Dear Editor,

Thank you for your feedback and decision, inviting us to resubmit with minor revisions on our manuscript, "*Old Carbon, New Insights: Thermal Reactivity and Bioavailability of Saltmarsh Soils*", submitted on 21/10/2024; revised and resubmitted on 07/05/2025; further revised and resubmitted on 14/07/2025.

We are now pleased to provide an updated and further revised manuscript for your consideration for publication in EGU *Biogeosciences*.

Below, please find our detailed responses to the second round of reviewer 1 comments. We have attached two copies of the revised manuscript, one with tracked changes and one cleaned, final version.

We believe that this revised manuscript is improved and that we have fully addressed all comments.

We now look forward to receiving your decision on its publication in *EGU Biogeosciences*.

Yours sincerely,

Alex Houston, on behalf of all co-authors

Review of Houston et al. "Old Carbon, New Insights: Thermal Reactivity and Bioavailability of Saltmarsh Soils" (Biogeosciences; https://doi.org/10.5194/egusphere-2024-3281)

Synopsis

This is a revised version of a previous manuscript focusing on Ramped Oxidation (RO) 14C activities (reported as "percent modern" or pMC) and d13C values for organic carbon (OC) from a set of saltmarsh soil cores from the Skinflats saltmarsh in Scotland, UK. Based on my comments and those of a second, anonymous reviewer, the authors have made considerable changes to the revised version. I believe this revised version represents a significant improvement, but I still have several issues, particularly related to the treatment and presentation of the inverse model results. I highlight these in detail below---it is not clear to me that the authors fully comprehend what is being calculated and reported in these inversions. Only after implementing these further changes would I then support publication in Biogeosciences. I believe this will require one more round of review. Please do not hesitate to contact me regarding any questions on this review.

Sincerely,

Jordon Hemingway

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We thank the reviewer for their second review of this manuscript, which we agree is much improved from the original submission. We have added detailed responses to each individual query below. We believe that we have fully addressed each query and look forward to the editor's decision on its publication.

(there are no line numbers given for the abstract, so I will just write my comments here and the authors can find the relevant lines).

- "...driven by the net contribution from the older fraction...": What does this mean? Are the authors saying that preserved OC in salt marshes is generally low in 14C activity?

Saltmarshes accumulate OC from different autochthonous (in-situ production) and allochthonous (externally derived) sources, which can be differently aged. Hence, a saltmarsh soil sample can contain both 'young' and 'old' components. This turnover of differently aged OC in saltmarsh soils is a key part of this work.

For example, the accumulation of differently aged OC is already mentioned in the previous sentence of the abstract:

"... accumulate organic carbon from both modern and aged sources through in-situ biological production and the capture of ex-situ sources which are deposited during tidal inundation."

- "We also present the first evidence to supprt...": I'll admit that I'm not very well-versed in the MRV side of CDR, but it seems wild to me to claim that thermally labile OC that is currently preserved in salt marshes could count as additional CO2 removal. This is carbon that is already sequestered. I understand that draining and disturbing these salt marshes would lead to remineralization of this OC, thus increasing CO2 emissions, but doing nothing will not lead to any additional CO2 being removed from the atmosphere.

What am I missing here?

The reviewer is correct that thermally labile OC preserved in a saltmarsh is not 'additional' in a business-as-usual scenario. However, management interventions which reduce the emission of stored OC to the atmosphere (e.g., protection from a degradation pressure) can in some cases be counted as delivering reduced emissions. A foundation of this manuscript is the evidence from Houston et al. (2024) that the Skinflats saltmarsh was respiring CO_2 from ^{14}C depleted OC pools in a simulated drainage degradation scenario. In this manuscript, we show that the respired ^{14}C-CO_2 content from the above study was closest (in most cases) to the ^{14}C content of the most thermally labile OC pool. Therefore, we propose that the thermally labile OC pool in saltmarsh soils which are protected against a drainage degradation pressure for the purpose of generating carbon credits or contributing to national Greenhouse Gas Inventories, could be counted as delivering emissions reduction.

