



Research article

Ultra-high resolution mass spectrometry of physical speciation patterns of organic matter in fire-affected soils



Nicasio T. Jiménez-Morillo^{a,*,1}, José A. González-Pérez^a, Gonzalo Almendros^b, José M. De la Rosa^a, Derek C. Waggoner^c, Antonio Jordán^d, Lorena M. Zavala^d, Francisco J. González-Vila^a, Patrick G. Hatcher^c

^a Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS, CSIC), Reina Mercedes Av., 10, 41012, Seville, Spain

^b Museo Nacional de Ciencias Naturales (MNCN-CSIC), Serrano St. 115-B, 28006, Madrid, Spain

^c Department of Chemistry and Biochemistry, College of Science, Old Dominion University, Norfolk, VA 23529, USA

^d Departamento de Cristalografía, Mineralogía y Química Agrícola, Facultad de Química, Universidad de Sevilla, Profesor García González St., 1, 41012, Seville, Spain

ARTICLE INFO

Keywords:

Charred biomass
ESI-FT-ICR/MS
Mediterranean soils particle size fractions
Pyrogenic organic matter
van Krevelen diagram
Wildfire

ABSTRACT

Fire is one of the most important modulating factors of the environment and the forest inducing chemical and biological changes on the most reactive soil component, the soil organic matter (SOM). Assuming the complex composition of the SOM, we used an ultra-high resolution mass spectrometry analysis technique to assess the chemical composition and fire-induced alterations in soil particle size fractions (coarse and fine) from a sandy soil in a Mediterranean oak forest at Doñana National Park (Southwest Spain). Electrospray ionization-Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICRMS) showed that the coarse fraction of soils not affected by fires consisted mainly of polyphenolic compounds consistent with little-transformed SOM and fresh biomass, whereas the fine fraction was enriched in protein and lipid like homologues suggesting microbially reworked SOM. In fire-affected SOM, the coarse fraction contained a high proportion of aromatic compounds, consistent with inputs of charred litter or *in situ* chemical transformation of the SOM. Analysis of the fine fraction revealed two differentiated chemical families pointing to the existence of two carbon pools; a native microbial-derived moiety composed of lipids and polypeptide compounds, and a secondary, pyrogenic or thermally-altered moiety rich in aromatic compounds. This work represents the first application of ultra-high resolution mass spectrometry to study the chemical composition of SOM in different particle size fractions.

1. Introduction

Soil is the largest carbon (C) reservoir on the Earth's surface, with over 2000 Pg C, of which ca. 70% corresponds to organic matter (Batjes, 1996; Scharlemann et al., 2014). Due to the large size of the C pool in soils, small deviations from soil C content could have a relevant effect in the global C balance and an outstanding impact on the climate (González-Pérez et al., 2004; De la Rosa et al., 2008; Moss et al., 2010). Soil organic matter (SOM) can be perceived as a mixture of biogenic components with variable proportions of constituents from plants and microorganisms at different evolutionary stages (Stevenson, 1994; Arias et al., 2005; Ikeya et al., 2015). Within this mixture, some organic constituents retain a clear biogenic signature (i.e., lignin, tannins, polysaccharides, protein, etc.), while others consist of complex

aggregates of macromolecules and with simple molecules through a hierarchy of links ranging from weak physical interaction, to covalent bonds. These form a continuum of domains formed by aromatic and aliphatic structures incorporating O-containing functional groups of different reactivity (Sleighter and Hatcher, 2007). The intrinsic physical and chemical characteristics of SOM, which also show large variability in space and time, is a valuable source of biogeochemical information that also play relevant roles on the biological, physical and chemical soil properties (Baldock and Nelson, 1999). The SOM may be sorted into three well-defined conceptual C fractions, concerning its turnover time i) active-labile; ii) active-intermediate (fast recycling); and, iii) passive or refractory, that may remain stable in soil for centuries to millennia (Balesdent and Mariotti, 1996).

Fire is considered to be one of the principal factors affecting SOM.

