

TG–DTA, DRIFT and NMR characterisation of humic-like fractions from olive wastes and amended soil

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Abstract

The purpose of the present study is to investigate, by means of thermogravimetric analysis (TG) and differential thermal analysis (DTA), diffuse reflectance infrared Fourier transform (DRIFT) and 2D nuclear magnetic resonance (NMR) spectroscopies, the structural features of the humic-like fraction (HLF) from olive pulp (OP), its effluents originated from the fermentation processes for hydrogen (EH₂) and methane production (ECH₄) and humic acid (HA) from soil amended with each of these materials. A considerable structural modification emerged between the HLF, in particular from the ECH₄ effluent, which was characterised by a high content of polyphenolic and polypeptidic substances. The short-term amendment trial with OP and EH₂ indicated that no chemical or structural changes in soil HA appeared. In contrast, the amendment with ECH₄ substantially influenced the chemical and structural composition of soil HA. The structural interpretation performed by 2D NMR indicated the presence of aliphatic and aromatic protons while the sugar-like content and O–CH₃ groups decreased with respect to the soil control HA. It emerges from this study that olive wastes contain stabilised humic-like material that may be recycled as an amendment in areas where olive trees are cultivated.

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1. Introduction

The disposal of olive mill wastes (OMW) represents a serious environmental problem in the Mediterranean basin where olive trees are mainly cropped [1], because of the high content of organic carbon (C) (cellulose, emicellulose, polyphenols and lipids) and their high electrical conductivity [2–4]. An alternative practice is the recycling of organic C and the nutrients present in OMW as an organic soil amendment, thus closing the C and nutrient cycles [5]. However, recycling of OMW in agriculture needs to minimise the phytotoxicity and negative environmental impact caused by the high content of phenols and easily decomposable organic substances [6,8].

Studies on a laboratory scale [9,10] indicated that the treatment of olive waste water (OW) under aerobic conditions leads to an increase in stable organic matter (OM) similar to soil humic

substances (HS), with a drastic reduction of phytotoxicity. The amount and quality of the humic-like fraction (HLF) found in OMW during various fermentation processes is considered an important parameter of OM maturity and stability [11].

Recently, Nastri et al. [12] demonstrated that olive pulp (OP) and its effluent obtained from hydrogen (EH₂) and methane production (ECH₄) are potential soil amendments. These materials were characterised by a high amount of OM, nutrients and a negligible concentration of heavy metals. Furthermore, the results obtained indicated that only OP at high concentration delayed both seed germination and seedling growth. These effects decreased when the OP was incorporated into the soil while an enhancement of seedling growth was detected with the addition of EH₂ and ECH₄. On these basis further investigation was considered useful to evaluate if soil amended with OP and its effluents EH₂ and ECH₄ could influence the structure of native soil HS.

The HS originated from microbial decomposition of plant and animal residues represent the most important component of soil OM [13]. The structural changes that occur in HS are complex

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and therefore a physical–chemical and structural approach is needed. In addition, few studies have investigated the effects of olive wastes on the status and quality of native soil HS in short- and/or long-term amendment trials [8,14].

Among analytical techniques, thermal analysis is a method used to investigate the thermal stability of soil OM. In particular, thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) have been used to study HS structure [15–19] and subsequently to monitor the composting process [20–22]. This technique involves a continuous and simultaneous measurement of weight loss (TG) and energy change (DSC) during heating of the sample [15,22]. Usually, during heating of HS a first exothermic reaction ($\approx 300^\circ\text{C}$) is produced by the decomposition of proteins and carboxyl groups, while the exothermic reaction at higher temperatures ($\approx 450^\circ\text{C}$) is originated by decomposition of refractory C such as aromatic rings and saturated aliphatic chains [23,24]. Additionally, by combining thermal analysis with spectroscopic techniques, important structural information regarding the OM transformation process can be obtained.

Particular attention was devoted to diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy as a technique for functional group analysis [19,25,26] and to liquid-state [27–29] and solid-state NMR [28,30–32] for molecular structure. The development of high-field magnets and of multi-dimensional techniques has improved the overlapped individual signals which are typical of one-dimensional liquid-state NMR spectra of HS [33]. The HS two-dimensional (2D) NMR study was introduced by Buddrus et al. [34] and more recently, detailed interpretations on the structural components of HS have been provided by other authors [33,35–38].

