

Interactive comment on “Ramped thermal analysis for isolating biologically meaningful soil organic matter fractions with distinct residence times” by Jonathan Sanderman and A. Stuart Grandy

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Reviewer #2

General comments: The combination of ramped thermal analysis, radiocarbon analysis, and pyGCMS is an interesting and innovative multi-technique approach to addressing one of the most important, ongoing scientific questions in the SOM community. It is worthy of publication, however there are a few areas for improvement. In particular attention needs to be focused on the correlation between RPO and pyGCMS with regards to reaction artifacts. The discussion is much too brief and would benefit greatly by referencing this work to more of the existing SOM-thermal analysis studies on chemistry,

thermal decomposition, mineral-association, etc.

RESPONSE: We thank reviewer 2 for the constructive feedback. As detailed below we have tried to address the reviewer's concerns about relating the data from the two methods and consistent with reviewer 1's comments, we have expanded the discussion section primarily in relation to setting our work in existing literature. We have purposely chosen not to take a deep dive into range of possible implications for SOM cycling research that our findings may have because this is just an initial investigation on one soil type.

Specific comments:

Line 26-28: Specify if this is referring to physical and/or chemical fractionation. Define or give examples of the homogeneous pools. Define the characteristic turnover rates

RESPONSE: We were referring generically to all fractionation schemes and go on to elaborate in the next paragraph. We have revised this first sentence to define "homogenous pools" to mean "in terms of reactivity, composition or microbial accessibility depending on the particulars of the study". "Characteristic turnover rates" has been reworded as "distinct mean turnover rates".

Line 79: why only the pasture treatment?

RESPONSE: This was a limited investigation and we chose to focus our limited budget on the trial with the greatest carbon flow to maximize our chance of "seeing" the bomb spike in ^{14}C propagate through the thermal fractions. This explanation has been added to this sentence.

Line 82: When was the end of the trial?

RESPONSE: 1996. Sentence revised to include end date.

Line 109-114: The methods need to be clarified. It is unclear how the final temperatures were reached, what happened after the ramp to 300C? Were samples held at the

final temperature? Also, how would the differences in ramp rates and moisture content between the pyGC (30K/min) and RPO (5K/min) affect the thermal decomposition and consequently the chemical composition of evolved species?

RESPONSE: We attempted to clarify this in response to the first reviewer. It seems that the reviewer may be confusing the pyrolysis temperature targets with the GC temperature ramp. The sample was pyrolyzed at one of the set temperature intervals for 20 s. Then, the pyrolysis product was transferred to the GC column where the compounds were separated with a starting temp of 40°C followed by the temperature ramp of 5° C min⁻¹ to 270°C followed by the final ramp (30°C min⁻¹) to 300°C, which was held for an additional 10 min. Hopefully this is now more clear.

Ramp rate has an effect on the formation of combustion/pyrolysis by-products and it should be discussed whether the products evolving at the same temperatures in the two methods are in fact identical. Susott, R., 1980. Effect of heating rate on char yield from forest fuels. Research Note, Intermountain Forest and Range Experiment Station USDA Forest Service INT-295, pp. 1–9. Broido and Nelson, 1975. Char yield on pyrolysis of cellulose. Combustion and Flame, 24 (1975), pp. 263-268.

RESPONSE: While we are not entirely sure what the reviewer is getting at here. We will respond first to the issue that pyrolysis at lower temperatures can produce by-products (primarily char) that are then fully decomposed at a higher temperature. There are multiple lines of evidence that charring is minimal at least in the RPO measurements – first the shape of the thermogram does not suggest a significant pool of very high activation energy OM (i.e. there is no distinct secondary peak as seen in some studies of simple compounds such as the Broido and Nelson 1975 reference the reviewer suggested). Second, the 14C data suggests the highest temperature fraction is the oldest. If there were significant charring of lower temperature OM then the 14C trend would be obscured by inclusion of this charred but young OM. The second part of this comment is that the two methods may not be releasing identical compounds in each temperature interval. This is a potential limitation that we have acknowledged

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in the manuscript and one of the reasons that we have considered this a preliminary investigation because this issue is really difficult to both confirm and to rule out entirely.

