

New analytical technique for establishing the quality of Soil Organic Matter affected by a wildfire. A first approach using Fourier transform ion cyclotron resonance mass spectrometry

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Introduction:

Fire is one of the most important modulator factors of the environment and the forest. It is able to induce chemical and biological shifts and these, in turn, can alter the physical properties of soil. Generally, fire affects the most reactive fraction, soil organic matter (SOM) (González-Pérez et al., 2004) resulting in changes to several soil properties and functions. To study changes in SOM following a wildfire, researchers can count on several traditional as well as new analytical techniques. One of the most recently employed techniques is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). This new powerful ultra-high resolution mass spectral technique, together with graphic interpretation tools such as van Krevelen diagrams (Kim et al, 2003), may be used to shed light on alterations caused by the burning of SOM. The objective of this research is to study fire impacts on SOM, using a sandy soil collected under a Cork oak (*Quercus suber*) in Doñana National Park, Southwest Spain. that was affected by a wildfire in August 2012.

Methods:

The impact of fire on SOM was studied in various different sieve fractions (coarse, 1-2 mm, and fine, <0.05 mm) collected in a burned area and an adjacent unburned control site with the same physiographic conditions. Alkaline extracts of SOM from each soil sample were examined using a Bruker Daltonics 12 Tesla Apex Qe FT-ICR-MS equipped with an Apollo II ESI ion source (operating in negative ion mode). The ESI voltages were optimized for each sample, and all spectra were internally calibrated following the procedure of (Sleighter and Hatcher, 2007), after which, peaks were assigned unique molecular formulas using a MatLab script written in house by Dr. Wassim Obeid of Old Dominion University.

Results:

The van Krevelen diagrams together with the relative intensity of each chemical compound, both obtained by FT-ICR-MS, allowed us to assess SOM quality for each sample and size fractions. The chemical compounds were grouped into the 7 main families; condensed aromatic compounds, unspecific aromatics, tannins, lignin, lipids, protein and carbohydrate derived.

The unburnt SOM in the coarse fraction was mainly composed of compounds with a high intensity in the tannin-like, lignin-like and carbohydrate-like regions of the van Krevelen diagram, whereas the SOM in the fine fraction showed a high intensity in the lipid-like and protein-like regions. These results suggest that the SOM in the coarse fraction was less altered than that of the fine fraction; the latter believed to be subjected to higher microbial activity. We suggest that the observed changes occurs via a methylation process, producing a SOM that is highly humified (Jiménez-Morillo et al., 2014).

The SOM in the coarse fraction affected by fire, showed a high relative intensity of chemical compounds in the carbohydrate-like and lignin-like regions, indicating the input of fresh organic matter. The presence of molecular formulas which plot in the aromatic and condensed aromatics regions also indicates that this fraction may have contributions from a second, more recalcitrant, organic carbon pool. The appearance of aromatic and condensed aromatic compounds could suggest that, in this fraction the fire induced condensation processes. In the burnt fine fraction, two different SOM sources of alteration could be identified; i) from microbial origin with high relative intensity of lipid-like and protein-like compounds and ii) fire origin with large amounts of condensed

aromatic compounds and a high contribution from the carbohydrate-like compounds region. We suggest that these results indicate both, condensation processes yielding black carbon like materials and additions from the coarse fraction during fire mediated distillation process.

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