SOIL Discuss., author comment AC2
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Reply on RC2

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., https://doi.org/10.5194/soil-2021-146-AC2, 2022

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

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 of 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 method, we believe that BPCA markers remain a very useful tracer of BC in soil and sediment matrices, certainly one of the most useful tool 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.

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).

- 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, and that therefore keep a specific thermal signature related to the higher binding energy of C atoms. Therefore they 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.

Figure 1. Y axis unit inconsistent with the other figures

Authors: On Figure 1 we have the "by default" layout of the Universal Analysis 2000 software that was used to calculate indicators from the curves. On the other figures you have "clean" curves after removal of the baseline, etc… We think that this is not an issue in the present form.

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

Authors: this is an interesting suggestion. We will give it a try for the revised version.

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.

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 soil amendment with biochar.

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 attached (Figure RC2-1).*

*On Figure RC2-1, 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 advocate for a possible incompletely rebuilt SOM pool at CKS soils from Germany.

- 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.

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: We agree and will add information to complete the statement in L 363 ff. after "…. condensed moieties (Brodowski et al., 2005; Glaser et al., 1998)." Apart of the criticised and discussed validity of the BPCA-C conversion factor (Glaser et al., 1998; Schneider et al., 2010) the BPCA method may produce biased results for soils rich in organic carbon (Kappenberg et al., 2016). Contrastingly Roth et al. (2012) confirmed validity of the BPCA method for charcoal detection, which is assumed to be most dominant source of BC in soils under study."

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Please also note the supplement to this comment:
https://soil.copernicus.org/preprints/soil-2021-146/soil-2021-146-AC2-supplement.pdf