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Quantifying the pluri-centennial soil organic carbon pool using Rock-Eval pyrolysis

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Soil C is a key component of climate change. Any alteration of the soil organic C (SOC) reservoir yields a rapid modification of the atmospheric CO_2 concentration. However, a part of the SOC reservoir will not contribute significantly to next century's land CO_2 emissions as its residence time exceeds this timescale. The size of the pluri-centennial SOC pool is supposed to be large (ca. one third of total SOC), but is in fact highly uncertain as it cannot be estimated accurately by any analytical method. This methodological gap hampers the proper initialization of SOC dynamics models, questioning their predictions on the evolution of the global SOC reservoir.

Here, using an exceptional soil sample set coming from long-term agronomic experiments in Western and Northern Europe, we show that a multivariate regression model based on Rock-Eval 6 (RE6) pyrolysis data can accurately predict the proportion of the pluri-centennial SOC pool in a soil sample with a prediction error lower than 6% for a wide range of soil types and land-uses.

One hundred and six soil samples coming from four sites (Grignon, FR; Rothamsted, UK; Ultuna, SW; Versailles, FR) with long-term bare fallow (LTBF) and associated non bare fallow treatments (organic amendments, cropping systems, grasslands) were used to calibrate and validate the model. In a previous study, the modelling of SOC decay in LTBF experiments allowed estimating the size of the pluri-centennial persistant SOC pool at each of these sites (Barré et al., 2010, Biogeosciences 7:3839-3850). Based on these estimates, we calculated the proportion of pluri-centennial persistant SOC (% of total SOC) in each of the 106 soil samples. They showed very diverse proportions of pluri-centennial persistant SOC pool (from 6 to 100% of total SOC, with total SOC concentrations ranging from 5 to 46 gC.kg-1soil). All samples were analysed using RE6 pyrolysis. Five RE6 pyrograms per sample were used to compute the temperatures at which a specific amount (5 to 95%) of CH, CO and CO_2 gas had evolved during the RE6 pyrolysis and oxidation steps. These RE6 predictors were used in a random forest (RF) multivariate regression model to predict the proportion of the pluri-centennial SOC pool. Our RE6-RF model showed an excellent predictive performance: out-of-bag R^2=0.93, out-of-bag error=6% of total SOC (n=86); validation R^2=0.96, prediction error=5% of total SOC (n=20).

We then applied our RE6-RF model on 50 cropland and forest topsoils (0-30cm) with contrasting geopedology (region of Grignon, FR). Despite its wide heterogeneity, this new sample set was within the prediction range of our RE6-RF model. The RE6-RF predicted proportion of the pluri-centennial SOC pool was consistently higher in cropland than in forest soils ($p<0.001$), while its concentration (gC.kg-1soil) was not affected by land-use. Conversely, the concentration of the pluri-centennial SOC pool was markedly dependent on soil type ($p=0.01$) and parent material ($p=0.001$), indicating a clear geochemical control on the pluri-centennial soil organic carbon reservoir.

Our study positions RE6 pyrolysis as a meaningful tool to quantify the pluri-centennial SOC pool, with the ability of detecting its landscape-scale heterogeneities.