



Pyrolysis compound specific isotopic analysis ($\delta^{13}\text{C}$ and δD Py-CSIA) of soil organic matter size fractions under four vegetation covers.

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A chemical characterization of soil organic matter (SOM) under different ground cover from a Mediterranean climate (Doñana National Park, Andalusia, Spain) is approached using bulk $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and δD isotopic analysis (C/TC-IRMS) and $\delta^{13}\text{C}$ and δD pyrolysis compound specific isotopic analysis (Py-CSIA: Py-GC-C/TC-IRMS). Soil samples were collected in sandy soils, Arenosols (WRB 2006) from the Doñana National Park (SW Spain) under different vegetation cover: cork oak (*Quercus suber*, QS), eagle fern (*Pteridium aquilinum*, PA), pine (*Pinus pinea*, PP) and rockrose (*Halimium halimifolium*, HH). Two size fractions; coarse (C: 1-2 mm) and fine (F: <0.05 mm) were studied from each soil. A complete conventional analytical pyrolysis (Py-GC/MS) of these samples have been studied in detail (Jiménez-Morillo et al., 2015).

Bulk isotopic analysis of stable light elements ($\delta^{15}\text{N}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and δD) revealed particular isotopic signatures showing differences related with the main vegetation cover and the different soil size fraction. All samples had a carbon isotopic signature between -26 and -29 ‰ which indicated that the organic matter in the two fractions of each soil sample derived from C3-type plants. The bulk δD isotopic signature in whole soil sample indicate a lower deuterium fractionation occurs in SOM under arboreal than under no-arboreal vegetation, this can be caused by the occurrence of a higher water evaporation rate under bush vegetation and/or to differences due to leaf morphology as previously described (Leaney et al., 1985). A $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ chart may provide some clues about N origin in the soil and particularly about the original source of nitrates (Kendall et al., 1996). In all sample and size fractions our values are in the chart area corresponding to NO_3^- in precipitation, with lighter $\delta^{18}\text{O}$ (c. 20 ‰) values compatible with fertilizers may be from adjacent crops.

In addition we were able to assign $\delta^{13}\text{C}$ and δD values for a number of specific SOM compounds released directly from pyrolysis (Py-CSIA); lipids (Alkenes), aromatic unspecific (alkylphenols), lignin (methoxyphenols) and polysaccharides (anhydrosugars) derived molecules. For all coarse fractions the $\delta^{13}\text{C}$ and δD values had the same general behavior with sugar derived molecules being enriched in the heavy isotope.

Regarding alkenes $\delta^{13}\text{C}$ isotopic signature, this was variable and dependent upon the main cover vegetation that may reflect different fractionations at different synthesis stages (Chikaraishi & Naraoka, 2001),

The δD values for specific compounds had a similar behavior to that for $\delta^{13}\text{C}$, being the sugar derived compounds the most deuterium enriched in comparison with lipid and lignin derived pyrolysis products. A conspicuous δD fractionation was observed for the sugar derived compounds in the fine fractions as compared with the coarse ones, with a depletion in deuterium, mainly for the PA sample where the depletion was the highest (c. -140 ‰). This may points to the occurrence of biological reworking with a higher microbiological activity fixing the lighter isotope in the soil fine organic fractions. It is known that lipid hydrogen is deuterium depleted relative to bulk organic hydrogen (Smith and Epstein, 1970). In line with this, in our study the lipid derived compounds had the largest deuterium depleted signature with a difference between bulk and lipid δD values was c. -35 ‰ . This fractionation was highest in Pine (PP) and Rockrose (HH).

The combination of traditional techniques for the study of SOM i.e. Py-GC/MS and IRMS, with new hyphenated analytical pyrolysis techniques i.e. Py-CSIA opens new possibilities and windows of information in SOM research. Our findings points to the occurrence of more or less complex processes that affects SOM chemical characteristics; whereas the coarse fraction resembles the chemical structure of the above vegetation, this SOM "memory" is less defined in the fine fractions, probably due to biologically mediated chemical conversions, additions and selective preservation of refractory chemical structures. SOM bulk IRMS and Py-CSIA are also informative about relevant plant physiological processes, OM sources and OM evolution status.

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