal with the convenience of studying the quality of SOM instead of only considering the total amount of soil organic C. In fact, even the quantitative composition of the major SOM fractions (i.e., free

organic matter, humic acid (HA), fulvic acid (FA), humin) shows a limited value as indicator of soil perturbation processes [7–9]. In addition, it has also been suggested that in agricultural soils under contrasted tillage practices the different fractions may have similar turnover rates [10].

One recognized way to approach the quality of SOM is the study of the different organic fractions at a molecular level. At this respect, the potential of analytical pyrolysis in analyzing the molecular composition of SOM, with similar success than alternative, time-consuming, wet chemical methods has been largely recognized [9,11].

In fact, previous pyrolytic analyses has succeeded in revealing the impact of no-till cropping systems on the composition of SOM, whereas complementary spectroscopic data (CP/MAS <sup>13</sup>C NMR measurements) failed in showing substantial effect due to the cropping systems [12].

\* Corresponding author. Fax: +34 91 564 08 00.

E-mail address: [humus@ccma.csic.es](mailto:humus@ccma.csic.es) (G. Almendros).

In the present study, a pyrolytic assessment of the impact of tillage practices on dryland farming systems from Central Spain is carried out. The field experiment, involving conventional, minimum and no-tillage as well as uncultivated plots, was designed in 1987. To date, no previous molecular-level characterization of the differences in the organic matter composition was done in this long-term experimental field.

Due to the massive incorporation of crop residues in agricultural fields subjected to minimum tillage practices, and in order to preclude trivial pyrolytical results mainly reflecting the quantitative contribution by non-decomposed crop residues (accumulated in the fractions referred to as free organic matter and humins) the study was focused in the comparatively stabilized HA fraction, which is considered to display a recalcitrant nature, mainly after its interaction with the mineral fraction.

## 2. Experimental

### 2.1. Field location and experiment design

The CSIC experimental farm “La Higuera” (UTM coordinates: zone 30; 4434290 m N; 377738 m E) under semi-arid continental climate (average temperatures of 6 °C and 23 °C in winter and summer, respectively; mean annual rainfall, ca. 400 mm, with an extended dry season from June to September [13]) is located in Toledo, Central Spain. The soil samples were collected from the 20 upper cm of a Calcic Haploxeralf [14] with loam–sandy texture (total sand =  $783 \pm 29$  g kg<sup>-1</sup>, clay =  $135 \pm 22$  g kg<sup>-1</sup>).

The experiment to compare the effect of different tillage systems was a randomized block design with three replications and two blocks. Plot size was 40.9 m. The tillage treatments consisted of: (i) conventional plow tillage (CT), i.e., tilling the soil with moldboard plow to a 20–22 cm depth, then using a rotovator; (ii) chisel (minimal) tillage (MT), i.e., chiselling the soil to a depth 14–16 cm and using the rotovator before sowing; (iii) no-tillage (NT), i.e., implementing direct drilling. In the NT plots, volunteer barley plants and weeds were sprayed with 0.54 kg ha<sup>-1</sup> glyphosate [N-(phosphonomethyl)glycine] before seeding with a triple-disk seed drill.

Samples from uncultivated plots near the experimental plots, with typical Mediterranean shrub consisting mainly of *Retama sphaerocarpa* (L.) Boiss and dense herbaceous layer, were also taken as a reference in order to assess the impact of the above agricultural practices.

### 2.2. Soil general analyses

Air-dried soil samples were homogenized to 2 mm. The chemical analyses included determination of pH (water suspension, 1:2.5 w:w), total N (micro-Kjeldahl digestion), available P [15], and available Na, K, Ca and Mg (1 M NH<sub>4</sub>OAc [pH 7] extraction). Oxidizable soil C was determined according to Walkley and Black method [16].