The aim of the present study, within the EU BIOTROLL Project, was to apply TG–DTA, DRIFT and NMR spectroscopies in order to compare OP and EH_2 , ECH_4 and their HLF to understand how soil humic acid (HA) was influenced by a short-term trial amendment with these products.

2. Materials and methods

2.1. Olive waste

The OP was collected from a two-phase decanter mill and was submitted to two different fermentation processes for hydrogen production (EH_2) and for methane production (ECH_4) as described by Gavala et al. [39].

2.2. Experimental design

The surface horizon (0–20 cm) of a Typic Udifluent soil (USDA, 1998) was sampled at the experimental farm of the University of Bologna's Agricultural Faculty (Cadriano, Bologna, Italy). The main physical–chemical characteristics of the soil were: pH (in water 1:2.5, w/v) 7.62; texture: sand 31%, silt 42% and clay 27%; electrical conductivity (EC, dS m^{-1}) 0.09; total calcium carbonate (CaCO_3) < 1%; total organic C (TOC) 7.6 g kg^{-1} ; humic C 4.8 g kg^{-1} ; total Kjeldhal nitrogen (TKN)

0.84 g kg^{-1} ; C/N ratio 7.8; cation exchange capacity (CEC) $22 \text{ cmol}_c \text{ kg}^{-1}$, Olsen-P (P) 12.3 mg kg^{-1} .

Aliquots of 5 kg of dry soil were placed in plastic pots (16 cm in diameter and 25 cm in height) and each treated with an amount of OP and EH_2 and ECH_4 corresponding to 120 kg ha^{-1} of TKN, respectively. Each treatment was replicated three times and compared to unamended controls. The pots were buried into the soil up to 4/5 times their height to create a micro-environment more similar to the field conditions. After 6 months each sample was air dried and stored for subsequent spectroscopic and thermal analyses.

2.3. Chemical analysis of olive wastes and soil

The elemental characterisation and phenolic and total lipid concentration analysis of OP, EH_2 and ECH_4 have been described by Natri et al. [12].

Total C and N in soil, HA and HLF were measured with an elemental analyser (Thermo Finnigan mod. EA 1110).

2.4. Soil HA and HLF extraction and characterisation

Each air-dried sample, about 10 g, was extracted under N_2 with 100 mL of 0.5 M NaOH and stirred for 24 h. The suspension was centrifuged at $5000 \times g$ for 30 min and then filtered through a $0.45 \mu\text{m}$ filter using a Minitan S System (Millipore, Bedford, MA, USA). The solution was acidified with 5 M HCl to $\text{pH} < 2$ to precipitate the HA and was subsequently centrifuged at $5000 \times g$ for 20 min in order to eliminate the supernatant. The HA and HLF were dissolved with NaOH 0.5 M to produce a Na-salt, and then dialysed against Millipore water, using tubing (Cellu Sep H1-USA) with a cut-off of 8000 Da, until a neutral pH was achieved. Finally, the solutions were freeze-dried.

The titrations of HA were carried out using a VIT90 Radiometer Auto titrator (Radiometer Analytical, France), whereas thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out using a TG-DTA92 instrument (SETARAM, France) details on these procedures are described by Montecchio et al. [19]. The DRIFT spectra were recorded with a Nicolet Impact 400 FT-IR Spectrophotometer (Madison, WI) equipped with an apparatus for diffuse reflectance (Spectra-Tech. Inc., Stamford, CT). Peak area integration from 3000 to 2800 cm^{-1} was used to compare the CH groups in aliphatic substances between samples [19].

NMR spectra were recorded with a Bruker FT-NMR Avance 400 spectrometer (Broad Band 5 mm probe, inverse detection). Nominal frequencies were 400.13 MHz for ^1H and 100.61 MHz for ^{13}C . An internal lock on the deuterium of D_2O and $\text{DMSO-}d_6$ was used for all spectra. The chemical shifts at 298 K were referred to TSP. ^1H NMR data was acquired using the bipolar longitudinal eddy current delay pulse sequence (BPPLD) [40,41] and the Carr–Purcell–Meiboom–Gill sequence, commonly known respectively as “ledbpgs2s” and “cpmg1d” in the standard Bruker library. As regards the “ledbpgs2s”, 4k scans were collected, implying a bipolar pulse pair ranging from 2 to 3 ms, with a diffusion time (D20) of 100–200 ms and a time

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