Reviewer #1

This paper tests the potential for differential scanning calorimetry (DSC) to be able to quantify char in soils in the presence of soil organic matter using a range of soils with and without historical inputs of char from 19th century charcoal kilns. A subset of the results have been benchmarked against BPCA analyses of the same samples. The results suggest that DSC does have considerable potential as a rapid low-cost tool for charcoal/biochar quantification in complex soil matrices. The results also suggest that a range of correction factors likely exist for converting BPCA analyses to 'total' char amounts.

This is a very well conducted, thoughtful, and well explained study that does add another technique to the BC/char/biochar analytical toolbox. It is particularly useful because it provides a rather nuanced view across the entire continuum of pyrogenic products rather than focusing on a narrow analytical window like many techniques. I have very little to criticize in the work, with the caveat that I am not an expert in the application of either DSC or BPCA analysis. I have made a number of grammatical and typographical suggestions on the pdf attached.

Authors:

On behalf of authors, I would like to thank Referee 1 for his time, helpful and overall enthusiastic comments on our work. We particularly appreciate the time spent for grammatical corrections/suggestions to improve the readability of the text in a clean English.

Answers to specific comments are provided here below, with propositions of revisions where needed.

Kind regards,

Brieuc

Some small points:

L59 – text in relation to NMR is not really necessary here?

Authors: Indeed the information is less relevant and will be removed from the revised version of the MS

L132 – the carbonate correction is not clear – elaborate

Authors: The inorganic C content was measured by the modified-pressure calcimeter method (Sherrod et al., 2002). This precision will appear in the main text in the revised version of the manuscript.

L155 – not clear what 'vertical drop' means here

Author: By 'vertical drop' we refer to the line perpendicular to the thermogram baseline delimiting the area of two peaks, i.e. joining the local minimum between two peaks and the

baseline of the thermogram. We removed the term ´vertical drop´ and rephrased this passage (and legend of figure 1)

L230 – not sure which direction the difference is here from the text alone – clarify

Authors: former formulation : “the content charcoal-C estimated by BPCA-C differs by a factor of c. five as compared to the amount estimated by DSC” changed to “as indicated by the slope of the regression line, total BPCA-C content underestimated by a factor of around 5 the amount of charcoal-C predicted by DSC”

L231 and elsewhere – dots or commas to indicate decimel places?

Authors: Thank you, we revised accordingly; dots are used systematically for decimals in the revised version: 0.18+/-0.03. Figure 3 and 5 were changed accordingly

L271 – not entirely sure ‘crystallinity’ is the term to use here, but I guess its OK?

Authors: Charcoal may have crystalline structures, this has been shown in the literature by XRD (e.g. Wiedemeier et al., 2015); We suggest to write: “Nevertheless, both degree of aromatic condensation and the presence of crystalline structures may govern thermal resistance beyond…”

L272 – stability also depends on ash content (McBeath, A.V., et al. 2015. Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis. Biomass and Bioenergy, 73, pp.155-173.)

Authors: Thank you for this comment.

Former sentence: “At comparable aromaticity, thermal resistance depends mainly on the degree of aromatic condensation of char (Harvey et al., 2012; Leifeld, 2007)”

Revised sentence: “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 (McBeath et al., 2015).

L392 – with regard to EGA – define acronym at first use, and – I wonder if you would simply get a different set of issues related to differing O2 access?

Authors:

- For EGA definition, acronym was deleted because used only twice in the text.
- About the technique in itself, actually evolved gas analysis can rather be seen as a complementary tool to DSC or TG, as it measures gas fluxes (CO2) over time released by the heating/combustion processes of the sample. The release of CO2 as measured by EGA is tightly coupled to the exotherm, i.e., an O2-issue would occur also in the latter but not be identifiable as such. Therefore we do not expect that O2-related issues would specifically arise from EGA; however, this is beyond the scope of our study anyway.