### 2.3. Soil organic matter fractionation and humic acid purification

The isolation and quantitative analysis of the soil organic fractions included the previous removal of the not-yet decomposed organic particles (*free organic matter*), which was separated by flotation in 2 M H<sub>3</sub>PO<sub>4</sub>. The resulting soil residue was treated with 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and 0.1 M NaOH, and the extraction was repeated up to 5 times with each solution. After centrifuging (2600 × g) the successive suspensions obtained with the use of these extractants, the supernatant fractions were aggregated and the final volume was measured. Aliquots were taken from this total extract for quantitative determination of the C in the acid-insoluble HA separated

after dropwise precipitation with H<sub>2</sub>SO<sub>4</sub> (1:1 by vol.) whereas the acid-soluble FA was determined as the difference in C concentration with the whole humic extract [17,18].

For preparative isolation of the HAs, the remaining humic extract was precipitated (pH 1) with 12 M HCl. The precipitate (HA) was redissolved in 0.25 M NaOH and centrifuged (43,500 × g) to remove the particulate impurities. The resulting sodium humate solution was reprecipitated with HCl overnight, purified with 1 M HCl-HF, dialyzed in cellophane bags for one week against distilled water, and desiccated at 36 °C.

### 2.4. Spectroscopic characteristics of the humic acids

The optical densities at 465 nm (E<sub>4</sub>) and 665 (E<sub>6</sub>) nm of HAs were determined from solutions of 200 mg CL<sup>-1</sup> of HA in 0.02 M NaHCO<sub>3</sub> [19] with a Shimadzu UV-240 spectrophotometer. The E<sub>4</sub> is classically considered to be related with the aromaticity of HAs [20,21], whereas the E<sub>4</sub>/E<sub>6</sub> ratio gives information about the polydispersity of the HAs [22].

### 2.5. Curie-point pyrolysis-gas chromatography/mass spectrometry

The HAs were analyzed by Py-GC/MS in a Horizon Instruments unit attached to a Varian Saturn 2000 gas chromatograph–mass spectrometry system (GC/MS). The samples on ferromagnetic wires were heated at the Curie temperature of 510 °C for 5 s. The pyrolytic interface was set to 250 °C, and the chromatographic temperature was programmed from 50 to 100 °C at 32 °C min<sup>-1</sup> and then up to 320 °C using a rate of 6 °C min<sup>-1</sup>. In order to enhance the chromatographic resolution, a liquid CO<sub>2</sub> cryogenic unit, fitted to the injection port, was adjusted from –30 °C (1 min) to 300 °C at 20 °C min<sup>-1</sup>. A 25-m × 0.32 mm × 0.4 μm fused-silica capillary J&W CP-Sil 5CB column (Agilent Technologies Spain S.L., Las Rozas, Madrid) was used.

The pyrolysis compounds were identified on basis to their electron impact mass spectra (70 eV) and by comparison with those in the Wiley (1986) spectral database. The ion traces for the main series of homologous compounds were obtained (e.g., 85 for alkanes, 69 for alkenes, 60 for fatty acids). In the case of aromatic compounds reconstructed ion chromatograms displaying the joint intensity of the major diagnostic fragments, in general [M<sup>+</sup>] and [M<sup>+</sup> – CH<sub>3</sub>], were used to identify the expected pyrolysis products in the whole chromatogram (e.g., *m/z* 109 + 124 for guaiacol, *m/z* 139 + 154 for syringol, etc.).

### 2.6. Data analyses

For comparison purposes, the amounts of the different compounds were considered to be proportional to the peak areas of the total ion chromatographic trace. These data were subjected to multivariate analyses in order to recognize some trends in the compound assemblages released by the HAs from the different experimental plots. The variables (descriptors) processed were the main groups of pyrolysis products from soil HAs, whereas the observations (samples, individuals) were the different spatial replications of the HAs isolated from soils managed with the different tillage systems. The program used (correspondence analysis, two-way table, no supplementary observations [23]) converts the original frequency table into a plot in which samples and variables are depicted as points in the space defined by factorial axes.

## 3. Results and discussion

Several general analytical characteristics of the soils are illustrated in Table 1, showing differences due to management. Thus,

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