Thermal signature and quantification of charcoal in soil by differential scanning calorimetry and BPCA markers

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Abstract. Black carbon (BC) plays an important role in terrestrial carbon storage and can sustainably improve soil fertility. Nevertheless, the accurate quantification of BC remains a critical issue to fully unravel the functions and dynamics of BC in soil. In this work, we explored the potential of differential scanning calorimetry (DSC) to identify, characterize and quantify charcoal in the soil of pre-industrial charcoal kiln sites from a diversity of forest and cropland soils in Belgium and Germany. Pre-industrial charcoals and uncharred soil organic matter (SOM) demonstrated a distinct thermal signature that allowed their discrimination, with charcoal being more thermally stable than SOM. The DSC pattern of charcoals is characterized by one to three specific exotherms varying in size and position depending on soil conditions. From our data, we assume that the thermal moieties within charcoal depend on the strength of chemical bonds of C atoms (increasing with the degree of aromatic condensation and decreasing with weathering) and on the activation energy required to initiate the combustion. Despite the specific thermal features of charcoal, its decomposition spans a wide range of temperatures that overlaps with the thermal signature of uncharred SOM. This stresses the challenge of BC quantification in soil and hinders the use of cut-off temperatures to accurately quantify charcoal in soil. Therefore, charcoal-C content was estimated from the relative height of exotherms attributed either to the combustion of charcoal or SOM. For a selection of 45 soil samples, charcoal-C content estimated by DSC was compared to benzene polycarboxylic acids (BPCA) abundance, a widely used method to quantify BC in soil. The two methods correlated strongly ($R^2 = 0.97$), with BPCA-C representing about one fifth of DSC-derived charcoal-C. This reinforces the view that operationally-defined BC content has an absolute quantitative value only if the recovery rate is controlled, which is very complicated for many case studies. Overall, our results demonstrate that dynamic thermal analysis is largely under-exploited despite providing quantitatively interpretable information across the continuum of soil organic matter.

1 Introduction

Black carbon (BC) is the solid residue of incomplete combustion of biomass and fossil fuel, which comprises a wide range of thermally altered materials from slightly charred biomass to highly recalcitrant condensates such as soot (Goldberg, 1985; Schmidt and Noack, 2000). A main fraction of terrestrial BC is stored in soil (Forbes et al., 2006; Leifeld et al., 2018; Preston and Schmidt, 2006; Reisser et al., 2016; Santín et al., 2016), where it has a longer residence time than uncharred organic matter (e.g. Wang et al., 2016; Wolf et al., 2013). The increased resistance of BC to (a)biotic degradation has been related to its fused aromatic ring structure (Solomon et al., 2007; Wang et al., 2016). BC has received much interest from soil scientists because it plays an important role in the provision of ecosystems services such as terrestrial carbon storage (Czimczik and Masiello, 2007; Knicker, 2011; Masiello, 2004; Preston and Schmidt, 2006; Schmidt and Noack, 2000) and sustainable soil fertility (Glaser et al., 2001, 2002; Glaser and Birk, 2012; Schmidt et al., 2021). Nevertheless, the accurate quantification of BC in environmental matrices remains as a critical issue that makes the role of BC unclear in geochemical processes (Mukherjee and Kumar, 2021).

According to the general definition reported earlier, BC comprises a wide range of materials with no clear-cut boundaries, which challenges quantification (Kappenberg et al., 2016; Roth et al., 2012; Schmidt et al., 2001). The various forms of BC cover a large molecular continuum (Hammes et al., 2007; Masiello, 2004) that reflects contrasting conditions of formation (Keiluweit et al., 2010; Wiedemeier et al., 2015a). Moreover, properties of chars produced at relatively low temperature overlap with that of uncharred organic compounds naturally present in soil. Consequently, quantification of BC relies on operational definitions depending on specific objectives defined by researchers from different fields in atmospheric, soil, sediment and paleo-environmental sciences (Hammes et al., 2007; Schmidt et al., 2001). The various methods record systematic differences because they recover different fractions of the BC continuum and do not all completely isolate BC from other carbon compounds (Hammes et al., 2007; Roth et al., 2012). As a result, Schmidt et al. (2001) reported that variation in the BC content estimated by four different methods for one individual sample was more than two orders of magnitude.

Typically, five categories of techniques of identification and quantification of BC in soil and sediments are distinguished: physical, thermal, chemical, spectroscopic and molecular markers techniques (Bird et al., 2015; Hammes et al., 2007). The principle of thermal and (thermo-)chemical separation techniques relies on the exposition of the sample to an oxidative treatment in standard conditions. Carbon surviving oxidation is determined by mass loss or elemental analysis and operationally defined as BC. A molecular marker technique that is widely used by soil scientists consists in the quantification of benzene polycarboxylic acid (BPCA) markers liberated by digestion of BC in an acid medium (Brodowski et al., 2005; Glaser et al., 1998). This procedure has two main advantages: (i) it relies on the chemical decomposition of BC into markers that are specific to BC, related to its high aromaticity and (ii) it provides information on the degree of aromatic condensation of BC according to the number of carboxyl groups on the edge of benzene of the BPCA markers (Glaser et al., 1998). Nevertheless, this method has known limitations, as soil type and soil organic matter content may affect both quantification of total BC and the pattern of BPCA markers (Brodowski et al., 2005; Kappenberg et al., 2016). In particular, the recovery of

BPCA-C may vary depending on the quality of BC (Hammes et al., 2007; Roth et al., 2012). The less condensed fraction of chars is suspected to be completely decomposed by the strong oxidative attack (Glaser et al., 1998) whereas the most refractory, graphitized forms of BC might resist digestion preceding BPCA analysis (Brodowski et al., 2005; Roth et al., 2012). As a result, BPCA-C was shown to correspond to a maximum of $\frac{1}{2.27}$ of total C in charcoal in optimal conditions of recovery (Glaser et al., 1998). This factor of 2.27 is often used as a conservative conversion factor to estimate total BC content from BPCA-C extracted from soil, although it has been criticized for its validity (Glaser et al., 1998; Schneider et al., 2010).

Among these techniques used for BC quantification, thermal methods are convenient because they are rapid, reproducible, inexpensive and require little sample preparation (Plante et al., 2009). Thermal resistance has been related to the biological availability of chars (Harvey et al., 2012; Plante et al., 2011) and to the residence time of BC in soil, as revealed by ^{14}C measurements (Leifeld et al., 2015; Plante et al., 2013). Static thermal methods rely on cut-off temperatures to distinguish between BC and non BC components (e.g. Gustafsson et al., 2001). Nevertheless, widely used chemo-thermal oxidation at 375°C is calibrated for soot (Elmquist et al., 2004) and was shown to recover only from 0 to 44 % of C in chars, with no survival for those produced at < 850 °C (Nguyen et al., 2004). In contrast to static methods, dynamic thermal analysis techniques like thermogravimetry (TG) and differential scanning calorimetry (DSC) have the potential to provide information for the entire continuum of materials that compose soil organic matter (SOM) by scanning a sample over a large range of temperatures (Leifeld, 2007; Plante et al., 2009). Leifeld (2007) highlighted that BC has a specific thermal signature that allows an unambiguous discrimination from uncharred SOM, as BC is systematically more thermally stable. Among materials potentially interfering with the signature of BC, only bituminous coal had a thermal stability comparable to that of chars.