Reviewer #2

This manuscript by Hardy et al. is a very fine addition to our knowledge regarding the use of the DSC method in soil science and the composition of SOM in RCH (or kiln) soils. The text is concise from title to conclusion and the figures are of very good quality and server their purpose ideally. The manuscript fits the scope of the journal well. However, I think the discussion can be revisited once more.

My knowledge regarding DSC is limited, but I have seen and studied quite a few kiln soils in the past, so my comments will be more general in nature. I will list them by line numbers in the following. I hope they can be used to improve the discussion of the results and methods.

Authors: On behalf of authors I would like to thank you Alexander for your time and sharing your views about char quantification in soil and your knowledge about charcoal hearth soils. This is highly appreciated.

Please find point by point answers to your helpful comments here below.

Best regards,

Brieuc

l. 59: The BPCA method is widely used in soil science, but it's also controversially discussed regarding its prediction quality for black carbon. There are several recent papers on this which are easily found. If it is not a specific indicator for BC, then this opens the question what is actually measured, especially in a very heterogeneous substrate like kiln soils.

Authors: We generally agree with your comment. The limitations of the BPCA method is well-known (and many known issues were already raised by the inventors of the initial method), as already critically addressed in L64 ff. Despite of the number of limitations related to the BPCA method, we believe that BPCA markers remain a very useful tracer of BC in soil and sediment matrices, certainly one of the most useful tools that we have at the moment. We would attenuate your statement about the fact that BPCA markers are not specific to BC. We do consider them as BC-specific, even though small interferences from other aromatic C sources may occur, and that the BPCA signature and recovery rates may vary according to the quality of BC and changes in analytical conditions. Yet, BPCA is more specific to BC than many of the other methods used to analyze BC. To our point, the main limitation of the BPCA markers is the current lack of control of the recovery rate, which make it an inappropriate approach for absolute quantification of char content in soil and sediment. This is one of the core working assumption of our work, and the motivation to look for other techniques of BC quantification in soil and sediment. Also other existing quantification methods have inherent limitations and generally focus on a narrow window of the BC continuum, which makes the application of complementary methods for BC quantification meaningful.

l. 70: The factor 2.27 is often used, and also often discussed critically, e.g. DOI: 10.1016/j.orggeochem.2010.07.001

Authors: Thank you for the reference, the sentence was completed to point out the weakness of the correction factor: "…BPCA-C extracted from soil, despite criticised for its validity (Glaser et al., 1998; Schneider et al., 2010).

l. 87. Minor point: not only western Europe, in the eastern parts as well. Also consider changing "former" to "mostly historical forest areas" or something similar.

Authors: Suggestion accepted: "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).

l. 135. So the DSC method is calibrated using charcoal pieces >1mm. All the kiln soils I saw were pitch black, often times with no or very little macroscopic charcoal pieces. What about fine charcoal dust and charcoal degradation products more humic in character, tar etc. Are they also detected by the DSC method at charcoal (>1mm) specific peaks?

Authors: Thank you for raising this point. Actually, in order to constrain the signature of aged charcoal in soil as good as possible, we had to isolate some charcoal from soil and avoid a significant contamination from natural SOM. Therefore, the collection of large charcoal fragments appeared to be the best solution. Again, you point out the difficulty of dealing with a continuum of material. In our view, this is not a major issue here as even microscopic charcoal fragments and dust will keep a specific signature with aromatic clusters that do not originate from other SOM sources in soil. Microscopic fragments will therefore keep a specific thermal signature related to the higher binding energy of C atoms and will be accounted for charcoal by our approach unless they are completely degraded to highly H and O rich molecules of small size with a molecular structure similar as that of lignin-derived SOM. In that case they would be accounted for "natural/humified" SOM rather than charcoal.

The comparison of the signature of pure charcoal powder with that of the kiln soil from which charcoal was extracted supports this view (see Figure 5a), and suggests that the use of large charcoal pieces is acceptable to constrain the DSC signature of charcoal remains in soil.

