

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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Received and published: 9 December 2019

Reviewer #1

General comments:

The combination of ramped thermal oxidation with ^{14}C determination is a relatively novel approach to study organic matter fractions of different turnover times. Therefore, it is worth to be published in an international journal. Overall, I have problems with the presentation of approach and discussion of data. In my view the authors failed to relate their study to existing knowledge from thermal decomposition studies. This could be

C1

overcome by revising the text and involving more literature. Following this it should be stated clearly which results confirm former findings and which really add to the existing knowledge.

RESPONSE: We thank the reviewer for constructive feedback and have addressed these overall shortcomings by better integrating our findings into the relevant literature as detailed in our responses to the specific comments below.

Specific comments:

Ins 5 ff. I miss state of the art and objective in the beginning of abstract. What does "preliminary" mean in this context? How is "biologically meaningful" defined in this respect?

RESPONSE: We had used the term "preliminary" because this research has focused on only one soil as it evolved over the course of a 30 year field trial and therefore we do not know if the results are applicable to other soil types. We had also used the term because the two pyrolysis techniques are not perfectly aligned resulting in some ambiguity in synthesizing results. We have replaced the word "preliminary" with "first". "Biologically meaningful" is the term that has been applied to the isolation of carbon fractions with distinct turnover times, but we have removed this term in the abstract to avoid having to further define it within the space constraints of an abstract. Otherwise, we feel that the first sentence clearly states the objectives of this paper and we disagree that an abstract needs to include a discussion of the state-of-the-art as that is more appropriate and is included in the introductory material.

In 10: Statement without prove up to here. What is the "activation energy of the fraction"? Not defined so far ...

RESPONSE: The abstract is a summary of the findings, we disagree that a proof of model fit is necessary to include in the abstract. Upon re-reading this part of the abstract with the reviewer's comments in mind, it is clear that this section can be confus-

C2

ing. We have reworded these two sentences to clarify.

In 35: py-GC/MS data only can show shifts in the composition of volatilized and ionized fraction - not in the bulk chemistry. Be more precise in descriptions....

RESPONSE: We assume the reviewer is referring to L.15. We clarified with the following edit, 'shift in the chemistry of pyrolysis products'.

In 16: "microbial derived" is not a chemical compound class (e.g., polysaccharides and lipids as well can be derived from microbes, e.g. the latter from microbial cell walls).

RESPONSE: "microbial derived" is an adjective describing the "compounds at middle temperatures" not the compounds (polysaccharides and lipids) found at low temperatures. We focus a lot of attention in the discussion to the fact that the lipids are likely of microbial origin yet they are the least thermally stable compounds because these compounds are often found to dominate the mineral-associated OM fraction in physical fractionation schemes.

Ins 17-20: This appears speculative to me (at least not logically following the previous statements).

RESPONSE: Abstracts often conclude with a broader integrative and forward looking statement that contextualizes the results of this particular study in the broader field (i.e. why should we care about these findings). We feel within the constraint of an abstract this sentence is a good summary how we chose to discuss the findings.

Ins 23-24: What is "multifaceted organic chemistries"? In my view there is only the (one) organic chemistry as a scientific discipline.

RESPONSE: This paraphrasing of our original sentence is not accurate but the reviewer's comment points out that this description may not precisely convey the meaning we intended, so we have revised this sentence for clarity. The sentence now reads: "This spectrum of turnover rates is due to a combination of organic matter composition with varying reactivity, various degrees of interaction between organic and mineral

C3

phases and greatly varying microclimates more or less suited to microbial activity".

In 110: How was the temperature set up? How was the transfer from Py-oven to GC capillary? Important: Has cooling & condensation been avoided? Describe ionization mode (at least briefly). How did you distinguish between protein-derived and (other) N-bearing compounds?

RESPONSE: At each temperature interval (330, 396, 444, 503, and 735), the sample was pyrolyzed at that temperature for 20 s. We have clarified the text this way, 'However, in contrast to our previous studies in which we used a single pyrolysis temperature, here we used a 'ramp' or stepped approach by pyrolyzing the same sample at five distinct, sequentially increasing temperatures (330, 396, 444, 503 and 735 °C; e.g. Hempflig and Schulten, 1990; Buurman et al., 2007; Williams et al., 2014). Thus, the same sample was pyrolyzed five times corresponding with each of these temperatures.