In this work, we explored the analytical potential of DSC to identify and quantify charcoal-C in the soil of pre-industrial charcoal kiln sites, also referred to as relict charcoal hearths in the literature. Charcoal kiln sites are platforms of *in situ* charcoal production by the earthmound kiln method (Schenkel et al., 1998), which operated at maximal temperatures of 400–450 °C (Emrich, 1985). They are widespread in the historical forest areas in Europe as charcoal has long been the unique combustible used for smelting and steel-making (Hardy et al., 2016; Samojlik et al., 2013). These sites have received increasing attention in recent years, particularly as proxies for long-term soil amendment with biochar (Borchard et al., 2014; Burgeon et al., 2021; Dehkordi et al., 2020; Hardy et al., 2017a; Hirsch et al., 2018; Kerré et al., 2017; Lasota et al., 2021; Mastrolonardo et al., 2019; Pollet et al., 2022; Schneider et al., 2018; Zanutel et al., 2021), which is a promising technology to sequester carbon in soil while maintaining or improving soil fertility (Laird, 2008; Lehmann, 2007).

Three specific objectives were addressed here: we aimed (i) to characterize the DSC thermal signature of charcoal in soil relative to that of uncharred SOM; (ii) to quantify charcoal-C in soil based on specific charcoal features of the thermograms; and (iii) to compare the content of charcoal-C in soil estimated by DSC to the content of total BC estimated by the BPCA method. To meet these goals, we analyzed charcoal-rich soils sampled at various pre-industrial charcoal kiln sites of Wallonia in Belgium and of the Siegerland and the Eifel in Germany.

2 Material and methods

2.1 Soil samples

2.1.1 Soils of Belgium

Two series of organo-mineral topsoil samples of kiln and adjacent reference soils from forest (sampled by (sub-)horizons of variable depth; N=38; described by Hardy *et al.*, 2016) and cropland (0-25 cm depth; N=34; described by Hardy et al., 2017a) were analyzed. Briefly, forest soils cover a wide range of textural classes, from sand to clay loam. Soil types of reference soils are Arenosols, Cambisols, Luvisols or Podzols according to the WRB 2014 classification (IUSS Working Group WRB, 2014). They are mainly strongly acidic, except for three Cambisols developed on calcareous parent rocks (limestone, dolostone and marl). In cropland, soil types of reference soils include mainly haplic Luvisols (15 sites) according to the WRB 2014 classification (IUSS Working Group WRB, 2014). One site was identified as an eutric Cambisol and one as a colluvic Regosol. The particle-size analysis of topsoil (USDA texture; IUSS Working Group WRB, 2014) indicated that soil texture is silt loam at 15 sites and loam at two sites. In Wallonia (Southern Belgium), the climate is oceanic and cold temperate, with mean annual temperature between 6.4 and 9.5 °C and rainfall from 750 to 1400 mm. Charcoal production virtually ceased in the early 19th century, when coke replaced charcoal as an industrial fuel in iron metallurgy, and had completely stopped by 1860 (Evrard, 1956). Therefore, we can reasonably assume that charcoal was deposited >150 years ago.

To investigate the effect of the mineralogical background on the thermal signature of soil, we also selected five subsoil samples from relatively clay-rich argic horizons from forested and cultivated Luvisols. Subsoil samples were treated with 6 % H_2O_2 at 70 °C during 30 days to oxidize SOM with a limited effect on soil mineralogy. The content of soil organic carbon (SOC) that survived oxidation ranged from 0.50 to 0.91 g kg^{-1} according to elemental analysis.

2.1.2 Soils of Germany

For comparison of DSC results with BPCA biomarkers, we also analyzed 45 kiln and reference forest topsoil samples (0–5, 5–20 and occasionally 20-25 cm) from 10 different sites. These had been previously BPCA-characterized (Borchard et al., 2014) following the procedure of Brodowski et al. (2005). Five sites were located in the Siegerland region and five in the Eifel region of Germany. In the Siegerland, soils were Leptic Cambisols (IUSS Working Group WRB, 2014) developed on acidic rock, whereas soils from the Eifel region were Haplic Luvisols, Mollic Leptosols and Leptic Cambisols (IUSS Working Group WRB, 2014) formed from the weathering of calcareous rock (Borchard et al., 2014). Soils from Siegerland were very acidic, with median pH values of 3.9 whereas soils from Eifel were base-rich and had a median pH value of 5.5 (Borchard et al. 2014). In both regions, the climate is cold temperate with mean annual temperatures of 8.9 and 7.7 °C and mean annual precipitations of 946 and 717 mm in the Siegerland and the Eifel, respectively. The sites were abandoned > 60 years ago (Borchard et al., 2014).

2.2 Sample preparation and carbon analysis

All soils were air-dried at a maximum of 40 °C until constant weight was reached. They were then gently ground and sieved to 2 mm. Before DSC and BPCA analyzes, the < 2 mm fraction of each soil was ground to powder with an oscillating rings crusher (samples from Belgium) or a ball mill (samples from Germany). The inorganic C content was measured by the modified-pressure calcimeter method (Sherrod et al., 2002). The total content of C was determined by dry combustion, and corrected for inorganic C to obtain the total organic carbon (TOC) content, which includes uncharred SOC and charcoal-C. Prior to DSC analysis, samples exceeding 60 g kg^{-1} of TOC were diluted with Al_2O_3 and homogenized in a ball mill.

2.3 Charcoal pieces

In order to constrain the thermal signature of aged charcoal in soil, macrofragments of charcoal were extracted from kiln soil for a selection of 20 sites from Belgium (Hardy et al., 2017b). By this approach, we assume that large charcoal particles have a thermal signature representative of charcoal residues in soil regardless of its size, provided that weathering over time didn't completely erase the aromatic character specific to chars. Charcoal particles > 1 mm were separated from about 2 kg of soil by way of wet sieving. The residue, containing charcoal particles, was rinsed abundantly with demineralized water and air dried. Charcoal pieces were separated from inorganic material by flotation in water, and then rinsed again several times with demineralized water in a 500 ml beaker, until the water was clear. Plant residues were removed manually. Between 50 and > 400 charcoal pieces were collected for each site.

To compare thermal characteristics of aged charcoal to that of a charcoal that was never deposited in soil (referred to here as "fresh" charcoal), we also analyzed a birch charcoal that was produced in a traditional mound kiln in August 2012 (Hardy et al., 2016). Prior to analysis, charcoal particles were ground to a powder with an agate pestle and mortar. In total, 21 charcoal samples were analyzed.

2.4 Differential scanning calorimetry analysis

Soils and charcoals were analyzed by heat flux DSC with a DSC 100 (TA Instruments), which measures the temperature difference between the sample and an empty reference beside of it, subjected to the same heating program. A heat flow rate is calculated based on the voltage signal corresponding to the difference in temperature between the sample and the empty reference (Plante et al., 2009). Between 15 and 25 mg of soil ground to powder were weighed into an aluminium pan and scanned under a flow of 50 ml min^{-1} synthetic air from room temperature to 600 °C, at a heating rate of 10 °C min^{-1} (Leifeld, 2007).

After subtraction of a linear baseline drawn between 150 °C and 600 °C, peak temperatures (°C), peak heights (W g^{-1}), temperature at 50 % heat release (T50) and total heat of reaction (J g^{-1}) were measured for each DSC thermogram with the Universal Analysis 2000 software (TA Instruments). Peak area (J g^{-1}) was measured for charcoal pieces only, by identifying the minimum between two peaks and splitting the peaks perpendicularly to the baseline (Figure 1). From repeated measurements (n=6) on one sample, we estimated a 95 % confidence interval for each DSC characteristic that was systematically < 2 % of the measured value.