The main text was slightly modified to clarify this point :
"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„ (l. 135-139)

Figure 1. Y axis unit inconsistent with the other figures (W/g vs. W g^{-1})

Authors: adapted

Figure 5c: could you show fresh and old charcoal overlaid?

Authors: Thank you for the suggestion. We gave it a try but superimposition of the thermogram of fresh charcoal on Figure 5b makes the figure unclear so we prefer to keep

them separate.

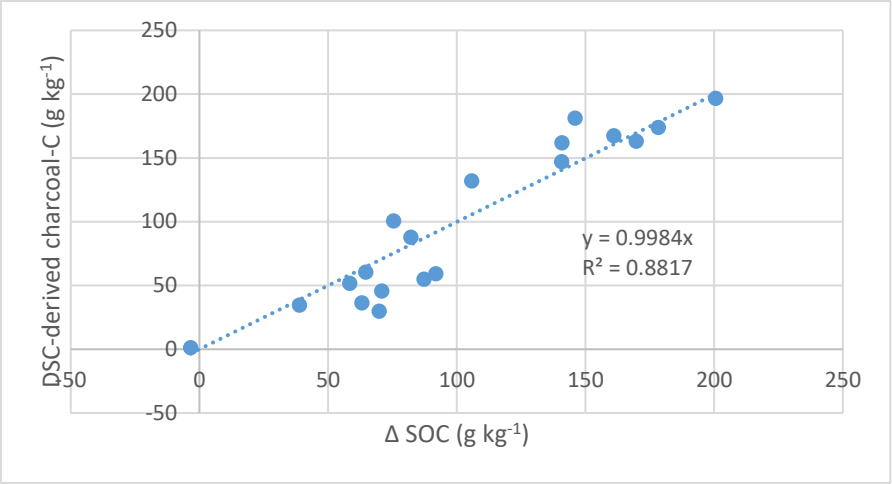
Section 3.3 I can't see appendix 1 (?). This section could greatly benefit from a table showing TOC, DSC-charcoal, BPCA, BC concentrations! Maybe just average values to save space.

Authors: Actually this is exactly what is contained in Appendix 1. The table is currently available online with the preprint (https://soil.copernicus.org/preprints/soil-2021-146/soil-2021-146-supplement.pdf). As the table is quite large we will keep it as a supporting information.

l. 350: You only discuss the kilns on cropland soils here? What about the kiln sites in forests? Maybe I missed it. These kilns on cropland soils are somewhat of a novelty compared to other sites discussed in the literature, which are predominantly in "undisturbed" forests.
Authors: First, about this last statement indeed, the occurrence of these sites in cropland makes them an interesting proxy for studying the long-term effects of biochar on agricultural soils.

Authors: Second, for the use of difference of total OC content between CKS and ref soils as an estimator of the content of charcoal-C in soil :

- For forest soils of Wallonia, the calculation of the excess of SOC at kiln site by difference with adjacent reference soil is made impossible because of the sampling procedure that was followed under forest. As you know, the activity of charcoal production has locally modified the topography of the charcoal hearth site, with the most common relief being a small elevation with the shape of an upside-down plate. For this reason, kiln and reference soils of Wallonia in forest areas were sampled according to soil horizons rather than soil depth. This prevents from calculating an excess of SOC at kiln site for a given depth.
- For cropland soils, the story is easier as the sites were diluted laterally and have no more specific reliefs. Therefore, the same depths were used in and out the sites when sampling.
- For forest sites of Germany, the same depths of sampling were respected for both kiln and reference soils, so the calculation of the excess of SOC at kiln site by difference with adjacent reference soil is possible but we hadn't tried. Please find the result here below.



DSC-derived charcoal-C content estimated for the CKS soils of Germany against the excess of SOC (Δ SOC) in CKS soils, calculated by difference with adjacent reference soils

The slope of about 1 between DSC-derived charcoal-C content and Δ SOC brings us further confidence on the fact that the DSC quantification method calibrated here for CKS soil is subject to little bias, and work probably better than the estimation made by BPCA-C * 2.27 (the coefficient factor being arbitrary and over conservative in this case).