Line 130: what is the basis for the fast cycling pool rate?

RESPONSE: This was an omission on our part. We have added a description of a simple sensitivity test which was used to determine k_{fast} : “Given the limited number of degrees of freedom, we decided not to allow for the simultaneous optimization of all three parameters. The value for k_{fast} was set at 0.25 yr^{-1} after performing a simple sensitivity analysis where k_{fast} was varied from 0.1 to 1.0 yr^{-1} and f_{slow} and k_{slow} were optimized. This exercise suggested that the overall lowest mean RMSE across thermal fractions was achieved with $k_{fast} = 0.25 \text{ yr}^{-1}$.”

Line 143 and 196: The effects of isotopic fractionation during thermal decomposition should be included in the discussion. Or are these values consistent with isotopic differences between compound classes? Benner, R., Fogel, M.L., Sprague, E.K. and Hodson, R.E., 1987. Depletion of ^{13}C in lignin and its implications for stable carbon isotope studies. *Nature*, 329(6141), p.708. Loader, N.J., Robertson, I. and McCarroll, D., 2003. Comparison of stable carbon isotope ratios in the whole wood, cellulose and lignin of oak tree-rings. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 196(3-4), pp.395-407.

RESPONSE: These are a good but very complex points the review raises.

First, isotopic fractionation during thermal decomposition for a complex mixture such as natural organic matter should be minor – the activation energy of ^{12}C versus ^{13}C of any given compounds would result in a few degree shift in the temperature peak for that individual compound. Given the wide thermal range of each of our fractions, this small kinetic effect would not be seen in the ^{13}C data.

Second, it is difficult to compare our results to isotopic differences of different compounds because within each temperature range, there is a mixture of compounds.

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Both of the studies the reviewer cites focus on the strong depletion in ^{13}C of lignin relative to other compounds but lignin is never more than $\sim 10\%$ of any given thermal fraction. Looking through the literature, palmitic acid is often a few per mil lower than the substrate the microbes were feeding on (Abraham et al. 1998) but given we do not know what fraction of the total SOM the microbes were feeding on, we do not want to make this a talking point in this paper. Also it is important to remember that our starting (or bulk) material isn't fresh plant material but rather it is a mixture of aged SOM.

Given that this is such a complex topic since we are not talking about transformations of fresh OM, we prefer not to get into this sort of speculative discussion in this current paper. As such, we have revised line 196 not to mention the ^{13}C data.

Abraham, W. R., Hesse, C., & Pelz, O. (1998). Ratios of carbon isotopes in microbial lipids as an indicator of substrate usage. *Appl. Environ. Microbiol.*, 64(11), 4202-4209.

Line 162: It would be interesting to see results for the whole soils. Were there compositional differences between years that might support the changes in MRT? Is there a reason only the mean data is shown?

RESPONSE: Changes in MRT were across the temperature fractions. The ^{14}C model assumes that MRT doesn't change with time. The compositional differences were so small between years within each thermal fraction that we decided to just present the mean data. The variance about the mean values are given in the text (lines 164-167) and the multivariate plot in Fig 4b shows the individual years.

Line 198-201: How does the presence of those pyrolysis products affect the calculated MRT of the higher temperature thermal fractions?

RESPONSE: We may not be understanding the reviewer's comment but presumably these compounds would have already been released at low temperatures in the RPO procedure (as they are using Py-GC/MS) and would have no effect on the MRT of compounds released at higher temperature.

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Line 206: The activation energy of lignin (or any other compound class) is not shown or discussed. This could easily be added and would offer an interesting comparison between the activation energies of the thermal fractions and the compositional analysis.

Williams, E.K., Rosenheim, B.E., McNichol, A.P. and Masiello, C.A., 2014. Charring and non-additive chemical reactions during ramped pyrolysis: Applications to the characterization of sedimentary and soil organic material. *Organic geochemistry*, 77, pp.106-114.

