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Responses to Reviewer 2

This manuscript and the associated data provide a high value set of SOC fraction gridded products for Australia and will be an important resource for land managers and the scientific community. There are some question marks over the reliability of the data due to bias in the original calibration samples (primarily agricultural soils) and in the method used to derive the PyOC and MAOC fractions for the calibration samples. The approach used can clearly be made more robust in future by starting with a larger, more representative and more reliable set of calibration data.

Thank you very much for the positive reception of our manuscript and your constructive comments. We will try to address the limitations of the current study and include some recommendations for improving the digital soil maps of SOC fractions in the future.

This are some weaknesses in the scientific methods/sampling that are the basis of this manuscript. The authors point out issues in the sampling, where there was insufficient range of soil types/biomes used in the initial calibration. What they do not point out is that the method used to estimate the fractions is not particularly reliable.

The SOC fractions used for calibration of the spectral methods were measured using a chemical approach (and data) developed for SCaRP a decade ago. The ^{13}C NMR based approach to determine PyOC is not widely used for estimating concentrations/stocks as it is a semi-quantitative method (e.g it often under-detects aromatic C and spectral assignment /integration is difficult in low-SOC samples). The current global data set of PyOC (black carbon) has been obtained using the Benzene PolyCarboxylic Acid (BPCA) approach, this approach gives a more realistic estimate of concentrations of PyOC in soil (see Jones, A. et al. "Fires prime terrestrial organic carbon for riverine export to the global oceans," *Nat. Commun.* 11, 2791 (2020). <https://doi.org/10.1038/s41467-020-16576-z>, Dymov, A.A. et al. Comparison of the Methods for Determining Pyrogenically Modified Carbon Compounds. *Eurasian Soil Sc.* 54, 1668–1680 (2021). <https://doi.org/10.1134/S1064229321110065>)

Thank you for your comment. In this study we capitalized on legacy soil datasets (SCaRP) and spectral libraries to produce a new set of SOC fraction maps with digital soil mapping methods, and as it is sometimes the case when using legacy soil datasets, the laboratory method analyses may not be the most cutting-edge but are still valid for the purposes of the study.

In the original publication by Baldock et al. (2013) the terminology referred to resistant organic carbon (ROC) instead of to pyrogenic organic carbon (PyOC). ROC has a chemical composition that is not incompatible with that of charcoal (or that is dominated in its majority by charcoal and charred plant residuals) but there is a potential presence of other poly-aryl carbon compounds that do not have a pyrogenic origin (Baldock et al., 2013). We decided to change the terminology from the publication by Baldock, which referred to particulate organic carbon (POC), humus OC (HOC) and ROC, to the terminology that is currently used by most SOC fractions' studies, although we may have incurred into some imprecisions with the terms. While POC and HOC have a clear correspondence with POC and MAOC, it is possible that ROC is not completely analogous with PyOC. We will indicate this in the revised version of the manuscript, as well as recommendations for a comparison with other methods for determination of PyOC in future studies in Australia.

Baldock, J.A., Sanderman, J., Macdonald, L.M., Puccini, A., Hawke, B., Szarvas, S., McGowan, J., 2013. Quantifying the allocation of soil organic carbon to biologically significant fractions. *Soil Research* 51, 561-576.

Specific Comments

Materials and Methods

1. PyOC was estimated by ^{13}C CPMAS NMR, this is excellent for identifying the types of carbon present but is generally regarded as only semi-quantitative in nature. The data for the fractions have not been cross-correlated with other approaches such as BPCA to ensure that they are in fact robust.

Thank you for your comment. As you mentioned before, we are using the legacy soil dataset from the SCaRP programme as basis for our study, and it was out of the scope of this paper, as well as far beyond our reach to perform additional fractionation analyses on the archive samples. While there may be some shortcomings associated to the determination of PyOC (or ROC) with ^{13}C NMR, in the comparison by Dymov et al. (2021) there seems to be a good correlation between this method and the preferred BPCA ($r = 0.88$, $p < 0.05$), so we still consider it appropriate for the determination of PyOC. We will indicate in the revised manuscript that future studies should carry a comparison between PyOC determined with BCPA and ^{13}C NMR.

MAOC is estimated by difference subtracting POC and PyOC from SOC, as a result there is also a question mark over the reliability of the estimates of this variable.

What is needed are measures of the error associated with PyOC and MAOC and how this transfers to errors in the subsequent estimates of these fractions using the irl1 and irl2 models.