The fact that we have a slope of about 1 here for forest soils whereas we found a slope of about 0.8 for cropland soils, as stated in the text, might be due to the dilution of the cropland soil and the better incorporation of natural SOM in cropland due to tillage, which probably has standardized site conditions and possibly accelerated the reconstitution of the natural SOM pool that had been destroyed by pyrolysis at the time of charcoal production. Moreover, historical sources indicate that CKS from Germany might be of younger age (> 60 years old) than that from Belgium (> 150 years old), which also advocates for a possibly incomplete rebuilt of the SOM pool at CKS soils from Germany.

The main text was completed to integrate the analysis by Δ SOC for forest soils from Germany and discrepancies with results from cropland soils from Belgium were discussed (l. 354-366)

l. 355. This is a very confident statement; I would be more cautious. Extra uncharred SOM could easily be charcoal derived products not detected by BC quantification techniques. The difference between BC and TOC in kiln soils is sometimes very large (as you know best), depending on which techniques are used. This cannot easily be explained by the presence of extra uncharred SOM. I guess this is the wrong paper to discuss this issue. But maybe try to be more careful with these assumptions in writing.

Authors : We also were quite doubtful on the validity of this statement a few years ago, but with the increasing bunch of evidence on this effect we have a more nuanced position today. The best evidence to date that the presence of charcoal in CKS soils may promote the storage of small amount of natural SOM is the delta 13C study of the PhD thesis of Bart Kerré (e.g. Kerré et al., 2016), who showed a larger amount of maize-derived biomass at CKS than at adjacent reference soils. Similar results were obtained more recently e.g. in the PhD thesis of Victor Burgeon (Burgeon et al., 2021).

Nevertheless, we agree with you that the effect of stabilization of natural SOM induced by biochar in soil is probably overestimated in some studies dealing with it, sometimes due to BC quantification biases.

l. 366. If you use the BPCA method as a benchmark for BC then please discuss its potentially shortcomings also, not only in terms of the conversion factor(s).

Authors: The most critical issue related to BC quantification by the BPCA method is already part of the discussion (l. 368-371). Other weaknesses of the BPCA method are already presented extensively in the introduction (l.63-70) and won't be repeated to avoid redundancy.

Reviewer #3

The manuscript from Hardy et al. investigates the potential for differential scanning calorimetry to characterise charcoal and quantify BC in soils. The paper uses soils from a croplands and forest soils with pre-industrial charcoal kilns to characterise the thermal signatures and quantify of charcoal C content. The manuscript also compared the accuracy of BC quantification from DSC to the benzene polycarboxylic acid (BPCA) method using a subset of samples. The paper provides an insight in to the continuum of chacoal and BC using DSC as a methodology of determining charcoal C content.

Overall the paper is well written and the authors address the aims of the manuscript clearly. The introduction and methods are concise and well presented. I have some minor comments about the methods and results in the specific comments below. The discussion follows the results well and places the study in the current literature. I believe this is a well conducted and presented manuscript with data that are unique, and findings that fit within the scope of the journal.

Authors: First we would like to thank Referee 3 for his time and helpful comments that will help improve substantially the quality of the manuscript. A point-by-point answer to specific comments raised is provided below.

Specific comments

Line 14: Consider rewording sentence, potentially, 'sustainably improve soil fertility'

Authors: Accepted as proposed by Ref 3 : "Black carbon (BC) plays an important role in terrestrial carbon storage and can sustainably improve soil fertility."

Line 33-34: Consider rewording to '...interpretable information across the continuum of ...'
Authors: Accepted

Line 101: For the soils collected in Belgium, what was the depth of topsoil sample?
Authors: for cropland soil the depth of sampling was 0-25 cm; in forest, soils were sampled by soil horizons (Hardy et al., 2016) so the depth of sampling was not constant. Organo-mineral (A) (sub-)horizons are considered here. The depth of the A horizon was generally about 0-10 cm for reference soils but generally much deeper (up to 50 cm deep) for CKS soils.
We propose to complete the sentence:
"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."