We direct interested readers to the following helpful resource:

Griscom, Bronson W., et al. "Natural climate solutions." *Proceedings of the National Academy of Sciences* 114.44 (2017): 11645-11650.

The above argument is already covered in the abstract:

"*Management interventions (e.g. rewetting by tidal inundation) to limit the exposure of saltmarsh soils to elevated oxygen availability may help to protect and conserve these stores of thermally labile organic carbon and hence limit CO_2 emissions.*"

We have added further clarification to the abstract:

"*We also present evidence to support the inclusion of thermally labile allochthonous OC stored in saltmarsh soils in additionality assessments for projects which aim to prevent the drainage of saltmarshes…*"

(here beings the line numbers)

L27: Hemingway et al. (2017) used an oxidizing carrier gas and should thus be cited along with Plante et al. and Stoner et al., not with Rosenheim et al.

We thank the reviewer for this clarification and have updated the text.

L26: "*(e.g., Hemingway et al., 2017b; Plante et al., 2011; Stoner et al., 2023), or other gases, typically Helium (e.g., Rosenheim et al., 2008).*"

L30: “CO2 evolved at low temperatures is deemd to be from… pools with greater thermal lability than CO2 evolved at higher temperatures”. Yes, of course it is---this is the definition of thermal lability! I don’t see what sentences like this are adding.

We feel that it is important to define this for readers, who may not be experts in the field. We have changed ‘deemed’ to ‘derived’ to clarify that this happens.

L30: “*CO_2 evolved at low temperatures is derived from soil OC pools with a greater thermal lability than CO_2 evolved at higher temperatures*”

L34 (and throughout): change to “14C activity”, as it is a radioactive isotope.

“^{14}C content” is standard in the reporting of radiocarbon as fraction or percentage modern, and we have retained this throughout the manuscript. We think it would be fine to use activity, but that this would add unnecessary confusion for readers when ^{14}C content is already being used as consistent terminology.

L57-59: “Crucially, the biological availability… depends on… thermal reactivity”. This is not true. Biological availability may correlate with thermal reactivity, but it does not depend on it per se.

This is fair, we have changed ‘depends on’ to ‘related to’ throughout the revised manuscript when referring a relationship between thermal reactivity and biological availability.

L108-109: “stream of high purity oxygen”: I suppose I didn’t realize in the first round of review that this is indeed a pure O2 stream (I now dug into the Gartnett et al. 2023 paper). Given this, do the authors think this difference in carrier gas will impact thermogram shape relative to other systems? Have they compared a reference material using their setup vs. using the setup at NOSAMS, ETH, etc.? It would be really nice to see the inter-laboratory reproducibility of this instrument (not just internal reproducibility, which looks quite nice in Gartnett et al.). For reference, most other systems use O2 in He. As a starting point for this comparison, the authors could look into Bolandini et al. (2025) Radiocarbon (https://doi.org/10.1017/RDC.2025.6), who investigated the impact of O2 flow rate on thermogram shape for the ETH instrument.

This is an interesting suggestion but is not within the scope of this study and not directly relevant to our findings.

L151-153: Fair point to the authors in their response that this is indeed how most labs used to do a 13C correction prior to AMS instruments including a 13C cup---I did not realize this is still how things are doing at SUERC. Still, I note that the authors mis-cited McIntyre et al. (2017) in their response, who indeed used the internal 13C correction of the MiCaDaS system, as is common practice at ETH (that paper instead focuses on the in-line EA-IRMS-AMS for singleanalysis %OC, d13C, and F14C analysis).

We do not agree that this is mis-cited. We were making the point that some labs use IRMS ^{13C} values for normalising ^{14}C results. Indeed, McIntyre et al. (2017) state in their Introduction "*In some laboratories, offline IRMS sample δ^{13}C is used for retroactive ^{14}C correction calculations*". P.894

L159-162 (and thoroughout): Please use μE, sE, and p(0, E) nomenclature.