There is an important clarification to make about the SOC fractionation protocol which has led to confusion on how the three fractions are quantified, and we thank the reviewer for pointing that out. We clarify the description of the SOC fractionation scheme in the revised version of the manuscript. MAOC is not estimated as $\text{SOC} - (\text{PyOC} + \text{POC})$. The first step of the fractionation protocol separates SOC by size. Next, ^{13}C NMR analysis were performed for both the fine ($<50\ \mu\text{m}$) and the coarse ($>50\ \mu\text{m}$) fractions to determine the proportion of poly-aryl C. The content of POC and MAOC were computed as the non-PyOC SOC present in the coarse and fine fraction respectively. We have rewritten this section as follows:

“A 10-g aliquot of air-dried soil $\leq 2\ \text{mm}$ was dispersed with $5\ \text{g L}^{-1}$ sodium hexametaphosphate and separated into coarse ($>50\ \mu\text{m}$) and fine ($<50\ \mu\text{m}$) fractions with wet sieving using an automated sieve shaker system (Baldock et al., 2013c). The TOC concentrations of the coarse and fine fractions were analysed with high-temperature oxidative combustion after the removal of inorganic carbon with 5-6 % H_2SO_3 if carbonates were present (method 6B3a, Rayment and Lyons (2011)). Solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy analyses were conducted on both the coarse ($>50\ \mu\text{m}$) and fine ($<50\ \mu\text{m}$) fractions. ^{13}C NMR is a semi-quantitative method that is commonly used to measure the proportion of aromatic C compounds in soil and organic matter samples. The proportion of poly-aryl C and aryl C that could be defined as lignin was determined and used as an estimate of PyOC. We note that whereas the chemical signature of the poly-aryl C is consistent with, and likely dominated by charcoal and charred plant residues, it may also indicate the presence of compounds non-pyrogenic origin (Baldock et al., 2013c). POC and MAOC contents ($\text{mg C-fraction g}^{-1}$ soil) were calculated by subtracting the proportion of PyOC in each fraction with the following equations (Baldock et al., 2013c):

$$\text{POC} = (2000 - 50\ \mu\text{m OC})(1 - f\text{PyOC}_{2000})\text{MF}_{2000} \quad (1)$$

$$\text{MAOC} = (\leq 50\ \mu\text{m OC})(1 - f\text{PyOC}_{50})\text{MF}_{50} \quad (2)$$

$$\text{PyOC} = (2000 - 50\ \mu\text{m OC})(f\text{PyOC}_{2000})\text{MF}_{2000} + (\leq 50\ \mu\text{m OC})(f\text{PyOC}_{50})\text{MF}_{50} \quad (3)$$

where $2000\text{-}50\ \mu\text{m OC}$ is the measured TOC content in the coarse fraction (mg C g^{-1} $2000\text{-}50\ \mu\text{m}$ fraction), $f\text{PyOC}_{2000}$ is the proportion of TOC attributed to poly-aryl C in the coarse fraction, MF_{2000} is the proportion of soil mass found in the coarse fraction ($\text{g } 2000\text{-}50\ \mu\text{m}$ fraction / $\text{g } \leq 2\text{mm}$ soil), $\leq 50\ \mu\text{m OC}$ is the measured TOC content in the fine fraction (mg C g^{-1} $\leq 50\ \mu\text{m}$ fraction), $f\text{PyOC}_{50}$ is the proportion of TOC attributed to poly-aryl C in the fine fraction, and MF_{50} is the proportion of soil mass found in the fine fraction ($\text{g } \leq 50\ \mu\text{m}$ fraction / $\text{g } \leq 2\text{mm}$ soil).”

The propagation of error from the laboratory fractionation, spectral predictive modelling, and digital soil mapping steps is out of the scope of this paper, but we will indicate these sources of uncertainty in the discussion.

2. The process of generating MAOC, POC and PyOC is reliant on an initial calibration and this was done on 312 samples a decade ago. A much larger number of samples were used in the spectral harmonisation and data set modelling but in the end they are reliant on this small number of samples (312) for SCaRP and an even smaller number of SCaRP samples (200) for the AusSpecMIR and AusSpecMIR2 and 309 for AusSpecIR. Again the authors need to justify how the use of this small set of samples, dominated by agricultural soil types, is able to successfully be used to provide calibration data for the much wider set of biome/soil types used in this study.

This may help to explain why the authors experienced difficulty with their preferred approach of modelling SOC fraction concentrations directly: *'The Pearson's r correlation coefficient 220 was 0.56, but the sum of SOC fractions showed some extreme values (Figure S1)'*.