Line 167: Can you explain the selection of charcoal concentrations in more detail?
Authors: Proposed reformulation : "…, 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 …"

Line 173 change ‘previously’ to ‘prior’
Authors: Accepted and already suggested by Ref1

Figure 4: Caption refers to soils from Wallonia and German, which is confusing because in the methods they are labelled as either German or Belgium soils. Suggest changing Wallonia to Belgium in the caption.
Authors: Accepted. The text will be harmonized accordingly, “Belgium” will be preferred to “Wallonia”.

Figure 6: figure has the R2 value but no line fitted or coefficients listed?
Authors: The coefficient is a correlation coefficient (r=0.935), the corresponding determination coefficient would be (R^2=0.874). As a correlation coefficient refers to a linear relationship by nature an extra line would be somehow redundant. The correlation coefficient was preferred here to the use of a R^2 because there is no intention of calibrating a regression line here, in contrast to e.g. Figure 7.

Figure 7: Too many significant figures
Authors: We guess too many significant digits? Will be harmonized between all figures and limited to two (coefficients of correlation or determination) or three (equations) in the revised version

Figure 7: caption doesn’t explain 7a or 7b explicitly

Authors: Thank you for this. Here is a proposition of revision of Figure caption : “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)”

Line 208: august to “August”

Authors: will be revised accordingly

Line 212: any statistical tests to measure these differences

Authors: Unfortunately, as we refer to only one single “fresh” charcoal produced by the mound kiln method, the application of a statistical test is impossible

Line 222: keep the naming of R2 consistent

Authors: We suggest to keep the use of correlation coefficient when the aim is to study the linear character of a relationship between two variables, whereas the use of the determination coefficient is useful when a regression line is necessary (e.g. on Figure 7 a) and b) where the slope of the relationship is critical for method comparison)

Line 226: change ‘more than twice smaller than’ to ‘less than half of’

Authors: Accepted in the proposed formulation

Line 230: “c. five”?
Authors: we propose to reformulate the sentence, according to comments of Ref1 and 3:

- Former sentence: “the content charcoal-C estimated by BPCA-C differs by a factor of c. five as compared to the amount estimated by DSC”
- changed to “total BPCA-C content underestimated the amount of charcoal-C predicted by DSC by a factor of around 5”

Line 235: consider changing ‘mineral background’ to ‘mineralogy’
Authors: Accepted

Line 242: consider changing “to get rid of” to reduce, remove, minimise.
Authors: “remove” will be preferred (cf Ref 1 who also suggested a change)

Lines 267-268 (“A positive ...”): Sentence is confusing, consider rewording
Authors: proposition of rephrasing => “Consistently, the content of aromatic-C estimated by 13C NMR spectroscopy correlates positively with the proportion of thermally refractory SOM (Harvey et al., 2012; Leifeld, 2007).”

Line 275: Consider rewording sentence.
Authors: proposition of rephrasing => “The temperature of the thermally most stable peak was proposed as the most reliable feature to assess the thermal stability of charcoal.”

Line 284: “which may explain the lower ...”
Authors: “smaller” will be changed to “lower”

Paragraph 1 of section 4.2 does not discuss any results. Whilst it is relevant information how it relates to the current study is not clear.
Authors: Indeed this short paragraph doesn’t refer to results of the manuscript but we believe that it brings critical information for the understanding of the thermal signature of charcoal compared to uncharred SOM. Therefore we propose to keep the paragraph in the text.

Some figures and captions use comma or a decimal point (i.e 96,3 vs 96.3). Figure 4 and 6 uses a decimal point, whereas 5 and 7 use commas

Authors: Thank you for this. Indeed we need to harmonize, and we propose to replace all commas by dots for decimals where needed (on the two mentioned figures and in the text where needed)

References:

Burgeon, V., Fouché, J., Leifeld, J., Chenu, C. and Cornélis, J. T.: Organo-mineral associations largely contribute to the stabilization of century-old pyrogenic organic matter in cropland soils, Geoderma, 388(July 2020), doi:10.1016/j.geoderma.2020.114841, 2021.

