

SOIL Discuss., author comment AC1
<https://doi.org/10.5194/soil-2021-146-AC1>, 2022
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Reply on RC1

Brieuc Hardy et al.

Author comment on "Identification of thermal signature and quantification of charcoal in soil using differential scanning calorimetry and benzene polycarboxylic acid (BPCA) markers" by Brieuc Hardy et al., SOIL Discuss.,
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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 not critical 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

Authors: 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. This will be clarified in the revised version of the text (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 "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 decimal places?

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

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

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 content (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 previously defined at l. 241.
- 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.

References:

Harvey, O. R., Kuo, L.-J., Zimmerman, A. R., Louchouart, 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.

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.

Sherrod, L. A., Dunn, G., Peterson, G. A. and Kolberg, R. L.: Inorganic Carbon Analysis by Modified Pressure-Calimeter 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., Wiesenberger, 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.