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Black carbon quantification in charcoal-enriched soils by differential scanning calorimetry

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Black carbon (BC), the solid residue of the incomplete combustion of biomass and fossil fuels, is ubiquitous in soil and sediments, fulfilling several environmental services such as long-term carbon storage. BC is a particularly important terrestrial carbon pool due to its large residence time compared to thermally unaltered organic matter, which is largely attributed to its aromatic structure. However, BC refers to a wide range of pyrogenic products from partly charred biomass to highly condensed soot, with a degree of aromaticity and aromatic condensation varying to a large extend across the BC continuum. As a result, BC quantification largely depends on operational definitions, with the extraction efficiency of each method varying across the entire BC range. In our study, we investigated the adequacy of differential scanning calorimetry (DSC) for the quantification of BC in charcoal-enriched soils collected in the topsoil of pre-industrial charcoal kilns in forest and cropland of Wallonia, Belgium, where charcoal residues are mixed to uncharred soil organic matter (SOM). We compared the results to the fraction of the total organic carbon (TOC) resisting to K2Cr2O7 oxidation, another simple method often used for BC measurement. In our soils, DSC clearly discriminates SOM from chars. SOM is less thermally stable than charcoal and shows a peak maximum around 295°C. In forest and agricultural charcoal-enriched soils, three peaks were attributed to the thermal degradation of BC at 395, 458 and 523°C and 367, 420 and 502 °C, respectively. In cropland, the amount of BC calculated from the DSC peaks is closely related (slope of the linear regression = 0.985, R^2=0.914) to the extra organic carbon content measured at charcoal kiln sites relative to the charcoal-unaffected adjacent soils, which is a positive indicator of the suitability of DSC for charcoal quantification in soil. The first BC peak, which may correspond to highly degraded charcoal, contributes to a larger part of the total BC amount in agricultural soils compared to forest soils, suggesting that cultivation might accelerate charcoal degradation. Regarding the K2Cr2O7 oxidation, 65 % of the TOC is oxidized in forest soils while 100 % is oxidized in agricultural soils, discrediting the method for old charcoal quantification in soil. In conclusion, DSC is a rapid and cost-effective technique for BC quantification in soil, covering the entire range of the BC continuum while giving information on the thermal stability of different BC pools. Oppositely, K2Cr2O7 oxidation in not a suitable method for old charcoal quantification in soil.