

Introduction :

Soil Organic Matter (SOM) is a crucial issue for agriculture and climate change mitigation. It plays a key role in the structural stability and fertility of soils and contributes to the global carbon cycle as the major reservoir of organic carbon on the Earth's surface.

The Rock-Eval® (RE) technology, known as a reference analytical method in the Oil & Gas industry, has been recently increasingly used for soil characterization. The use of RE device in soil science is based upon a straightforward adaptation of the analytical protocols conventionally applied in the petroleum industry with a modification in the temperature program (Disnar et al., 2003). Lately, some authors proposed new indicators derived from RE analysis to characterize soil organic carbon (SOC) in terms of labile and stable organic carbon as far as these new parameters are well related to SOC biogeochemical stability (Cécillon et al., 2018).

Objectives :

A first objective of this preliminary study was to evaluate the influence of soil sample physical characteristics on the RE signals. In this respect, the influence of sample amount and, of sample preparation (solvent extraction, decarbonation, particle size fractionation), on RE pyrolysis and oxidation signals was evaluated for two soils characterized by contrasted textures: clayey and sandy samples. The relationship between the SOM thermal stability and the molecular composition of the corresponding SOM lipid fractions of increasing polarity was also investigated for both samples using liquid chromatography separation followed by GC-MS (Gas Chromatography - Mass Spectrometry) analysis. Pure straw constituent (lignin, ...) RE analyses were performed and their signals recombination was compared with straw RE analysis.

A second objective was to assess the potential of RE analysis to discriminate soil samples parameters, mainly according to vegetation, soil textures and Total Organic Content (TOC). For that, 10 soil samples from various forest ecosystems were selected. They show either similar amount of organic carbon content, but contrasting texture (sandy vs clayey), or similar textures, but different TOC. This resulted in data referring to multidimensional statistics with clustering and principal component analysis.

Results :

The response of the different RE detectors is proportional with the initial amount of soil sample. However, the correlation of certain oxidation signals (S4CO and S5) gets poor for the lowest amounts. As grain size fractions are known to be associated with different mineralogies, four sub fractions (<63 μm , 63-125 μm , 125-280 μm , >280 μm) were separated by sieving on each soil sample. The RE signals of these sub fractions were recombined using a linear recombination based on the mass balance and compared to the one obtained on the initial sample. By this way, the impact of particle size fractionation on bulk sample was pointed out. For the sandy sample, the TOC was increasing with decreasing size fraction contrary to the clayey one with the same TOC value. For both soils, the RE response, derived from the linear signal recombination from the 4 size fractions, was consistent with the bulk sample one. Nevertheless, slight S2 peak differences were observed due to this fractionation. For both samples, the recombined signal shows a carbon mass loss (estimated by RE) compared to native signal. The loss of organic compounds on the recombined signal resulting in a S2 peak decrease is only detected in a temperature range from 430 to 470°C for the clayey sample. For the sandy sample, this carbon loss (S2) is spotted over the entire temperature range. It could be argued by a selective granulometry loss (on the 125 μm sub fractions) for the clayey sample while for the sandy one, this carbon loss seems to be due to the fractionation procedure.

RE shows that sample classical decarbonation (HCl solutions) also leads to a loss of organic compounds (S2 and TOC decrease) in addition to an incomplete destruction of carbonates (S5 peak). The fact that a part of S5 peak is still present may be explained by the presence of specific carbonate type but clearly indicates that care has to be paid when using acid attack. As RE parameters are commonly estimated based on petroleum samples with an average carbon content assumed to be around 83 wt.%, they have been modified in order to account for the specific soil composition ($C/O \approx 1$); the resulting TOC relative standard variations can reach up to 10 to 20% for the studied samples. The RE calculated TOC values were confirmed by elemental analysis.

The analysis of pure compounds (such as (hemi)-cellulose, lignin, ...) representative of the chemical compounds, constitutive of the vegetal biomass, highlights a relationship between them in the native sample; RE oxidation profiles are different when compared together resulting in the absence of specific chemical compound peaks. Despite the reference compounds were present in the straw sample, some of their pyrolysis and oxidation signals were out of the temperature range when compared to those of the straw. This preliminary test evidences that the use of pure compounds is not appropriate to study the chemical composition of soil samples.

The study of 10 selected forest soil samples discriminated two distinct families depending mainly on texture: more or less silty sand and clayey. Even though the number of considered samples is not enough to be representative, the statistical approach comforts these RE results. Limited correlated RE parameters accounting for a strong contribution (more than 70%) emphasize the mineral texture. In contrast, no combination of variables clearly points out domains to distinguish the initial vegetation.

Conclusion :

In conclusion, preliminary issues were identified when analysing soil samples using Rock-Eval®. Attention has to be paid when soil samples preparation is needed due to carbon loss and to the removal of crosslinking/intermolecular interactions compared to the native soil samples. Work is in progress to propose an improved RE method.

RE parameters to discriminate the forest soils have not been clearly identified yet. RE analysis are currently performed on additional samples to complete the set of samples.

References :

Cécillon L., Baudin F., Chenu C., Houot S., Jolivet R., Kätterer et al., 2018. A model based on Rock-Eval thermal analysis to quantify the size of the centennially persistent organic carbon pool in temperate soils. *Biogeosciences*, 15, 2835–2849.

Disnar J.-R., Guillet B., Keravis D., Di-Giovanni C., Sebag D., 2003. Soil organic matter (SOM) characterization by Rock-Eval pyrolysis: Scope and limitations. *Organic Geochemistry* 34, 327–343.