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## The energetic and chemical fingerprints of persistent soil organic carbon

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A better understanding of soil organic carbon (SOC) persistence is needed to better predict SOC vulnerability to global change. The absence of convincing physical or chemical procedures to define, characterize or isolate relatively labile versus persistent SOC pools makes the study of persistent SOC difficult. Long-term bare fallow (LTBF) experiments, in which C inputs have been stopped for several decades, provide a unique opportunity to study persistent SOC without the inherent artefacts induced by extraction procedures, the hypothesis being that SOC is gradually enriched in persistent C with time as labile components decompose. We determined the evolution of thermal and chemical characteristics of bulk SOC in five LTBF experiments across Europe: Askov (DK), Grignon (FR), Rothamsted (UK), Ultuna (SW) and Versailles (FR), using a multi-technique approach involving Rock-Eval pyrolysis, thermogravimetry and differential scanning calorimetry (TG-DSC), mid-infrared diffuse reflectance spectroscopy (DRIFT-MIRS), and Near Edge X-Ray Absorption Fine Structure (NEXAFS).

Results of Rock-Eval and TG analyses showed that the temperature needed to combust the SOC increased with bare fallow duration at all sites. Conversely, SOC energy density (in mJ mg<sup>-1</sup> C) measured by DSC decreased with bare fallow duration. Rock-Eval pyrolysis results showed that hydrogen index (HI) tended to decrease with bare fallow duration whereas the oxygen index (OI) did not show consistent trends across sites. NEXAFS signals presented little differences and were dominated by carboxyl peak. Nonetheless, NEXAFS results showed a trend of increasing carboxyl groups and decreasing ketone and amide groups with bare fallow duration. Due to the mineral matrix, only a reduced part of the DRIFT-MIRS signals has been used. We observed that the bulk chemistry of aliphatic SOC (CH<sub>3</sub> vs. CH<sub>2</sub> functional groups) showed different trends for the different sites.

Our results showed that in spite of the heterogeneity of the soils at the 5 LTBF sites, organic carbon that has persisted in soils for several decades have similar and defined thermal and energetic properties: persistent SOC burns at higher temperature and its combustion generates less energy. Persistent SOC in the studied temperate soils also shares some chemical properties: it has a lower HI values and is consistently enriched in carboxyl groups. Nonetheless, the chemical trends were less obvious than the results given by thermal techniques confirming that organo-mineral interactions are the key driver of long-term SOC stabilization. The increased burning temperature and lower energy density of persistent SOC suggest that SOC stability may be a function of the high energy cost and low energy gain from decomposition of this material. It also suggests that decomposition of the stable C pool should be more temperature sensitive and thus vulnerable to increased temperature as previously observed in several incubation studies.