We have implemented this change in nomenclature throughout.

L162-166 (and Table A2): I don't understand this---one can simply tell the software to perform a blank correction or not using the "blank_corr" flag (see documentation). How do the "13C values generated [vary] significantly from our IRMS measured values"? If the software does not perform a blank correction, then the d13C values used by the software are simply identical to the ones inputted by the user---there is nothing to be "modelled" here. I don't understand how the numbers in Table A2 were generated.

We are grateful to the reviewer for informing us on how to disable the blank correction in the *rampedpyrox* software. We have therefore removed the sentence and Table A2 as they are not required.

Fig. 1-2/Table 1-4: (I'm not sure exactly where to put this comment, so I will put it at the first place that I think is relevant, which is Fig. 1.) Here, the authors need to report much more information related to the inversion before these results can be interpreted. For example:

- what regularization values, l, were used for each sample?

We used the best-fit values which were generated by the model based on our data, following the model documentation. We have added these values to the supplementary information (rp_outputs -> sample -> Figure_2).

- How do the resulting p(0, E) distributions for each sample look? The authors show the thermograms, but never show p(0, E) distributions. It is difficult to judge results without seeing the distributions themselves. This is particularly the case since some of the samples appear to not reach baseline at high temperature (e.g., T3 5.5, T2 15.5). This is important as it is known that the inversion is sensitive to boundary effects, so baseline must by reached or forced (see documentation).

We have added these distributions to the supplementary information (rp_outputs -> sample -> Figure_3). Per model documentation, we forced the baseline to be reached. This does not change our findings.

- It would be incredibly useful for the subsequent discussion to know what fraction of each sample is contained within each thermal window. For example, is the 150-325 °C fraction 10% of total C? 20%? This sould be added, e.g., to Table 1 or 2.

We have added this table to the supplementary information (Table A3), for both the total C released for each temperature fraction and the % of each sample which was evolved for each temperature fraction. There were no significant changes in the proportion of C released from each fraction with burial depth and we have added a sentence on this to the discussion to clarify:

L338: "*This interpretation is supported by the lack of change in both the amount and the proportion of* CO_2 *evolved from each change temperature fraction with depth (ANOVAs,* $p > 0.05$*. Table A3).*"

- I am again missing the a comparison of mass-weighted RO results vs. bulk measured results. That is, if you simply sum the F14C or d13C values for each thermal window weighted by the fraction of total carbon within that thermal window, do you recreate the measured bulk values within uncertainty? This is again an important "sanity check" and can easily be added, e.g., to Tables 1-2 (or Table A3).

We cannot do this 'sanity check' for these samples because, as stated, the bulk soils were acid-treated, whilst the RO samples were not (as discussed in our previous response letter), so we would not be comparing like-for-like.

Although we can't do this check for these samples due to the different pretreatments, previous work using this analytical set-up have done this for other samples and shown that the combined ROx fractions do equal the bulk isotope values (Garnett et al 2023).

Garnett, M. H., et al. "A new ramped oxidation-14C analysis facility at the NEIF Radiocarbon Laboratory, East Kilbride, UK." *Radiocarbon* 65.5 (2023): 1213-1229.

We have included above explanation to the revised manuscript; see:

L186: "*The RO samples were not pre-treated with acid, but the samples for bulk soil-^{14}C were (Houston et al., 2024b), so we cannot verify that the weighted RO-^{14}C contents amassed to the bulk soil ^{14}C content. However, previous work using this analytical set-up have done this for other samples and shown that the combined RO fractions do equal the bulk isotope values (Garnett et al., 2023).*"

- In Table 3, what does the p(0, E) column mean? p(0, E) iss a probability density function-

--that is, a distribution whose integral is equal to unity. It is not a single scalar number.

