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Direct soil organic matter compound specific δ13C analysis using pyrolysis (Py-CSIA): identification of biomarkers in a dehesa from Southern Spain

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Dehesa are woodlands typical of southern Mediterranean climate species modified by human to seasonal wood-pastures adapted to the unpredictability of the Mediterranean climate. Changes in climatic and environmental conditions can affect both, plant biomass chemical and isotope composition that will eventually be reflected in soil organic matter (SOM). Nowadays, many ecological studies use bulk isotope values, which represent a weighted mean average of the different necromass compounds. An isotopic characterization of individual compounds is desirable to differentiate the isotopic composition of the main plant components. Soil organic matter is composed mainly of high MW biopolymers i.e. polysaccharides, polypeptides, polypeptides, polyesters, etc. not amenable to most chromatographic techniques without the use of intense extraction and sample preparation steps.

Here, an analytical pyrolysis technique combining Py-GC with a continuous flow isotope ratio mass spectrometer (IRMS) (Py-CSIA) is described and validated for the direct study of compound specific isotope composition in soil samples.

The consistency of the Py-CSIA was tested using a standard n-alkanes mixture (dissolved C16 to C30 series with increasing concentrations along three pentads, Indiana Univ. SIL mix. Type B). The values obtained fitted to a straight line (R^2 > 0.999). No induced thermal cracking nor deviations from the acclaimed isotope composition (fractionation) was observed up to high pyrolysis temperature (< 500 °C).

Composite dehesa (Pozoblanco , Córdoba, Spain) surface soil samples were taken under evergreen oak canopy . A detailed SOM study was performed using conventional analytical pyrolysis (Py-GC/MS) and $\delta^{13}C$ for specific compounds released after pyrolysis was done using Py-CSIA.

Well-resolved chromatograms were obtained by Py-GC/MS and a total of 40 pyrolysis compounds were detected that represented the chemical variability of soil organic matter and consisted mainly of polysaccharide, lignin-derived compounds (G- and S- units), fatty acids and n-alkanes.

When coupling Py with GC-C-IRMS, many c peaks were well resolved and with a sufficient chromatographic separation to give accurate $\delta^{13}C$ readings. Nonetheless, there were compounds with high $\delta^{13}C$ standard deviations considered not sufficiently resolved for a reliable estimation of their isotope composition due to coelution and were discarded.

The $\delta^{13}C$ for specific biomass compounds released by pyrolysis of soil was in line with the expected values for C3 plants i.e. Quercus spp. Polysaccharide derived products (furans, cyclopentanones), showed slightly enriched $\delta^{13}C$ values (-26.0 ± 0.47 ‰) in accordance with their naturally ^{13}C enriched composition. Although no statistical differences were found, lignin-derived units showed slightly depleted $\delta^{13}C$ (-27.4 ± 0.78 ‰). Accordingly, depleted $\delta^{13}C$ values for lipids (-35.1 ± 2.41 ‰) and alkanes (-35.5 ± 2.20 ‰) were found, the latter with lighter isotope composition with increasing the hydrocarbon length.

Here we show the possibility of using this particular analytical pyrolysis technique (Py-CSIA) for the direct measurement of $\delta^{13}C$ in relevant specific soil organic matter components including those from polysaccharides (cellulose/hemicellulose), lignin, lipid/waxes and also peptide/protein-derived compounds.

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