Ultrahigh-resolution mass spectrometry to elucidate the variability in $\delta^{13}C$ of water-extractable organic matter in soils

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The molecular characterization of natural organic matter is a challenging objective, because of the great heterogeneity of this material. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is an advanced non-targeted investigation technique allowing an ultrahigh-resolution molecular analysis of complex organic systems. On the basis of a previous study conducted on 120 soil samples from the Burgundy region that revealed clear differences in the C stable isotopes concentrations between water-extractable organic matter (WEOM) samples from soils with different land covers (cropland, grassland and forest), our hypothesis is that the relative contribution of the vast assemblage of molecules constituting WEOM regulates this variation in the C isotope composition.

We analyze the WEOM samples of these 120 soil samples using FT-ICR MS and used multivariate statistical analysis to link specific molecular assemblages with the variability in $\delta^{13}C$ for each land cover class. Our objective was to determine if similar molecular patterns are responsible for the $\delta^{13}C$ variability in the different land cover classes.

For the whole dataset, $\delta^{13}C$ values showed clear differences in the C isotope composition between the three land covers, as well as variations of the C isotope abundances within each category. The WEOM of grassland soils, with an average $\delta^{13}C$ of -27.1±0.7 (mean±SD), is isotopically lighter than WEOM of forest soils, averaging at -24.2±0.9. In cropland soils, we measured intermediate $\delta^{13}C$-WEOM values (-25.8±1.1). We evaluate the relation between the highly resolved molecular information (m/z as X variables) and $\delta^{13}C$ (y variable) of WEOM by setting up an OSC-PLS (Orthogonal Signal Corrected - Partial Least Square) statistical model for each of the three different classes.

This approach revealed that hundreds of molecular formulas, mainly specific to each land cover class (for about 80%) but also few common to two or three land-cover classes, were correlated with the variation in the $\delta^{13}C$-WEOM. The assigned molecular formulas were composed of CHO, CHON, CHOS and CHONS molecular categories. We determined that the variation in the WEOM-$\delta^{13}C$ values under each of the three land cover is primarily controlled by different identifiable compound classes and molecular trends, while molecular fingerprints common to several land covers are much more scarce.

Keywords: soil organic matter SOM, C stable isotopes, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, regional scale