The content of charcoal-C was estimated from DSC thermograms by the method described by (Hardy et al., 2017a), based on the relative height of the peaks derived from the combustion of charcoal and of that from the combustion of uncharred SOM (Leifeld, 2007). For acidic forest soils, only one peak was systematically discernable for charcoal and therefore used for quantification. In contrast, in cropland and Ca-rich forest soils, three peaks were clearly identifiable for charcoal and used for quantification. The relationship between thermal signature of charcoal and soil environmental conditions was attributed to the presence of abundant Ca^{2+} adsorbed to carboxylate groups at the surface of aged charcoal under neutral pH, which decreases the thermal resistance of the O-rich, aged fraction of charcoal (Hardy et al., 2017b).

2.4.1 Sensitivity analysis

To test the influence of the pattern of heat fluxes related to the combustion of charcoal on the estimation of charcoal-C content, we mathematically simulated soil-charcoal mixtures (n = 18) over a representative range of charcoal-C concentrations (from 5 to 90 % of TOC) based on the DSC pattern of heat release from 9 pre-industrial charcoals from different kiln sites. Simulated mixtures were obtained by summing the thermogram of pure charcoals, at different doses, to the thermogram of a charcoal-free soil. By comparison of predicted values with calculated values, we obtained a root mean square error (RMSE) of 1.39 % of the amount of charcoal-C added.

2.5 BPCA analyzes

Prior to analysis, samples were dried at 40 ºC to a constant weight and sieved to 2 mm. Benzene polycarboxylic acids were extracted from the 45 soils of Germany as specific markers for BC in soil, according to the procedure of Brodowski et al., (2005). An estimation of total BC content was obtained by multiplying total BPCA-C content by 2.27 (Brodowski et al., 2005).

3 Results

3.1 Thermal analysis of soils

Independent from soil conditions, reference soils had a characteristic DSC pattern, with a main maximum between 300 and 330 °C, at 310.3±10.0 (mean±s.d.) °C on average for forest reference soils and at 319.2±3.7°C for cropland reference soils (Figure 2). This peak was asymmetrical and spread systematically towards higher temperatures. A smaller peak was sometimes visible in the range of 400–450 °C, particularly in cropland reference soils (Figure 2).

Soils from pre-industrial charcoal kiln sites had a more variable signature. In addition to the signal in the 300–330 °C range, they had from one to three additional exotherms of higher thermal stability (Figure 2). We observed two main types of DSC signature for kiln soils. In the first category, (very) acidic forest soils were pooled (Figure 2a-d). These soils showed a characteristic main exotherm at 391.8±14.7 °C, and a small peak of higher thermal stability at around 494.8±19.2 °C that was not always clearly visible. The second category comprised calcareous forest soils (Figure 2e, f) and cropland soils (Figure 2g-i). The main difference to the thermal pattern of forest soils from the first group was the presence of multiple peaks, with an exotherm at 374.7±6.3°C and another at 422.6±2.7 °C in place of a unique peak at around 400 °C. Regardless of the presence of charcoal, most thermograms had a small, sharp endotherm at about 575 °C.

The deep Argic horizons that were H_2O_2 treated and therefore contained almost no residual organic carbon (OC content < 0.91 g kg^{-1}) recorded very limited heat fluxes by DSC analysis (Figure 3). In contrast to organo-mineral soils, no heat was released, and a small endotherm was even recorded between 350 and 600 °C, in addition to the same sharp endotherm at ~575°C as observed in most soils. This result suggests that, for the soils of this study, soil minerals have minor effects on the DSC signature. Accordingly, regression of total heat of reaction against TOC content provided a very high determination coefficient ($R^2 \geq 0.97$), regardless of the dataset (Figure 4a-c), which highlighted the close relationship between heat released during DSC analysis and the combustion of soil organic materials. Small intercepts of the linear regressions might express some influence of the mineralogy on heat fluxes.

3.2 Thermal analysis of charcoals

By superimposing the DSC thermogram of charcoal particles with that of the kiln soil from which particles were extracted, it clearly appears that peaks recorded at temperature higher than 350 °C were related to the combustion of charcoal (Figure 5a). Nevertheless, as suggested by the variability of the thermal signature of kiln soils, the pattern of heat release of pre-industrial charcoals varied to some extent. From one to three main peaks were visible on the thermograms of pure charcoals (Figure 5b). The least stable peak (peak 1) showed the highest variability, with temperatures ranging from 360.5 to 415.6 °C and an average value of 378.1±15.6 °C (mean±sd). Temperature of the second and third peaks was less variable, with average values of 424.4±3.0 °C and 506.6±9.2 °C, respectively.

The pattern of heat release of pre-industrial charcoals was also compared to that of one birch charcoal that was never aged in soil, produced in a traditional mound kiln (Figure 5c). It is interesting to note that fresh charcoal had a thermal signature very different from that of pre-industrial charcoals. Fresh charcoal had a main peak at 477 °C with a shoulder at 329 °C, which was lower in temperature than the temperature of the lowest maxima recorded in pre-industrial charcoals. Additionally, T50 of the fresh charcoal was 438°C as compared to that of pre-industrial charcoals ranging from 388 to 418 °C with average values of 400.3±7.9 °C.

3.3 Quantification of charcoal-C in soil with DSC and comparison with BPCA-C content

Data describing the selection of 45 soil samples from Germany used for the methodological comparison between the quantification of BC content by DSC and by BPCA molecular markers is presented in Appendix 1. By quantitative analysis of the DSC thermograms based on relative heights of peaks attributed to charcoal and uncharred SOM, we estimated a content of charcoal-C of 13.5±7.8 g kg^{-1} for kiln soils in cropland and 0.9±0.7 g kg^{-1} for respective reference soils. In forest, charcoal contents estimated with DSC were much higher, as the sites were never diluted laterally by tillage. Forest kiln soil samples from Belgium contained 68.7±35.3 g kg^{-1} of charcoal-C on average and up to 173.2 g kg^{-1} whereas in kiln soil samples from Germany, charcoal-C content is 79.7±68.9 g kg^{-1} on average and up to 199.7 g kg^{-1}.

Thermal characteristics of soils from Germany were compared to their total BPCA-C content. We found a strong positive correlation (r=0.935) between T50 and the total amount of BPCA-C in soil (Figure 6). However, the BPCA-C content recovered for the forest kiln soils of Germany of 13.2±10.8 g kg^{-1} was by far lower than the content of charcoal-C estimated by DSC of 79.7±68.9 g kg^{-1}. After multiplication by the conversion factor of 2.27, total BC content estimated from BPCA was 30.3±24.4 g kg^{-1}, which remains less than half of the content of charcoal-C estimated by DSC. Nevertheless, both variables were strongly correlated. A significant linear relationship between DSC-estimated charcoal-C content and the content of BPCA-C recovered from the soil was found, both expressed as a fraction of TOC content (Figure 7a) or in absolute terms (Figure 7b), with coefficients of determination of 0.89 and 0.97, respectively. The slope of the regression lines (Figure 7a, b) showed that total BPCA-C content underestimated the amount of charcoal-C predicted by DSC by a factor of around 5 . Accordingly, the ratio BPCA-C:Charcoal-C was 0.18±0.03 on average.

4 Discussion

4.1 Thermal analysis of soils

For the soils of this study, the strong correlation between total heat release measured by DSC and TOC content supports the idea that the mineral background of soil had little effect on the shape of exotherms from the combustion of SOM. Therefore, in the present case exotherms can directly be related to reactions of combustion of organic components of soil. Nevertheless, in other soils the mineralogy may interfere strongly with exotherms from SOM combustion. In addition to the inversion of quartz-α to quartz-β at 573 °C (visible on most thermograms of Figure 2), gibbsite, kaolinite and halloysite generate endotherms between 300 and 550 °C (Tan et al., 1986). These minerals, absent or present in relatively small amount in temperate soils of this study, are expected to be present in large amount in many clay-rich tropical soils (Uehara and Gillman, 1981). Nevertheless, the direct measurement of CO_2 emissions by evolved gas analysis rather than heat fluxes recorded by DSC, alone or the combination with TG, have the potential to remove most interferences from soil minerals (Peltre et al., 2013) and to generalize the use of dynamic thermal analysis for the characterization and quantification of SOM pools.

