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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

Anonymous Referee #2

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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.

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 Line 79: why only the pasture treatment? Line 82: When was the end of the trial? 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? 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. Line 116: these appear to be compound classes, not sources. Line 130: what is the basis for the fast cycling pool rate? 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 13C 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. 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? Line 198-201: How does the presence of those pyrolysis products affect the calculated MRT of the higher temperature thermal fractions. 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. 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 systems.

Technical comments: Line 9 and 11: clarify “fraction” to “thermal fraction”. Line 38: “virtually” implies nearly/almost or in effect, replace with computationally, statistically, or digitally? 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. Line 80: why are “Wheat/Pea” 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”. Line 146-147: this information should also be in the figure caption. Line 162: omit “that” Lines 174 and 177: there is no “Table C1” or “Table C3”, I assume the authors are referring to Table D1. 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. 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. Figure 4: Capitalize the thermal fractions for consistency. 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? Table D1: the shading needs to be defined. Also “source” should be compound class?

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