

Responses to Reviewer: 1
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General Comments

The paper presented by Dobarco and colleagues represents an ambitious undertaking to map the fractional contribution of three different organic matter fractions (MAOM, POM, and PyOM), building on previous work from Grundy et al. (2015) and Viscarra Rossel et al., (2019). Using fractional carbon data predicted via mid- and near- infrared spectroscopy and quantile regression random forest model, they produce a useful gridded dataset of MAOC, POC, and PyOC to a depth of 30 cm. Generally, I found the paper to be well-written and insightful and have only few comments which I detail below.

Thank you very much for your comment. We are very glad that both reviewers considered overall the paper a good contribution.

Line Comments

Lines 41 – 43: It's not clear whether SOM or SOC is being discussed in this sentence. I think the sentiments expressed are true in both instances, but it's worth rephrasing to improve clarity.

Thanks for your comment. We agree with the reviewer that these characteristics apply to both SOC and SOM, although the variety of chemical composition and organic compounds may be more pertinent for SOM, and in these organic molecules C is just one component (although the origin of that SOC is the same of the SOM it is part of, etc.). But regarding the turnover time and temporal dynamics we are thinking more of SOC. We have rephrased as follows:

Soil organic matter consists of a continuum of compounds with different chemical compositions, origin (aboveground litter, dead roots, rhizodeposition, microbial-derived), degree of microbial processing and decomposition, and turnover times (Lehmann and Kleber, 2015). SOC is the main component of soil organic matter and varies in spatial and temporal dynamics.

Lines 47 – 49: Is this true for PyOC as well? What is the primary mechanism of preservation for pyrogenic organic matter if not some level of biochemical recalcitrance?

You are correct, the primary mechanism for protection of PyOC is presumably biochemical recalcitrance, and we indicate this in lines 77-78 (original manuscript). Here we refer to the main stabilization mechanisms of SOC as a whole, not of each fraction separately. There has always been a good debate on this subject, but I think that in the last 10 years there has been more evidence of the importance of the physico-chemical protection vs the biochemical recalcitrance alone. We have added at the end of the paragraph the sentence:

However, the hierarchy between stabilization mechanisms varies with the pedoclimatic context, land use and SOC fraction.

Line 74: In the MAOM fraction, what is the mechanism of preservation of PyOM in the MAOM fraction? Is it occlusion within microaggregates that are smaller than 60/53 μm ? Or can PyOM form organo-mineral association? I think in this section it would be worth discussing this fraction in a little more depth.

Thanks for your question. Intuitively I would imagine that PyOC is able to be found inside microaggregates smaller than 53 μm and also to be adsorbed to mineral surfaces. There does not seem to be many studies performing size/density fractionation and determination of PyOC under field conditions, but most of them investigate biochar additions. Zimmerman and Mitra (2017) suggest that PyOC (added as biochar) may enhance SOC stabilization via sorption and physical protection inside aggregates.

We searched in the literature regarding the physico-chemical stabilization of PyOC and found the following reference:

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, 114841, <https://doi.org/10.1016/j.geoderma.2020.114841>, 2021.

The authors found that PyOC is found in the free light fraction (analogous to free POM), and also occluded inside aggregates (macro and microaggregates) and sorbed onto mineral phases of the clay and silt fraction. We have rephrased the paragraph as follows:

PyOC can be found in both POC and MAOC fractions (Lavallee et al., 2019). Beyond the biochemical recalcitrance, which would be the main mechanisms of PyOC in the POC fraction (e.g., free PyOC non-associated to clay and silt sized mineral particles), PyOC can also interact with mineral phases and be protected inside microaggregates or adsorption (Burgeon et al., 2021). Zimmerman and Mitra (2017) suggest that PyOC (e.g., naturally occurring or added as biochar) may promote the stabilization of non-PyOC by enhancing the creation of microaggregates and sorption onto existing organo-mineral complexes.

Lines 77 – 78: This is kind of what I mean in my comment above, it seems contradictory.

Thanks for your comment. I don't think it is necessarily contradictory. I believe that the main SOC stabilization mechanism varies depending if we consider bulk SOC or a specific SOC fraction, and will also change on a case by case. Although globally, I think that physico-chemical stabilization is more important than biochemical recalcitrance. Also, at some point these mechanisms are working simultaneously. In the case of the PyOC fraction it is generally accepted that biochemical recalcitrance is the main protection mechanism, but that is not the case for MAOC.

Lines 88 – 89: It would be great to have a citation here for either how fractions can inform management, or how they can be incorporated into policy.

For example, the Australian National Soil Strategy has among its objectives to increase and maintain SOC, and this includes to develop cost-effective ways to estimate and model SOC. We hope that our maps could be used for that purpose in the future. In the meantime, we include a reference to Dangal et al. (2022) where they use maps of measurable SOC fractions as input for a biogeochemical model and project future SOC under future climate and land cover scenarios. Maybe it does not show how management is informed, but it is an application of similar maps in that direction.

Dangal, S. R. S., Schwalm, C., Cavigelli, M. A., Gollany, H. T., Jin, V. L., and Sanderman, J.: Improving Soil Carbon Estimates by Linking Conceptual Pools Against Measurable Carbon Fractions in the DAYCENT Model Version 4.5, *Journal of Advances in Modeling Earth Systems*, 14, e2021MS002622, <https://doi.org/10.1029/2021MS002622>, 2022.