Thermal analysis of charcoal-rich kiln soils, adjacent reference soils and individual charcoals has highlighted that both charcoal and uncharred SOM are composed of a continuum of materials. Reference soils are dominated by thermally labile uncharred SOM compounds that degrade at around 300–330 °C. Spreading of the thermograms towards higher temperatures (Figure 2) suggests that more stable compounds are also present in smaller amount. The degradation of SOM in the 300–350 °C range has been related to the decomposition of aliphatic C molecules, such as carbohydrates (Dell'Abate et al., 2002; Kucerík et al., 2004) and in the range of 400–450°C to the combustion of aromatic C (Satoh, 1984). Accordingly, Li et al. (2002) reported that thermal stability of lignin is higher than that of cellulose but depends on its structure. More recently, Sanderman and Grandy (2020) confirmed, by means of combining thermal analysis and analytical pyrolysis of molecules released in different thermal windows, that polysaccharides and lipids are thermally more labile, whereas higher temperature volatiles comprise phenols, aromatics, and N-containing compounds. Therefore, the pattern of heat release of reference soils suggests that they are composed mainly of aliphatic-C from microbial residues as well as cellulose- and hemi-cellulose-derived SOM, mixed to a small amount of aromatic-C that decompose at higher temperature. Small differences in the shape of the thermograms from cropland and forest reference soils probably result from a difference in the composition of SOM, possibly related to contrasting quality of organic matter inputs. Reference cropland soils systematically showed a small peak at ~400 °C, which corresponds to the temperature of the main peak attributed to charcoal in kiln soil. By visual inspection of bulk soils, black particles looking like charcoal were found in each of them. These particles might result from (i) from contamination of charcoal from the kiln site or (ii) burning that generally followed deforestation when land was converted from forest to agricultural land in the past (Hoyois, 1953). Moreover, plant residues left on the field after harvest were commonly burnt until the 1980s (personal communication of Joseph Dufey).

4.2 Thermal analysis of charcoals

The properties and composition of charcoal are known to depend largely on conditions of production such as temperature and heating rate that control the degree of aromaticity and crystallinity of chars (Keiluweit et al., 2010). Accordingly, the high thermal stability of BC has been attributed to its polycondensed aromatic structure (De la Rosa et al., 2008). Consistently, the content of aromatic-C estimated by ^{13}C NMR spectroscopy correlates positively with the proportion of thermally refractory SOM (Harvey et al., 2012; Leifeld, 2007). The thermal stability of aromatic compounds larger than that of aliphatic compounds or O- and H-rich C functionalities (Leifeld, 2007) is in line with the higher binding energy of C=C bonds (520 kJ/mol) as compared to that of C-C, C-O or C-H bonds (350-412 kJ/mol) (Plante et al., 2009). Nevertheless, both degree of aromatic condensation and the presence of crystalline structures (Wiedemeier et al., 2015b) may govern thermal resistance beyond aromaticity. Leifeld (2007) showed that hexane soot, charred wood and charred rice straw had the same aromaticity but different thermal stabilities. At comparable aromaticity, thermal resistance depends mainly on the degree of aromatic condensation of char (Harvey et al., 2012; Leifeld, 2007) and can be further influenced by other factors such as ash content (McBeath et al., 2015).

The temperature of the thermally most stable peak was proposed as the most reliable feature to assess the thermal stability of charcoal (Leifeld, 2007). Leifeld (2007) showed that the thermal stability of pine wood charred under N_2 increases with charring temperature, and recorded a complete loss of thermally labile compounds at 400 °C, in line with the process of aromatization of charcoal that occurs in the 280–400 °C range (Antal and Grønli, 2003; Bird et al., 2015). Leifeld (2007) also found that the most stable peak of charcoals and charred plant biomass occurred at a temperature > 500 °C. In contrast, fresh charcoal of this study had a main maximum at 477 °C and exhibited a signal in the low range of temperature (< 350 °C). These discrepancies might be explained by (i) differences in the quality of charcoal and (ii) differences in the experimental parameters of the DSC analysis. Leifeld (2007) analyzed his samples with heating rate of 20°C min^{-1} whereas in this study we used a heating rate of 10°C min^{-1}. Temperature of heat release is decreased by slower heating rates (Fernández et al., 2010; Leifeld, 2007), which can explain the lower temperature of the most stable peak measured for our fresh charcoal. On the other hand, the survival of thermally labile compounds for charcoal produced in a traditional mound kiln suggests that temperature of charring was < 400°C. This is not surprising, as wood pyrolysis by the traditional mound kiln method is expected to reach a maximum of 400–450°C (Emrich, 1985), and the local maximum temperature of pyrolysis varies within the mound according to the distance from the hearth. In contrast, no signal was recorded in the lower range of temperature (< 350 °C) for pre-industrial charcoals. The presence of aliphatic C compounds, such as proteins and sugars, were detected in chars produced at low temperature and related to the biological accessibility of chars, with the amount of labile compounds decreasing with temperature of pyrolysis (Fabbri et al., 2012). The disappearance of the thermally labile fraction for pre-industrial charcoals aged in soil suggests that this fraction was biologically reactive, probably made of residual incompletely transformed organic molecules dominated by aliphatic C. Therefore, it was more subject to (a)biotic decomposition than the thermally stable fraction of charcoal and was completely degraded since the time of charcoal production, > 150 years ago. Accordingly, the presence of a labile fraction in engineered biochars was found to contribute to early emissions of CO_2 after introduction to soil (Sagrilo et al., 2014).

Interestingly, the thermal signature of fresh and aged charcoals is quite different. Aged charcoals are thermally less stable than fresh charcoals and generally have multiple exotherms in the 360–525 °C range. The main process in aging of charcoal is oxygenation starting from the surface and propagating to the core of the particle (Lehmann et al., 2005). Charcoal was produced at relatively low temperature at kiln sites (400–450 °C; Emrich, 1985) and therefore may contain aliphatic-C and amorphous aromatic clusters of small size that would not be recovered as BC by the majority of existing BC quantification procedures. Moreover, physical, chemical and biological weathering occurring over time in soil is supposed to decrease the stability of charcoal (Ascough et al., 2011), and create H- and O-rich C functionalities (Cheng et al., 2008; Hardy et al., 2017b; Lehmann et al., 2005) that have a decreased resistance to thermal oxidation. By relating thermal characteristics to the elemental composition of charcoal, Hardy *et al.*, (2017b) highlighted that the O-rich fraction of charcoal had a specific thermal signature, corresponding to the peak of least thermal stability of charcoal (peak 1, Figure 5b). This is in line with the smaller binding energy of C-O bonds compared to C=C bonds of aromatic clusters in charcoal (Plante et al., 2009). As a result of weathering, the overall thermal stability of aged charcoals is smaller than that of fresh charcoal. Hardy *et al.*, (2017b) also found that the temperature of peak 1 was strongly negatively correlated to the content of Ca in charcoal. The most abundant O-rich functional groups in aged charcoals are carboxyl groups (Hardy et al., 2017b; Lehmann et al., 2005; Mao et al., 2012). These are known to have a strong affinity with Ca^{2+} (Kalinichev and Kirkpatrick, 2007). The presence of Ca^{2+} adsorbed to (poly-)carboxylate groups of charcoal might catalyze thermal decomposition by decreasing the binding energy of C-O bonds (e.g. Hu et al., 2018). Similarly, the presence of Al and Fe in the form of trivalent cations complexed to humic compounds of Podzols was shown to alter thermal stability of SOM (Schnitzer et al., 1964). This highlights the importance of soil conditions on the thermal signature of BC, and, more generally, SOM.