Glaser, B., Haumaier, L., Guggenberger, G. and Zech, W.: Black carbon in soils : the use of benzenecarboxylic acids as specific markers, Org. Geochem., 29(4), 811–819, 1998.

Hardy, B., Cornelis, J. T., Houben, D., Lambert, R. and Dufey, J. E.: The effect of pre-industrial charcoal kilns on chemical properties of forest soil of Wallonia, Belgium, Eur. J. Soil Sci., 67(2), 206–216, doi:10.1111/ejss.12324, 2016.

Harvey, O. R., Kuo, L.-J., Zimmerman, A. R., Louchouarn, P., Amonette, J. E. and Herbert, B. E.: An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars)., Environ. Sci. Technol., 46(3), 1415–21, doi:10.1021/es2040398, 2012.

Kappenberg, A., Bläsing, M., Lehndorff, E. and Amelung, W.: Black carbon assessment using benzene polycarboxylic acids: Limitations for organic-rich matrices, Org. Geochem., 94, 47–51, doi:doi:http://dx.doi.org/10.1016/j.orggeochem, 2016.

Kerré, B., Bravo, C. T., Leifeld, J., Cornelissen, G. and Smolders, E.: Historical soil amendment with charcoal increases sequestration of non-charcoal carbon : a comparison among methods of black carbon quantification, Eur. J. Soil Sci., 67, 324–331, doi:10.1111/ejss.12338, 2016.

Leifeld, J.: Thermal stability of black carbon characterised by oxidative differential scanning calorimetry, Org. Geochem., 38(1), 112–127, doi:10.1016/j.orggeochem.2006.08.004, 2007.

McBeath, A. V., Wurster, C. M. and Bird, M. I.: Influence of feedstock properties and pyrolysis conditions on biochar carbon stability as determined by hydrogen pyrolysis, Biomass and Bioenergy, 73, 155–173, doi:10.1016/j.biombioe.2014.12.022, 2015.

Roth, P. J., Lehndorff, E., Brodowski, S., Bornemann, L., Sanchez-García, L., Gustafsson, Ö. and Amelung, W.: Differentiation of charcoal, soot and diagenetic carbon in soil: Method comparison and perspectives, Org. Geochem., 46, 66–75, doi:10.1016/j.orggeochem.2012.01.012, 2012.

Samojlik, T., Jędrzejewska, B., Michniewicz, M., Krasnodębski, D., Dulinicz, M., Olczak, H., Karczewski, A. and Rotherham, I. D.: Tree species used for low-intensity production of charcoal and wood-tar in the 18th-century Białowieza Primeval Forest, Poland, Phytocoenologia, 43(1–2), 1–12, doi:10.1127/0340-269X/2013/0043-0511, 2013.

Schneider, M. P. W., Hilf, M., Vogt, U. F. and Schmidt, M. W. I.: The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200 °C and 1000 °C, Org. Geochem., 41(10), 1082–1088, doi:10.1016/j.orggeochem.2010.07.001, 2010.

Sherrod, L. A., Dunn, G., Peterson, G. A. and Kolberg, R. L.: Inorganic Carbon Analysis by Modified Pressure-Calcimeter Method, Soil Sci. Soc. Am. J., 66, 299–305, 2002.

Wiedemeier, D. B., Abiven, S., Hockaday, W. C., Keiluweit, M., Kleber, M., Masiello, C. A., McBeath, A. V., Nico, P. S., Pyle, L. A., Schneider, M. P. W., Smernik, R. J., Wiesenberg, G. L. B. and Schmidt, M. W. I.: Aromaticity and degree of aromatic condensation of char, Org. Geochem., 78, 135–143, doi:10.1016/j.orggeochem.2014.10.002, 2015.