Lines 139-142: Could you add a discussion either here or later in section 2.3 related to the pre-processing of the data from the different libraries? Were the data smoothed and corrected using Savitzky-Golay or the like, and how did that differ across the different libraries? If they are raw spectra, please specify that they were received in that form.

Thanks for your comment. We have indicated the pre-processing of the different spectral libraries but later in the section, before the piecewise direct standardization step.

SCaRP spectra were baseline-corrected and mean-centered prior subsequent analyses but were not subject to additional pre-processing. Pre-processing of the AusSpecNIR spectra consisted of spectral trimming (453-2500 nm), a Savitsky-Golay smoothing filter, conversion of reflectance to absorbance, and standard normal variate transformation. AusSpecMIR and AusSpecMIR2 were both pre-processed with the following steps: 1) spectral resolution and range harmonisation. All spectra were resampled using a smoothing spline function to a common 2 cm^{-1} resolution. The spectral range was set to 6500 cm^{-1} to 598 cm^{-1} , 2) Savitsky-Golay smoothing filter with 22 cm^{-1} local neighbourhood, 3) conversion from reflectance to absorbance units, and 4) standard normal variate transformation.

Line 219-220: Are there data associated with the C recovery of the fractions that might explain some of the poor matching between TOC and fraction sums? Soluble and dissolved carbon can be lost throughout the fractionation process, which may bias predictions.

Thanks for this question. Baldock et al. (2013) reported that the TOC recovery from the laboratory SOC fractionation (SCaRP samples) ranged from 76 to 142%, with an average TOC recovery of 102% and a standard deviation of 7.4%, and 86% of the samples yielded a recovery of 90–110%. In this case, I think the mismatch comes mainly from the prediction error of the spectral models, although some propagation of error from the

SOC fractionation data occurs as well. For example, for AusSpecNIR, AusSpecMIR and AusSpecMIR2, the SOC fraction concentration was calculated from predictions of SOC distribution between the three fractions, and predicted TOC. We have added:

The mismatch between the sum of SOC fractions and measured TOC is most likely derived from the prediction error of the spectral models, and in minor extent from the TOC recoveries of the laboratory SOC fractionation data.

Line 235: Can you clarify the difference between ilr_1 and ilr_2 in this line? Looking through the equations and text I think I can piece it together, but it would be helpful to the reader to make it explicit.

Thank you for the suggestion, but in this case, I think that if the reader is interested in understanding the ilr transformation in depth, they can read the reference Egozcue et al. (2003). I think that the essential information is that this transformation allows to model compositional data and reduces the variables in one dimension (in these case, from three to two variables). But also, given the nature of the transformation it is hard to interpret ilr_1 and ilr_2 . They can also write the equation for ilr_1 and ilr_2 by substituting the terms ($i=1$ and $i=2$) in equation 4 (equation 1 in the previous version), so that we don't add more equations to the manuscript.

Line 280: How much of the dataset was void-filled? Can you provide a percentage for total data interpolation across covariates?

We did not calculate the exact percentage but it would be minimal. I would say less than 0.5% of the study area. These voids corresponded to some waterbodies in the DEM mainly.

Line 387 and on: As my fellow reviewer noted, there are inconsistencies in the reporting of significant digits and errors in the results section of the manuscript. At the risk of being redundant, I recommend the authors carefully check the figures they present for consistency and utility.

Thanks for your comment. We will revise the number of significant digits throughout the manuscript.

Line 498-499: Are most agricultural lands in the Mediterranean biome irrigated? It could be worth highlighting the proportion irrigated either here or in the discussion.

Thank you for this question. We have calculated the proportion of irrigated agricultural land (pastures and cropping) for the Mediterranean biome using the land use map of 2018 (ABARES), and surprisingly we found that it is less than 2% of the area (1.6%). We have included this in the text:

where around 1.6% of the agricultural area (pastures and cropping) was irrigated (Abares, 2022)

Australian Bureau of Agricultural and Resource Economics and Sciences (ABARES). Land use: <https://www.agriculture.gov.au/abares/aclump/land-use>, last access: 20/09/2022.

Line 517: Higher mean sand content or higher mean SOC concentration?

I have corrected the manuscript. It is sand content.

Line 522-523: I think this sentence is confusing, I recommend rewording. Currently it reads as if the authors are discussing the total proportion of MAOC across Australia.

Thanks for your suggestion. We have reworded the sentence as "Conversely, the proportion of SOC found as MAOC is around 60% in Australian temperate grasslands, savannas and shrublands, 50% in Mediterranean forests and woodlands, ~ 54-64% in temperate forests and 65-65% in tropical (Table 3)."

Line 541: Please clarify the directionality of the relationship between POC and MAT.

Thanks for the suggestion. We have clarified that "The content of free POC decreased with an increase of MAT in topsoils (0-30 cm), whereas free POC increased slightly with MAT in subsoils, and occluded POC increased with MAT at all depths".

Lines 552 - 554: I'm glad you mention this here -- I was going to recommend something along these lines as a justification for not including these co-variates.

Thanks for your comment. I extracted the available data on exchangeable Ca and Mg, oxalate and dithionite extractable Fe and Al from the SoilDataFederator, but the spatial coverage was very irregular. Different regions had just few observations for each chemical property, which I could barely match with MAOC data. Definitely it would be great to examine these relationships in the future, as it has been done in other regions of the world.