Transmission electron micrographs of modern and fossil charcoals have provided evidence of organized and disorganized domains in the matrix of charcoal (Cohen-Ofri et al., 2006). The degree of organization, or aromatic condensation (McBeath and Smernik, 2009; Wiedemeier et al., 2015a) refers to the size and arrangement of aromatic clusters in BC, which increases with temperature of pyrolysis > 350 °C, once the aromatization of BC is complete or close to (Keiluweit et al., 2010; McBeath et al., 2015). Bird et al. (2015) proposed the existence of three pools of different resistance (labile C, semi-labile aromatic C and stable aromatic polycyclic C) to explain the reactivity of BC. According to the conceptual model of Bird et al. (2015), labile C corresponds to the fraction of BC that is composed of minor pyrolysis products such as anhydrosugars and methoxylated phenols, mineralizable on the (very) short-term; semi-labile aromatic C corresponds to aromatic C with a low degree of aromatic condensation; and stable aromatic polycyclic C to polycyclic aromatic clusters with a ring size > 7. Unfortunately, this view of charcoal stability made of three pools of distinct chemistry and reactivity cannot be directly translated to the presence of three exotherms measured for aged charcoals of this study. Indeed, fresh and aged charcoals of this study were produced at a comparable temperature of about 400 °C (and are hence supposed to be both dominated by amorphous aromatic C). However, they have very contrasting DSC pattern of heat release. Therefore, we hypothesize that the thermal resistance of charcoal might rather be controlled by (1) the binding energy of C bonds, which is driven by both pyrolysis conditions (aromaticity and aromatic condensation) and the degree of weathering (oxygenation and hydrogenation) of charcoal; and (2) the accessibility to combustion of C moieties, or the activation energy necessary to initiate combustion. As the reaction is partially surface-controlled, it is expected that highly weathered outer surfaces of aged charcoal oxidize more readily at lower temperatures whereas the inner parts have no access to O_2 despite the temperature being high enough for reaction. In contrast, an onion-shaped soot particle can only be oxidized layer by layer, and probably requires a higher activation energy to onset combustion. According to this view, the DSC peaks of contrasting thermal resistance found in aged charcoals might correspond to (i) C bonds that are weakened by the presence of O in their direct proximity (first peak, less thermally stable); (ii) aromatic C in clusters of small size that are partially weathered but that are not directly bound to oxygen (second peak); and (iii) unweathered aromatic C in clusters of large size (third peak, high thermal resistance). The process of aging of BC in the environment is still incompletely understood and is of prime importance to unravel the role that BC plays in geochemical cycles. In that sense, dynamic thermal analysis has the potential to offer rapid, inexpensive continuous information on the complete BC continuum related to the binding energy of C bonds, which can bring useful new information on the degree of weathering of BC aged in soil.

4.3 Quantification of charcoal-C by DSC: advantages and limitations.

Thermal analysis of charcoal-rich kiln soils, adjacent reference soils and individual charcoals has highlighted that both charcoal and uncharred SOM are composed of a continuum of materials. These two continuums largely overlap, which stresses the issue of BC quantification in soil by static thermal methods: the choice of a cut-off temperature to discriminate quantitatively between charcoal-C and uncharred SOC is not reliable. Therefore, the relative height of peaks attributed either to charcoal or SOM were exploited here to quantify charcoal-C in the soil of pre-industrial kiln sites. For cropland soils, the DSC-derived content of charcoal-C stored in the topsoil of kiln sites correlated strongly (r=0.98) to the excess of OC (ΔOC) accumulated in the kiln soil relative to adjacent reference soil, as shown by Hardy et al. (2017a). The slope of the relationship between the two variables is 0.80. By a similar approach for forest soils from Germany, we obtained a slope of 1.0 for the regression line between ΔOC and charcoal-C content estimated by DSC (r=0.94). For forest soils from Belgium, sampling by soil sub-horizons of varying depth prevented from implementing the comparison between charcoal-C content and ΔOC. The consistency between estimates of charcoal-C content by DSC and ΔOC brings confidence about the reliability of our DSC quantification procedure. Nevertheless, the slope of 1 for forest soils of Germany supports the view that ΔOC is exclusively made of charcoal-C, whereas the slope of ~0.8 for cropland soils from Belgium indicates that only ~80 % of ΔOC is charcoal-C. This result suggests that the presence of aged charcoal has promoted the stabilization of a small amount of extra uncharred SOM in cropland soils of Belgium, which is consistent with other findings on similar sites (Burgeon et al., 2021; Hernandez-Soriano et al., 2015; Kerré et al., 2016). The fact that this increase in uncharred SOM is not measured in forests soils from Germany might originate from e. g. (i) the younger age (>60 years) of the sites; (ii) a contrasting effect of charcoal on biomass production or the dynamics of natural SOM depending on soil conditions; and (iii) the effect of repeated tillage over time in cropland that has diluted charcoal laterally (Hardy et al. 2017a) and might have accelerated the reconstitution of the natural SOM pool and its incorporation in soil.

Although the relationship between BPCA-C and DSC-derived charcoal-C was strongly linear (Figure 7), the content of charcoal-C obtained by DSC was more than five times higher than the content of BPCA-C in soil. This result is in line with the findings of Brodowski et al. (2005) who stated that BPCA-C may underestimate total charcoal-C content by a factor up to 4.5 or higher, either due to a complete digestion of the less condensed moieties of char or to an inaccessibility of the most refractory, condensed moieties (Brodowski et al., 2005; Glaser et al., 1998). This confirms, for charcoal kiln soils of this study, that the 2.27 multiplicative factor for the estimation of BC content from BPCA-C is overly-conservative. Overall, this result reminds us that the quantitative interpretation of operationally-defined BC measurements, regardless of the method, must be done with great caution and be presented as an absolute value only if the recovery rate is controlled, which is practically very complicated for most field case studies. Another source of uncertainty comes from DSC, particularly because of the variability in the shape of soil thermograms according to mineralogy and SOM quality. The shape of thermograms from pre-industrial charcoals did not seem to have much effect on the estimates. Indeed, we obtained very accurate estimates (RMSE = 1.39 %) of charcoal-C content with our peak index for soil-charcoal mixtures numerically simulated from the thermograms of nine different pre-industrial charcoals with different shapes. Nevertheless, we were unable to test how the variability of thermal properties of uncharred SOM affects the accuracy of the estimation because of the difficulty to find soils completely free of BC. This point should be addressed in the future by setting up a strong calibration and validation dataset by adding known amounts of charcoal to a variety of soils initially free of charcoal (or to artificial mixtures of minerals and SOM) as conducted by e. g. Hammes et al. (2007) or Roth et al. (2012) for other methods of BC quantification. To overcome the issue raised by the variability in both SOM and BC depending on their composition and interactions with soil minerals, another improvement might come from peak decomposition of thermograms (Plante et al., 2005), as is done for example with X-Ray photoelectron spectroscopy (XPS) spectra for atomic quantification. This approach would require the identification of the thermal patterns associated to the different C moieties in SOM and BC and to model the shape of each associated exotherms in order to decompose the thermograms on a rational basis.