Once the sample was pyrolyzed at that temperature, pyrolysis product was transferred into the GC injector through a heated transfer line (200°C), operated in split flow mode (He flow rate of 1.0 ml min⁻¹, split ratio 50:1, 250°C). This process was repeated for each temperature interval, thus pyrolysis product of one sample was run through the GC/MS 5 times total for each temperature. The pyrolysis product for each temperature interval did not cool because it was injected into the GC through the heated transfer line immediately after pyrolysis. We have now more clearly articulated this in the methods. We have added text to the methods that the separated pyrolysate was ionized in the mass spec at 70 eV in the EI mode with the source temp held at 200°C. We have used the protein class in a number of papers, beginning with Grandy et al. 2007, Soil Biology and Biochemistry. This class consists of previously identified pyrolysis products (e.g. pyridines, pyrroles, indole; Schulten and Schnitzer, 1997, Biology and Fertility of Soils). We have now added the following text to the methods, 'Proteins include pyridines, pyrroles and indole that have been previously identified as pyrolysis products of proteins (Schulten and Schnitzer, 1997; Leinweber et al. 2014).'

C4

Ln 165: I think this is incorrect; compounds cannot dominate a pyrolysis temperature. You mean the compounds released at a certain temperature.

RESPONSE: We edited this in line with the reviewer's suggestion.

Ins 185-190: This in fact is not new: analytical pyrolysis (i.e. the combination of in-source pyrolysis with field ionization mass spectrometry) has shown this many years ago and for numerous samples (published in many articles and reviews).

RESPONSE: We appreciate the review pointing out that there is existing literature on the topic of soil organic matter chemistry varying with pyrolysis temperature. The exact statement the reviewer is referring to here is a brief summary of the integrated ¹⁴C and pyrolysis data which we then spend the rest of the discussion detailing. This is in fact new. However, for the ramped temperature py-gc/ms we have now included the following references in the methods.

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

Hempflig, E. and H.R. Schulten. 1990. Chemical characterization of the organic matter in forest soils by Curie point pyrolysis-GC/MS and pyrolysis-field ionization mass spectrometry. *Organic Geochemistry* 15:131-145.

Buurman, P., F. Peterse, G.A. Martin. 2007. Soil organic matter chemistry in allophanic soils: a pyrolysis-GC/MS study of a Costa Rican Andosol catena. *European Journal of Soil Science* 58.

Ins 194-195: This is unproven statement in my view. Which new insight in detail are you referring to?

RESPONSE: If we only wrote this one sentence, we would completely agree with the reviewer's sentiment here but the next three paragraphs expand on this broad statement.

C5

Ins 196-200: All this (esp. thermal lability and possible origin of carbohydrates) in fact is not new but has been published many times years ago.

RESPONSE: What is new and novel about this study is the integration of the ¹⁴C data with the pyrolysis data. That has not been published on before. We also think the time-series analysis provides an interesting context. We are not making claims that the pyrolysis data is novel in the sense that we are the first users of it or the ramped approach. Just because an approach has been used previously, in this case ramp py-gc/ms or ramp py-oxidation, doesn't mean it should not be used again especially given the fact that soils varies so greatly in composition and reactivity. We agree that there is some existing literature of analytical pyrolysis data on soil organic matter and as detailed in a previous response we have incorporated several of these studies into the discussion section.

Ins: 205 ff. From these analyses no indication of any association of compounds with minerals can be made. In contrast to author's discussion higher temperatures for thermal release may origin from binding to minerals. But whether this or chemical complexity of rather intact lignin is the reason for the higher activation energy cannot be judged from the present results. Thus, this discussion should be tuned down or better arguments for the one or the other point of view should be provided.

RESPONSE: This is a fair critique and we have reworded this paragraph to focus more on the fact that lignin does not persist in soils and the ¹⁴C data supports this notion.

Ln 209: This has been reviewed already in 2000 (*Biol Fertil Soils*, 30:399–432).

RESPONSE: We appreciate the reminder to revisit this great paper and have now included the Schulten and Leinweber (2000) paper in our list of references supporting this point.

Page:8 This discussion is misleading by restricting to humic substances fractions and the pyGC/MS technique which is not the very best for detecting native N-heterocycles.

C6

For discussing this issue first carefully study "Advances in understanding organic nitrogen chemistry in soils using state-of-the-art analytical techniques". *Advances in Agronomy* 119 (2013) 83-151 Overall this whole sections is not convincing (only 1 reference for "now considered").

RESPONSE: Thanks for pointing this out. We've attempted to clarify and expand this part of the discussion, and included several additional references.

Ins 235: "aromatic" is not an origin but a chemical structure property.

RESPONSE: Correct, thanks for catching this.

Ins 245-254: None of this is a conclusion. It is all summary. Either write true conclusions or omit this whole section

RESPONSE: We have expanded this final paragraph to induce short discussion of important next steps in this line of research but we agree with the reviewer that a standalone conclusions section is not necessary so we have shifted this paragraph back to the Discussion section.

Interactive comment on SOIL Discuss., <https://doi.org/10.5194/soil-2019-44>, 2019.