

Reappraisal of soil C storage processes. The controversy on structural diversity of humic substances as biogeochemical driver for soil C fluxes

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The functional relationships between the macromolecular structure of the humic substances (HS) and a series of biogeochemical processes related with the C sequestration performance in soils have been recently questioned. In this communication we collect recent data from a wide array of different ecosystems where the C storage in soils has been studied and explained as a possible cause-to-effect relationship or has been found significantly correlated (multivariate statistical models) with a series of structural characteristics of humic materials. The study of humic materials has methodological analytical limitations that are derived from its complex, chaotic and not completely understood structure, that reflects its manifold precursors as well as the local impact of anyiranmental/densitional factors. In this work we attempt to design an axploratory, multionic approach based

and not completely understood structure, that reflects its manifold precursors as well as the local impact of environmental/depositional factors. In this work we attempt to design an exploratory, multiomic approach based on the information provided by the molecular characterization of the soil organic matter (SOM).

Massive data harvesting was carried out of statistical variables, to infer biogeochemical proxies (spectroscopic, chromatographic, mass spectrometric quantitative descriptors). The experimental data were acquired from advanced instrumental methodologies, viz, analytical pyrolysis, compound-specific stable isotope analysis (CSIA), derivative infrared (FTIR) spectroscopy, solid-state C-13 and N-15 nuclear magnetic resonance (NMR) and mass spectrometry (MS) data after direct injection (thermoevaporation), previous pyrolysis, or ion averaging of specific m/z ranges from classical GC/MS chromatograms.

In the transversal exploratory analysis of the multianalytical information, the data were coded for on-line processing in a stage in which there is no need for interpretation, in molecular or structural terms, of the quantitative data consisting of e.g., peak intensities, signal areas, chromatographic (GC) total abundances, etc.

A series of forecasting chemometric approaches (aiming to express SOM biodegradability, or soil C resilience as a function of intrinsic molecular characteristics of the SOM) were especially successful in the case of: a) linear multiple regression models (LMR) with automatic backward variable selection, b) supervised removal of internal redundancy of the variables based on multidimensional scaling (MDS), and c) partial least squares (PLS) regression to obtain the variable importance for projection (VIP) which is useful to identify new environmental proxies.

At least the results obtained from differing continental Mediterranean soils showed that a large influence of local (soil-dependant) abiotic factors in the final variance (of the total soil C quality and quantity) was explained by the SOM molecular structure. This conclusion is relevant as regards the recent (in our opinion hermeneutic and speculative) controversy disregarding the importance of the structural features of HS in biogeochemical and environmental processes controlling C sequestration in soils.