5 Conclusion

The main advantage of dynamic thermal analysis to characterize SOM comes from the fact that it provides a complete view of the continuum of organic materials present in soil. DSC analysis of the soil of pre-industrial charcoal kiln sites and adjacent charcoal-unaffected soils has stressed the complexity of BC quantification by highlighting the fact that the thermal properties of charcoal and uncharred SOM are variable and overlap to a large extent, invalidating the use of cut-off values for an accurate discrimination between aged charcoal and uncharred SOM. Thermal analysis by DSC turned out to be a very useful tool to identify and characterize charcoal in the soil. Aged charcoal was shown to have a characteristic thermal signature, overall remaining more thermally resistant than uncharred SOM despite the decrease in thermal stability due to aging in soil. This thermal pattern was successfully used to quantify charcoal-C in cropland and forest soils. We found a strong linear relationship (R^2=0.97) between DSC-derived charcoal-C content and BPCA-C content in the soils of this study, with BPCA-C representing about one fifth of DSC-derived charcoal-C. Despite the successful use of DSC to quantify charcoal-C in the soils of this study, our approach based on peak height and position has no general character because of the high variability in the pattern of heat release of BC and SOM depending on its composition. An approach by peak decomposition might help to overcome this issue, whereas the use of evolved gas analysis rather than DSC has the potential to get rid of the interference of soil minerals with exotherms from SOM combustion. Overall, we believe that the potential of dynamic thermal analysis to characterize and quantify soil organic materials is largely under-exploited despite providing information on the whole range of organic materials present in soil. In the perspective of amending soil with biochar at large scale to mitigate climate change, dynamic thermal analysis might be a very useful tool to assess biochar stability prior to application and to quantitatively and qualitatively trace its evolution in soil.

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7 Appendices

Appendix 1. TOC content, PLFA-C content and DSC-derived charcoal-C content for the selection of 45 soil samples from Germany.

8 Author contributions

BH characterized soil samples from Belgium and NB characterized soil samples from Germany. BH & JL ran DSC analyzes, made the calculations from the DSC graphs and interpreted DSC data. NB ran BPCA analyzes for the selection of samples from Germany. BH drafted the text revised by JL and NB.

9 Competing interests

Authors declare no conflict of interest

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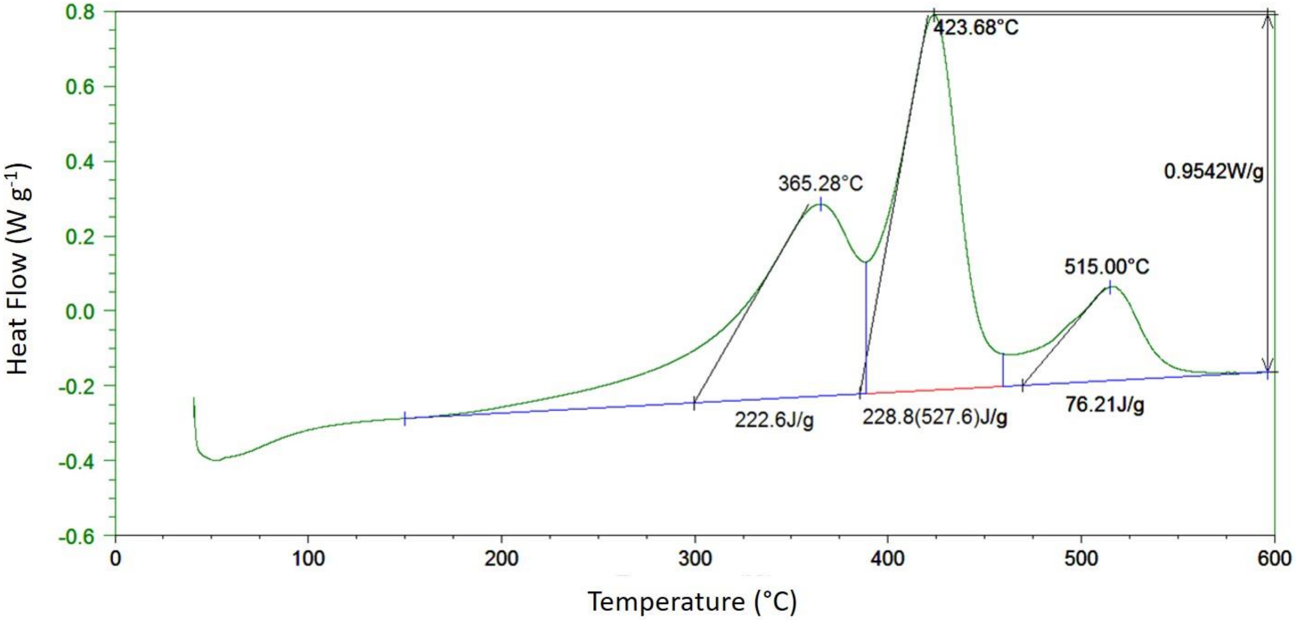


Figure 1. Measurement of characteristics from DSC thermograms (green line). After identification of peak maxima, peak height (W g-1) was measured as the maximum deviation from a linear baseline drawn between 150 and 600 °C, as illustrated for the main peak of the thermogram (0.9542 W g-1). Total heat release (527.6 J g-1) corresponds to the surface of the graph delimited by the linear baseline. Peak area (J g-1) was obtained by identifying the minimum between two adjacent peaks and splitting the peaks perpendicularly to the baseline. The black lines indicate the maximum rate of reaction associated to each maximum, and cross the baseline at the onset point (Temperature at which oxidation of the material starts).