* Corresponding author. Departamento de Fitotecnia, Escola de Ciências e Tecnologia, ICAAM, Universidade de Évora, Núcleo da Mitra, Ap. 94, 7006-554, Évora, Portugal. Tel.: +351 266 740 800.

E-mail address: njtm@uevora.pt (N.T. Jiménez-Morillo).

¹ Present address: HERCULES, Universidade de Évora, Palácio do Vimioso, 7000-089 Évora, Portugal.

Fire strongly influences C cycling and storage on temperate forests, being also the cause for rapid ecosystem changes (Nave et al., 2011). Wildfires exert alterations in the physico-chemical properties of soil and this depends on several factors, which may be categorized on: i) intrinsic to fire e.g. heating duration, type of burning, oxygen availability (Santín et al., 2016) and, ii) extrinsic to fire e.g. soil morphology, type and amount of organic material present in soil, the hydrologic conditions of soil during the fire event, etc. (De la Rosa et al., 2008).

Fire affects both the total quantity and quality (chemical composition) of SOM. Concerning SOM quantity, some authors observed that the effect of fire may vary from its almost total depletion to increases over 30% in the surface layers. The latter is usually attributed to inputs of fresh and partially charred biomass from the burnt vegetation (Chandler et al., 1983; González-Pérez et al., 2004). On the other hand, fire may induce the chemical alteration of SOM through several chemical reactions i.e. decarboxylation, dehydration, dealkylation and cyclization, which lead to the accumulation of condensed structures, including pyrogenic polycyclic hydrocarbons and heterocyclic nitrogen forms (Almendros et al., 2003, 2018; Kramer et al., 2004; Knicker et al., 2008).

Charred materials produced by fire contain high quantities of refractory C forms known as “black carbon” (BC) (De la Rosa et al., 2008). This is defined as a continuum of thermally altered products ranging from slightly charred, still degradable biomass, to highly condensed, refractory soot (Goldberg, 1985). This BC-continuum is chemically heterogeneous, but typically contains a great contribution of aromatic structures (Hedges et al., 2000; De la Rosa et al., 2008). In fact, the aromaticity of the charred material tends to increase with fire intensity (temperature and duration) (Shafizadeh, 1984).

Owing to the heat-insulating properties of soil, the highest alterations to SOM are usually confined to the first few centimeters of soil (Badía et al., 2014), where the highest amount of SOM is accumulated (e.g. Faria et al., 2015; Jiménez-González et al., 2016). Within this shallow layer, different C pools with different response to impacts of fires can be distinguished by using laboratory fractionation protocols based either on particle size or density fractions (Jiménez-Morillo et al., 2016a, 2017). In fact, it is frequently found that SOM in the coarse soil fractions consists mainly of fresh material, whereas, fine fractions contain comparatively more evolved or humified SOM due to the microbial activity (Hatcher et al., 1983; Nelson and Oades, 1998). Nonetheless, there is still limited information concerning the effect of fire in the case of chemical and physical soil fractions and the organic materials encompassed. This is in part due to the high heterogeneity and chemical complexity of SOM that requires the use of advanced analytical, more sensitive, techniques.

In recent years, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS) has emerged as one of the most effective tools for the analysis of chemically complex samples such as SOM. This analytical technique was first used for the chemical characterization of organic materials like humic and fulvic acids by Fievre et al. (1997). Since then, FT-ICR/MS has been effectively applied to the study and detailed characterization of terrestrial, aquatic, and atmospheric organic matter at the molecular-level (e.g. Stubbins et al., 2010; DiDonato et al., 2016; Willoughby et al., 2016). Concerning the study of fire-affected SOM, the technique has been used to detect BC particles within the aforementioned “environmental C reservoirs” (Kramer et al., 2004; Hockaday et al., 2006; Ikeya et al., 2015).