I don't know what 0.02, 0.02, 0.01, etc. refer to. Is this the maximum value in the p(0,

E) distribution? But this is arbitrary and depends on the size of the discretized energy

step, ΔE...

p(O, E) refers to the maximum value of the probability density distribution. In the revised text, we have removed the p(O, E) column from Table 3 and from the text; we acknowledge that it was not a helpful addition.

- Table 4 (and throughout): please update the nomenclature so that it is clear to the reader

when the authors are referring to μE, sE, and p(0, E) of the entire sample vs. for a given

thermal window; following previous studies, I recommend μE, sE, and p(0, E) when

referring to the bulk sample and μf,E, s f,E, and Pf (E) when referring to a given thermal

window, f.

We have now made these requested nomenclature changes throughout the revised manuscript.

L222-223: "...no significant changes in μE, sE, nor activation energy distribtuion (p(0, E))".

But p(0, E) is a distribution, not a scalar value, so how can it be compared across samples in

the same way as the other metrics?

We have removed the discussion of p(O, E) trends from the revised manuscript, without altering the interpretation of the overall results. We thank the reviewer for pointing out this mistake.

L232: “…μf,E [here using my recommended nomenclature]… increased sequentially…we therefore infer that the thermal recalcitrance of RO fractions is greater at higher temperatures…”. As for my comment on L30, of course it is---this is the definition of thermal recalcitrance! Higher temperature thermal fractions will have a higher μf,E value by definition---there is nothing to infer!

We have removed the quoted text from the revised manuscript as we agree that thermal recalcitrance is greater at higher temperatures. This is a point we make in the introduction to aid the reader and it does not need to be repeated here.

L252: What is meant by “…wider μE ranges…compared to the first three RO fractions”? μf,E [here using my recommended nomenclature] is a mean value so it cannot have a “range”. Do the authors mean that the difference in μf,E is greater between the highest two thermal windows than between the lowest three? But if so, then this is simply a function of the chosen temperature windows and doesn’t say anything inherent about the OC being combusted.

This sentence has been removed from the revised manuscript because the model results do not show any significant trends and are redundant to further discussion.

L253-254: “…may have been caused by non-first order decomposition of carbonates”. How would this cause “wider μE ranges… and increased bond strength diversity”? Non-first order behavior implies that the resulting thermogram (and thus p(0, E)) shape depends on the mass of sample loaded into the instrument (c.f., Fig. 4d of Hemingway et al. (2017) Biogeosciences).

Because of the equivocal nature of these results and the fact that they are not necessary to support our overall findings, we have removed this discussion point as being redundant.

L255: change “rampedpyrox model” to “distributed activation energy model”; rampedpyrox is simply the name of the python package.

We have made this change throughout.

L298-299: "…although the thermal reactivity of OC decreases with 14C content…" The causeand-effect should be flipped here: 14C activity decreases with decreasing thermal reactivity (i.e., thermal reactivity is the independent variable).

We have made this change.

L289: "*although ^{14}C content decreases with decreasing thermal reactivity*"

L344-347: Here the logic seems to be: (i) low-E components are consumed prior to deposition in the Skinflats; this leads to (ii) thermally recalcitrant material being deposited and thus (iii) no change with depth in the salt marsh (i.e., due to no further remineralization). But this somewhat contradicts the thermograms shown in Fig. 1 (and presumably the corresponding p(0, E) distributions, if they were shown), which shows a fair amount of carbon in the ~200-400 °C range. This is quite thermally labile. In fact, one does observe a decrease in the peak height of the ~250 °C peak with depth (relative to the ~450 °C peak). This instead points to a continued remineralization of this thermally labile material with burial depth. This is one instance where it would be very useful to know what fraction of total carbon is contained within each thermal window, as this could then be easily quantified. An alternative appraoch is to use the fraction of total carbon contained in "low-E", "middle-E", and "high-E" bins, as was done for example in Hemingway et al. (2018) Science (https://doi.org/10.1126/science.aao6463).

We agree that there is clearly some thermally labile C in the samples, this is already discussed in the next paragraph.