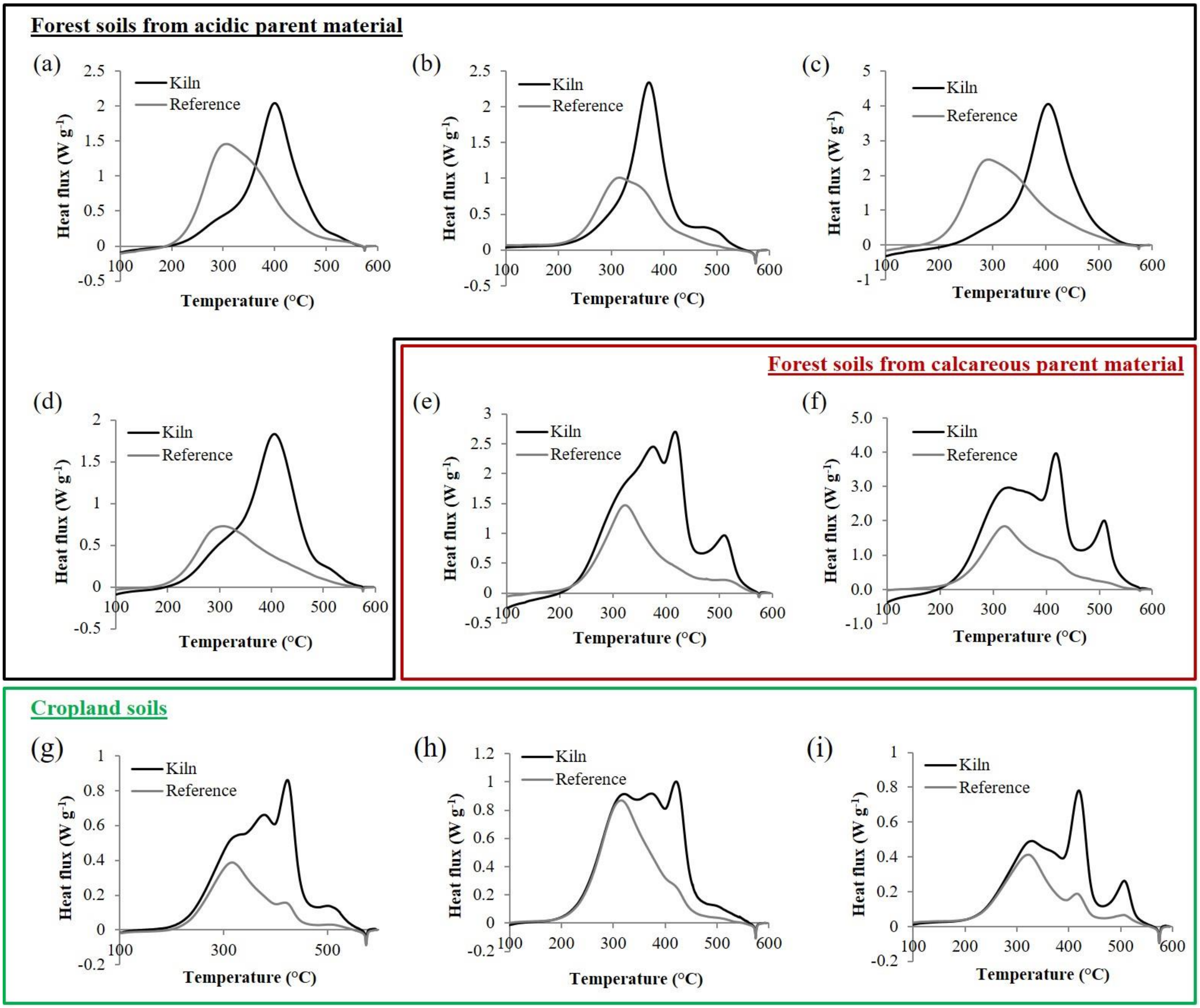


Figure 2. Differential scanning calorimetry thermograms of a representative selection of soils from pre-industrial charcoal kiln sites (black curves) and adjacent reference soils (grey curves). Four sites are located on (very) acidic forest soil (a, b, c, d), two sites located on calcareous forest soil (e, f) and three sites on cropland soils (g, h, i).

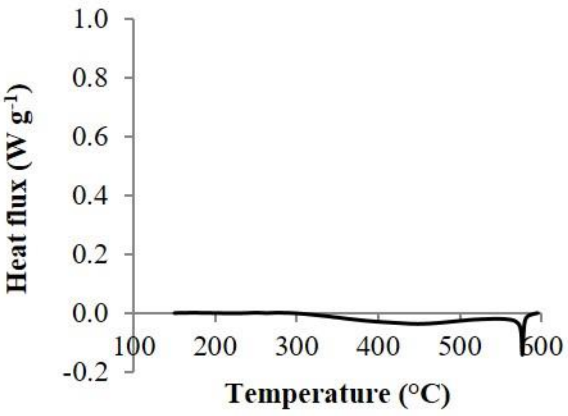


Figure 3. Differential scanning calorimetry thermograms of the subsoil (argic horizon) of a Haplic luvisol, H_2O_2 treated.

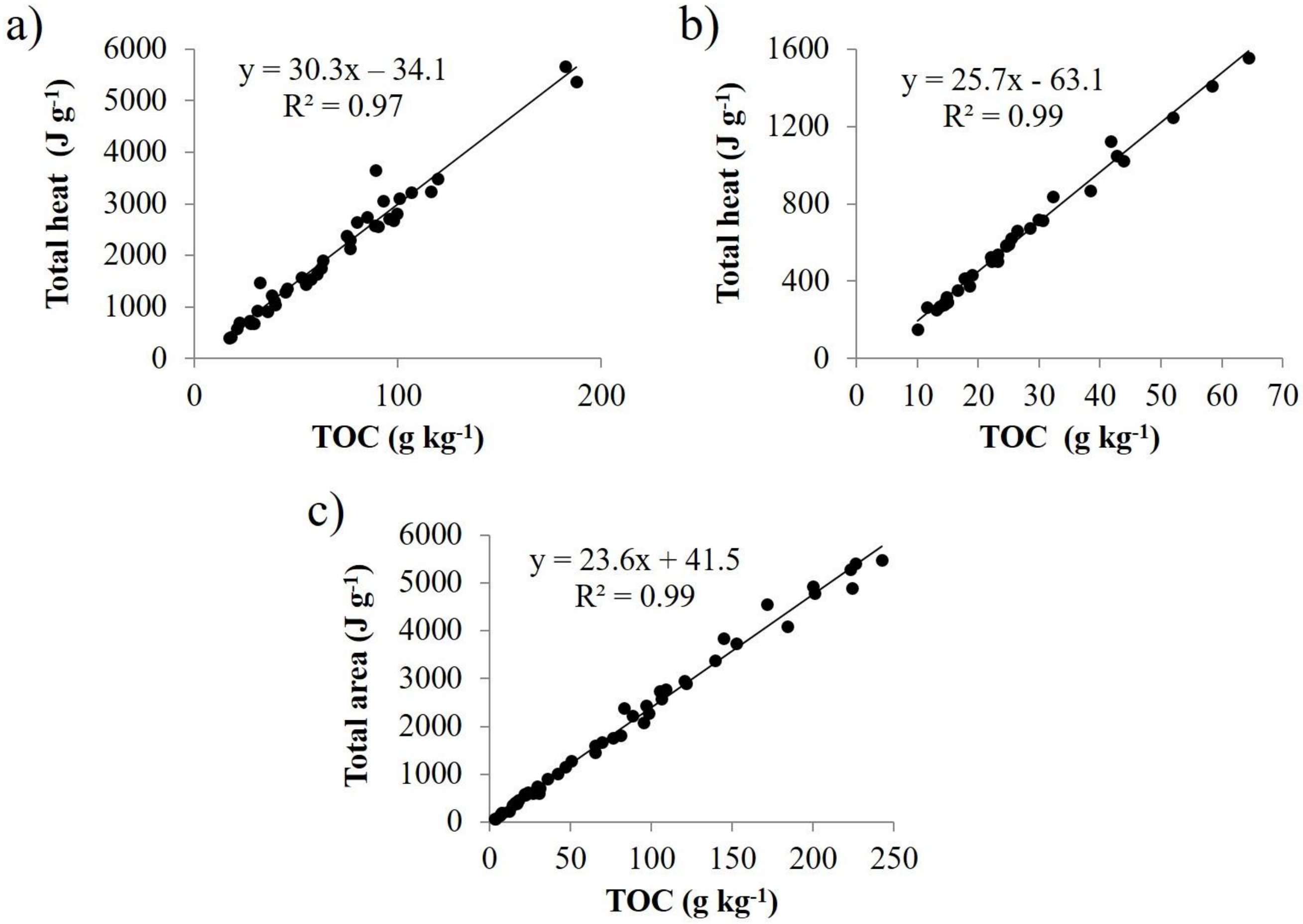


Figure 4. Total heat released between 150 and 600 °C from kiln and reference soils as a function of TOC content; a) forest soils from Belgium; b) cropland soils from Belgium; c) forest soils from Germany.