RESPONSE: The Williams paper presents an excellent example of one of the numerous reasons that comparing thermal profiles from individual compounds to natural organic matter is potentially problematic. Fig 3 in Williams et al. 2014 shows cellulose peak at 360 degrees and a lignin peak at 705 but when an apple leaf that is primarily a mix of cellulose, hemicellulose and lignin is run they get one sharp peak at 440. This finding suggests that the physical structure of a real plant greatly alters the thermogram.

This comment raises a broader point about interpretation of thermal analysis data in soil and sediment systems is complex interplay between inherent activation energy of different compounds and bonding between organic-mineral components as well as organic-organic binding. Interestingly, in the Williams paper there was only a very minor difference in calculated activation energy between cellulose and lignin (88 v. 90 kJ/mol) which contrasts with previous values reported in the literature (taken from Williams Table 2) ranging from 23-361 kJ/mol for lignin and 111-251 kJ/mol for cellulose. Given these large differences across studies, we are hesitant to compare our E_a values which fall squarely in middle of these ranges.

Line 232-237: This is very important and needs to be discussed in greater detail. It seems that the combined activation energy of these mineral associated OM and covalent bonds is still smaller than the activation energy of the aromatics measured during thermal analysis and that this is may not be directly reflected in natural/enzymatic sys-

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tems.

RESPONSE: This is an excellent point that the reviewer raises – namely, the SOM community generally considers mineral associated OM (MAOM) to have a high barrier to decomposition by extracellular enzymes but the thermal data suggests a lower than average activation energy. This is perhaps a broader critique of thermal analyses measuring something that is not directly relevant to microbial processes. There is a lot of speculation we can do on this point but we feel that is better left until we assemble a more comprehensive dataset. In the concluding paragraph we have added a sentence acknowledging this point and the need for specific follow on research.

Technical comments:

Line 9 and 11: clarify “fraction” to “thermal fraction”. RESPONSE: We have now tried to be consistent in the use of thermal fraction throughout the MS.

Line 38: “virtually” implies nearly/almost or in effect, replace with computationally, statistically, or digitally? RESPONSE: “virtually” has been replaced with “mathematically”.

Line 60: insert comma between oldest and most Line 71: change to “comes”. Also this is a run on sentence and should be split into two. RESPONSE: Done.

Line 80: why are “Wheat/Pea” capitalized? RESPONSE: No longer capitalized.

Line 85: I believe this is the first usage of SOC in the paper; it should be defined here or change to SOM?

Replace “a” with “the”. RESPONSE: SOC is only used twice in the entire paper but SOM is used much more often. We have switched to consistently using SOM throughout.

Line 146-147: this information should also be in the figure caption. RESPONSE: Caption has been revised as suggested.

Line 162: omit “that” RESPONSE: Removed. Lines 174 and 177: there is no “Table

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C1” or “Table C3”, I assume the authors are referring to Table D1. RESPONSE: Thanks for catching this error. Corrected.

Figure 1: If the y-axis is simply the normalized CO₂ signal, relabel as such and delete the tick labels/numbers for clarity. It is very hard to differentiate the greys for the sampling years. RESPONSE: Axis and tick marks revised as suggested. We found it difficult to better differentiate the curves but the point we make is that they are essentially identical so perhaps the grey scale doesn't matter.

Figure 2: Explain all missing data in the caption. It may also be helpful to have the bulk soil data in the figures as well. RESPONSE: Caption has been revised. The bulk data is already in Table 1. We decided not to show it here because there is already a lot of overlap for the ¹³C data around these mean values.

Figure 4: Capitalize the thermal fractions for consistency. RESPONSE: Revised as suggested.

Figure C1: Panel a and b, the 'X' needs to be defined. If representing missing data, why no X in panel i and j? Panel j, are RPO F5 and slow overlapping? RESPONSE: Caption was revised so that it is clear the x refers to an outlier. Panels (i) and (j) there was no sample to measure so we don't know where to put an x.

Table D1: the shading needs to be defined. Also “source” should be compound class? RESPONSE: The shading needed to be removed as colour is not allowed in tables. Caption has been revised accordingly.

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