Among the advantage of FT-ICR/MS is the enormous amount of detailed molecular-level information (empirical molecular formulas) yielded, precluding molecular fractionation and providing meaningful compositional information that can be readily associated with groups of natural biopolymers (Sleighter and Hatcher, 2007). However, the huge number of molecules detected by FT-ICR/MS and additional data associated greatly hinders the interpretation of the results, making ways to visualize such datasets indispensable. The van Krevelen diagram has been, and continues to be, one of the most used resources for visual

analysis in geochemical studies. It was developed for the classification of coal and its precursor materials based on elemental analysis data (van Krevelen, 1950), and later applied to FT-ICR/MS analysis of organic matter (Kim et al., 2003). This tool has also been used to study SOM affected by fires (Almendros and González-Vila, 2012), as well as to the detection of charred materials in soils (Nocentini et al., 2010). Recently, van Krevelen diagrams, based in atomic H/C and O/C ratios of compounds released by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), were also found helpful to assess chemical reactions produced by fire (Jiménez-Morillo et al., 2016a).

The formulas generated following FT-ICR/MS analysis plot in different regions of the van Krevelen diagram, which in turn reflects their origin from different biomacromolecular domains in the SOM (e.g. lipid polymers, tannins, lignin, carbohydrates, charred particles, BC, etc.). This graphical tool may be also used to assess the main chemical reaction pathways produced by both biotic and abiotic factors. Therefore, FT-ICR/MS assisted by van Krevelen diagrams can be employed to determine organic material sources, evolution, microbial influence and potential structural families in the SOM in terms of its original environmental scenarios (Kim et al., 2003; D'Andrilli et al., 2015).

In a previous research we found the existence of two organic C pools in shallow soil layer (0–3 cm depth) chemically well differentiated, with a distinctive response to fire events (i.e., different thermal degradation patterns) (Jiménez-Morillo et al., 2016a). However, the analytical technique used, Py-GC/MS, provided a window of information, very limited to part of the chemical reactions induced by fire. Therefore, in this work, ultra-high resolution mass spectrometry technique (FT-ICR/MS) is applied for a more detailed chemical characterization of SOM from different soil size-fractions in fire-affected and unaffected sandy soils from the Doñana National Park (SW Spain). The main hypothesis to be tested is that formulated elsewhere (González-Pérez et al., 2004) that postulates that fire exerts transformation in SOM, not only in quantity but also in its quality, either by transforming existing SOM molecules into new chemical structures or by producing new compounds entering the soil from the burnt biomass.

2. Material and methods

2.1. Area of study and sampling

The area of study is located at Doñana National Park (South-West, Spain). This is a single natural landscape established as natural reserve in 1969. Doñana Park has a mild, typically Mediterranean climate, characterized by dry summers and relatively wet winters with an elevated average rainfall (> 800 mm) compared to inland and an average air temperature of ca. 17 °C (Siljeström and Clemente, 1990). Doñana National Park has been recurrently affected by wildfires, which have been considered the main cause of changes in its geomorphology and vegetation patterns during the last centuries (Granados, 1985). The study site was affected by a severe wildfire (> 300 ha) during the summer of 2012. Soil samples were taken in October 2014 from a Typic Xeropsamment/Haplic Arenosols (IUSS, 2015) under cork oak (*Quercus suber*) “QS” canopy. Burnt (B) soil was affected by the wildfire (B: 37° 7'21.95"N; 6° 26'53.44"W) and a nearby control of unburnt (UB) soil (UB: 37° 7'23.69"N; 6° 26'51.53"W), with the same physiographic characteristics but no recent histories of forest fires, were sampled. The UB and B soil samples consisted of composite samples obtained by combining five sub-samples taken within a circular area of ca. 20 m² under the unaffected and fire-affected trees nearest (Fig. S1). The samples were collected from the first 3 cm of soil after removing the litter layer. Earlier studies demonstrated that fire-effects are not significant at soil depths greater than 3 cm in sandy soils under Mediterranean climate conditions (Badía et al., 2014; Aznar et al., 2016). The samples were transported in clean glass flasks, air-dried under laboratory conditions (at 25 °C and approximately 50% relative humidity) during 1-week and sieved to fine earth (< 2 mm) to remove

Download English Version:

<https://daneshyari.com/en/article/7475520>

Download Persian Version:

<https://daneshyari.com/article/7475520>

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