

## Pyrolytic indices of diagenetic transformation of lignin as biogeochemical proxies for soil organic matter quality and C storage potential

Marco A. Jiménez-González (1), Gonzalo Almendros (1), Ana M. Álvarez (2), Nicasio T. Jiménez-Morillo (3), and Francisco J. González-Vila (3)

(1) National Museum of Natural Sciences, MNCN-CSIC, Madrid (Spain), (2) Autonomous University of Madrid, UAM, Madrid (Spain), (3) Institute of Natural Resources and Agrobiology of Seville, IRNAS-CSIC, Sevilla (Spain)

The environmental factors involved in soil organic carbon sequestration remain unclear. The functional relationships between the macromolecular structure of the soil organic matter (SOM) and its resilience has been a constant in classical biogeochemical models. Other more recent hypotheses have postulated that preservation by soil minerals may play a chief role in the accumulation of stable SOM forms. However, additional experimental data are required to demonstrate a cause-to-effect relationship between preservation and stabilization. Some authors might consider that models neglecting the role of macromolecular structure are swapping cause and effect i.e. that SOM structurally flexible, weakly condensed and having 'open' structures is the one with high potential to interact with the soil mineral matrix, leading to stable microaggregates.

In this study up to 35 topsoil samples (0–5 cm) were collected from different Spanish soils with contrasted values of organic C (the dependent variable), geological substrate and vegetation type. A wide array of uni- and multivariate chemometric models were applied to independent variables consisting of total abundances of the major aromatic compounds, i.e. alkylbenzenes and methoxyphenols released from whole soil samples using pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). These two families of compounds were selected since they are classically considered to inform on the degree of microbial reworking of lignins, which is an important precursor of the aromatic moiety of the SOM.

A series of pyrolytic surrogate indices (aiming to express SOM diagenetic transformation in relation to the original biogenic molecular composition) were especially successful in forecasting SOC, viz: a) ratio between alkylbenzenes and methoxyphenols, b) ratio between short-chain (C0–C4) and long-chain (>C4) alkylbenzenes, c) ratio between methoxyphenols and short-chain alkylbenzenes, and d) ratios between methoxyphenols with different side-chain length, i.e. methyl-, ethyl-, vinyl-, propenyl- and aceto- derivatives of guaiacyl and syringyl rings. In particular partial least squares regression (PLS) models led to very significant prediction of SOC based exclusively on the major aromatic pyrolytic compounds as predictors, i.e. methoxyphenols and alkylbenzenes. The PLS coefficients showed high positive loadings for methoxyphenols (i.e. these compounds were diagnostic for soils with high C-storage potential), and negative for alkylbenzenes (which were characteristic for C-depleted soils). This may be explained as if selective preservation of lignin were the most efficient process in soils behaving as active C sinks. Conversely, the progressive smoothing in the lignin signature and the accumulation of methoxyl-lacking aromatics (i.e. short-chain alkylbenzenes) was typical in the soils with low SOC content but high levels of diagenetic alteration of lignin. The progressive alteration of C6–C3 phenylpropanoid lignin units also corresponded to the fact that heavily altered lignin, presumptively accumulated in SOM depleted soils, tended to release typical pyrolytic markers consisting of C0–C1 methoxyphenols instead of its vinyl and propenyl counterparts, in addition to major proportions of short-chain (<C4) alkylbenzenes.

The SOM forecasting model suggested that the SOM storage potential in continental Mediterranean soils does not parallel SOM quality, at least when the latter is defined as the extent to which the structural components of biomacromolecules are transformed into H- or alkyl-substituted condensed structures (i.e. in the case of lignin: demethoxylation, dealkylation, phenylpropanoid side-chain breakdown...) which characterizes the matured, structurally complex SOM forms. This finding could challenge the current policies incentivizing SOM sequestration regardless the qualitative descriptors of its maturity, or the analysis of local mechanisms responsible for the temporary retention of the SOM under different bioclimatic scenarios.