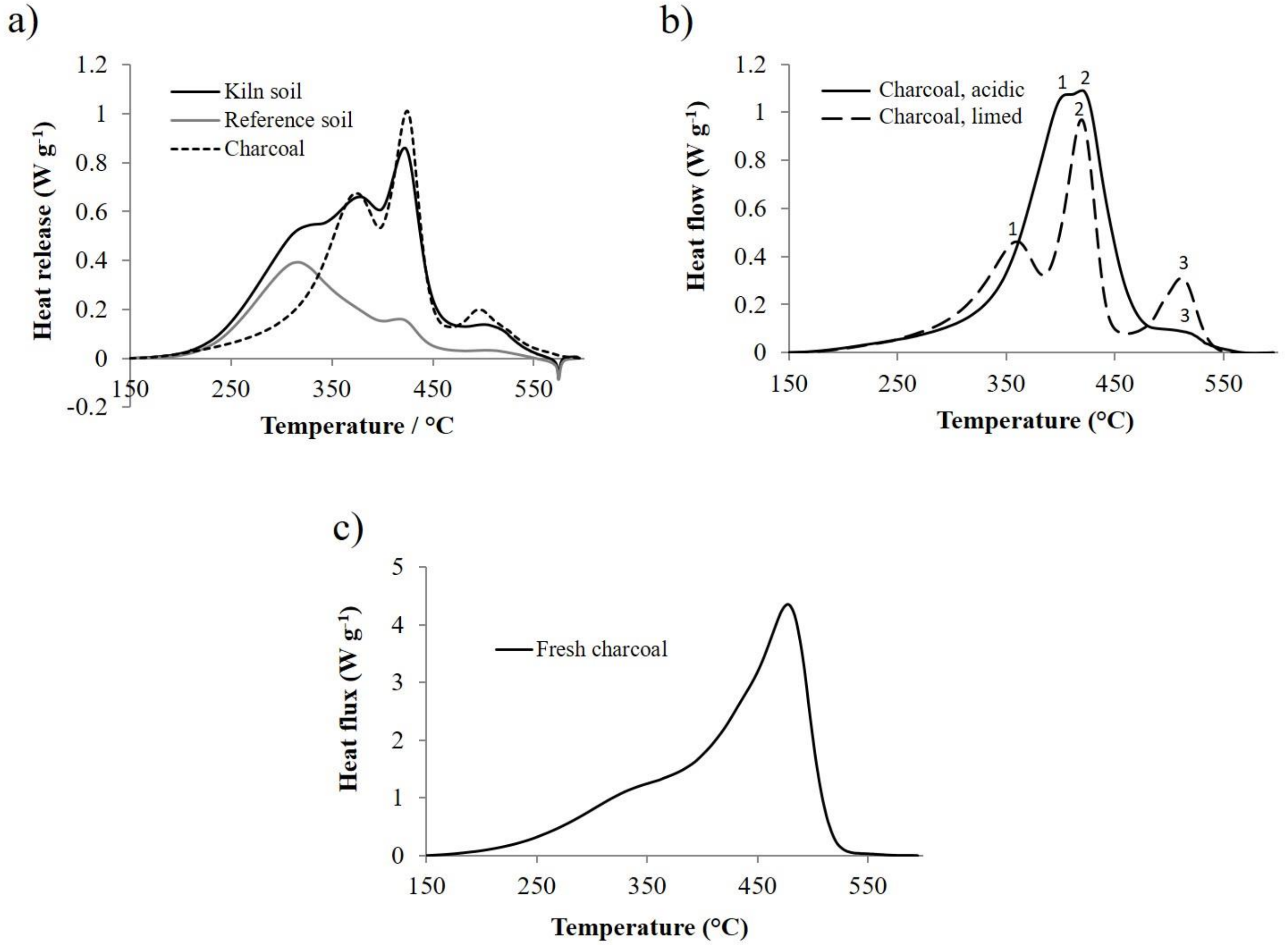
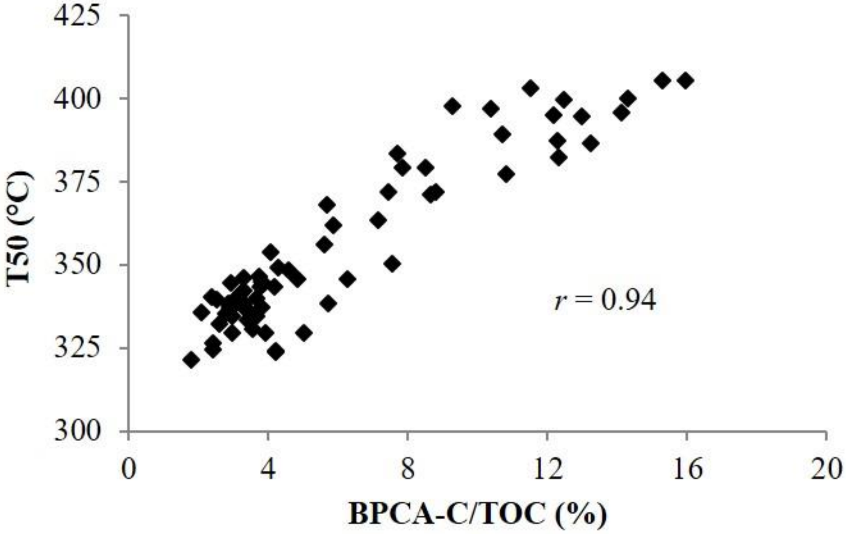


Figure 5. Differential scanning calorimetry thermograms of several charcoals; a) Thermogram of charcoal particles superimposed to the thermogram of the soil of the pre-industrial charcoal kiln site from which particles were extracted, and to the thermogram of adjacent reference soil (adapted from Hardy *et al.*, 2017a); b) Thermograms of charcoals extracted from an acidic forest soil and from a limed cropland soil. Numbers on the graph identify the maxima of exothermal peaks specific to the combustion of charcoal; c) Thermogram of a birch charcoal that was not aged in soil, produced in a traditional mound kiln.



670 **Figure 6. Temperature of 50 % heat release of bulk soils from Germany against the fraction of C from BPCA (BPCA-C/TOC).**

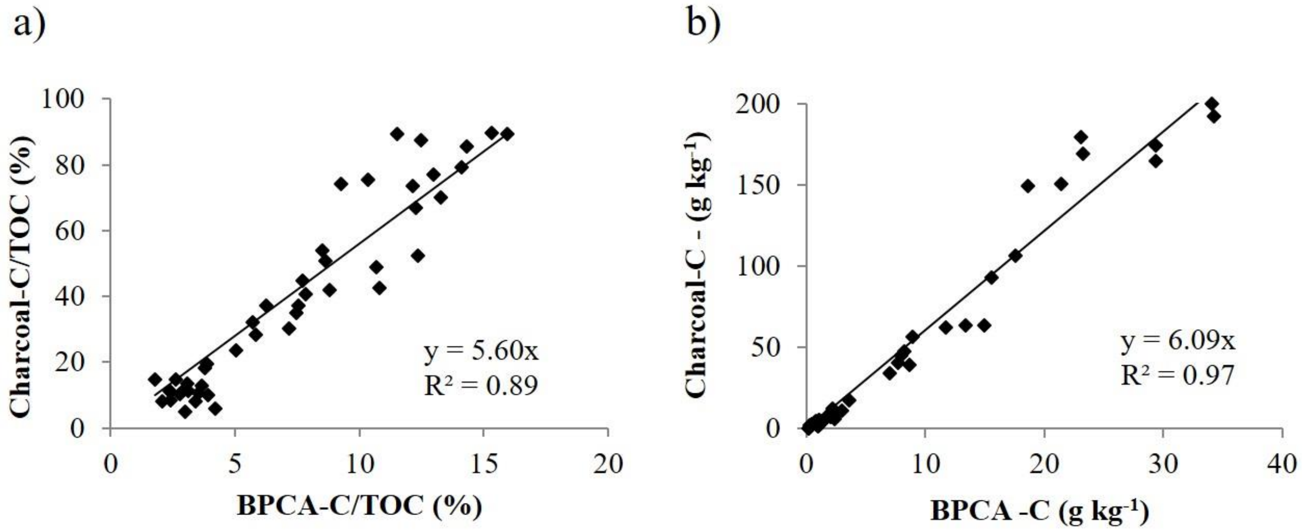


Figure 7. Charcoal-C content estimated by DSC against BPCA-C content in the soils from Germany, expressed as a fraction of TOC content (a) or in absolute terms (b).