L341: "*Not all old OC is degraded or thermally recalcitrant, and our results show that the Skinflats saltmarsh is also a store of old (^{14}C-depleted), thermally labile OC (Fig. 1).*"

Whilst we agree that visually it looks like there may be trends in the proportion of C evolved from each temperature fraction with depth, and we had discussed this in our original submission, there were no significant trends with depth in either the amount or the proportion of C evolved from each temperature fraction. We have added this data to the supplementary information (Table A3) and added a sentence to the discussion.

L338: "*This interpretation is supported by the lack of change in both the amount and the proportion of CO_2 evolved from each change temperature fraction with depth (ANOVAs, $p > 0.05$. Table A3).*"

L360-361: "…more energy is required …to decompose older…carbon than younger…carbon".

Careful with statements like this; thermal activation energy is merely an analytical tool to separate carbon; there is no requirement that older carbon necessarily has a higher thermal recalcitrance.

We agree with the reviewer for the need to be careful here, but feel it is important to state that our findings are consistent with much previous research on different soil/sediment systems. We have altered the text to state '*in most cases'* to make it clear that it is not a requirement that older carbon has a greater thermal recalcitrance than younger carbon.

L353: "*which have found that in most cases, more energy is required (higher temperature/μE) to decompose older (^{14}C-depleted), degraded/microbially derived (^{13}C-enriched) C than younger (^{14}C-enriched), less processed (^{13}C-depleted) C*"

L365-266: Schmidt et al. (2011) do not mention thermal reactivity. Also, biological turnover time does not depend on thermal reactivity per se; the latter is merely an analytical tool.

We have changed 'depends on' to 'related to' and removed the Schmidt et al. (2011) reference. No reference is required as we have stated this fact previously in the manuscript.

L359: "*As the biological turnover time of OC is related to the prevailing environmental conditions as well as thermal reactivity*"

L380-382: This statement is well-known in the RPO literature (see, e.g., some of the initial papers from the Rosenheim group that focused on using RPO as a means of dating sediments).

We are aware, but we still need to report it as it occurred for our samples. We have added a sentence stating that this has been found in previous research.

L376: "*Similar findings of mixing within thermal fractions has been reported in previous RPO work (e.g., Rosengard et al., 2025, Rosenheim et al., 2008).*"

L389-390: I don't think you can say that, "...the biologically evolved CO2...was therefore not from a thermally labile OC pool." It very well could have been from a labile pool if said pool was composed of several compounds of different 14C ages, as is likely.

We have altered the wording to make it clear that the pool was potentially not from a thermally labile pool, although it is possible that it was as all pools are mixtures.

L385: "*... potentially derived from less thermally labile OC pools than the other samples, although it is possible that the thermally labile pools were composed of multiple OC sources with different ^{14}C contents.*"

L399-401: I don’t know what this sentence is trying to say. Reword.

Reworded.

L396: “*Degradation of some of the thermally labile OM components during burial may reduce the range of differently aged OC sources within the most thermally labile RO fraction for the deeper samples in this study.*”

L432-433: This relates to my comment in the abstract, but can this really be considered as

additional C storage for MRV? This carbon is already naturally sequestered…

See our reply to the comment on the abstract. This is covered in the previous paragraph.

L420: “*Protecting saltmarshes from degradation following drainage is listed as an eligible activity for generating carbon credits for blue carbon ecosystem (BCE) projects (VERRA, 2023) and there is significant potential for climate mitigation by avoided emissions from protecting vulnerable stocks of soil OC in BCEs (Goldstein et al., 2020; Griscom et al., 2017; Kwan et al., 2025; Sasmito et al., 2025). Similarly, the re-creation of saltmarsh habitat through managed realignment (rewetting by tidal inundation) of historic saltmarsh habitats which were previously reclaimed for land use purposes (e.g., agriculture) could reduce (and possible reverse) the emissions of aged OC to the atmosphere, both locally to Skinflats, and globally.*”

L485-487: Same as previous comment

See above.