Thanks for your comment. We agree with the reviewer that this is one of the limitations of the study and we indicate it as such in the revised version of the manuscript. We also justify the use of the calibration dataset because the 312 samples, despite coming mainly from agricultural soils, were representative of a range of TOC content (1.2 - 90.9 mg C / g soil) and different soil types and biomes.

3. The authors have used a very thorough and well thought through approach to generate a spatially and depth consistent gridded set of SOC fraction data for the continent.

Figure 2 (I think) shows where the spectral training data sets were located. It would be useful to see where the original SCaRP SOC fraction calibration data was collected, either on a map of Australia or in a table by soil/biome type, this would provide the reader with a clearer idea of the limitations due to type of calibration data used.

Thank you for your comment. Figure 1 indicates the location of the spectral datasets (calibration data and predicted samples), including SCaRP (in red), and in Figure 2, the predictions of the spectra models at these same locations are used as calibration data for the digital soil mapping process. We have included an additional panel in Figure 1 indicating the location of the 312 SCaRP samples that were subject to fractionation at the laboratory. In addition, we have changed the caption of Figure 2 as "Location of the spectral predictions standardized for the depths 0-5 cm, 5-15 cm, and 15-30 cm, which were used as calibration data for digital soil mapping."

Results

4. The reporting of errors is an issue in the manuscript.

The authors need to do a major check over all sections of the text and tables to ensure that precision is treated correctly. Errors should have 1 or at most 2 significant digits.

The problems start in the abstract, $59\% \pm 17.5\%$, whereas $28\% \pm 17.5\%$ was PyOC and $13\% \pm 11.1\%$ in this case the errors have more decimal places than the values and there are too many significant digits for such large errors. The estimate of stocks 12.7 Pg MAOC, 2 Pg POC has inconsistent precision, possibly this is correct but given the other issues possibly not.

As a clearer example the authors report (L388) $13.1\% \pm 11.1\%$, this should be 13 ± 11 which indicates 85% error, reporting to ± 0.1 (0.7%) clearly makes little sense. The decimal place in the error sets the decimal place in the value, they should always agree.

Things get worse : Table 3. 2.49 ± 118.3 0.64 ± 23.8

We apologize for this issue and have corrected the reporting of errors with the appropriate number of decimal places through the manuscript.

5. It would be very useful to have stocks with errors estimated based on the data generated from the grid. The authors estimate stocks but then they provide no errors because of an issue around soil thickness. Without an error then these stocks are of limited use (see above). It would be better to have some estimates of error for these stocks that sum over the best estimates for soil thickness, issues around soil bulk density estimates etc.

Thank you for this suggestion. We have performed 500 simulations in a subset of pixels across Australia to incorporate the uncertainty of soil thickness, bulk density, coarse fragments, TOC concentration, and distribution of Soc among fractions in the estimates of the SOC stocks for 0-30 cm depth. It was not possible to generate maps for all Australia at 90 m resolution due to time constraints for carrying the simulations, but the results inform on the variation and uncertainty of SOC stocks spatially and across biomes. We hope this additional analysis addresses the concern of the reviewer.

Discussion

6. Mention is made of a likely underestimate of SOC in forest systems and it is clear the authors were aware of the lack of calibration sampling in forest systems. *'or the fact that the fractionation in the original dataset was applied to agricultural soils and some pastures but lack forest soils.'* *'The uncertainty on the spatial predictions*

of SOC fraction stocks was driven mainly by TOC and the proportion of SOC fractions predictions, which in turn rely on spectral predictive models developed with soil samples originating mainly from agricultural soils.'

Australia has 134 million hectares of forest, 17% of the land surface area.

<https://www.agriculture.gov.au/abares/forestsaustralia/australias-forests#forest-area>

It is somewhat surprising that they did not add additional calibration samples from the forest estate into the early stages of this study. The potential magnitude of this underestimation might be mentioned.

Thank you for your comment. We agree with the reviewer on the need for sampling and analysing additional samples from natural systems (forests, woodlands, shrublands, etc.) in future studies. We tried to indicate this limitation in the discussion but we may not have been explicit enough, and we will emphasize it in the revised manuscript. We wish that we had more samples from forested areas, but that was out of our reach since we used legacy soil datasets and spectral libraries. We include this as a recommendation for future studies.

Technical Comments

We thank the reviewer for these corrections. We have incorporated them in the revised version of the manuscript.