Authors response to:

Interactive comment on "Combining a coupled FTIR-EGA system and in situ DRIFTS for studying soil organic matter in arable soils" by M. S. Demyan et al.

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The manuscript by Demyan et al. reports on a new method for the characterization of soil organic matter (SOM) composition and stability, which represents a potentially important advancement of our knowledge of SOM dynamics. The application of thermal analysis techniques to the characterization of SOM has gained increasing traction, but many problems with the technique remain unresolved. The coupling of EGA and in-situ DRIFTS represents a potential means of addressing some of these problems, particularly the attribution of thermal reactions to particular chemical components of SOM. While the manuscript is of high quality and appropriate for the journal, I found that it lacked the reporting of some important results. The authors report on the optimized results, but as a method development manuscript, more results from the non-optimal conditions should also be reported for the reader to be able to make their own judgments. Also, I found the most novel part of the work to be the attribution of thermal reactions to chemical components, but the manuscript lacked most of the DRIFTS results, which should instead be highlighted. I think the manuscript needs some major revisions before I would recommend it for full publication. I provide specific guidance through the comments below.

We thank A. Plante for his thorough review, input, and suggestions on improving the manuscript. We have addressed each point below and have included revised or additional figures which are intended for the revised manuscript, in addition to a supplemental file which includes pre-testing results during the method development.

p.15384, ln.2-3: The citation Blumstein (1965) is not in the reference list.

This citation has been added to the reference list.

p.15384, ln.7: The method of DTA is not the measure of differential mass loss, that it TG. Instead, DTA measures a differential in the temperature between a sample and reference.

This has been corrected in the text to "DTA measuring the difference in temperature between a sample and a reference material."

p.15384, ln.15: This is a very important point, and one of the major challenges and opportunities in thermal analysis for SOM characterization. I will refer to this point in later comments.

This is one reason why we have explored the use of other characteristics (measurement of evolved CO_2 and CO_{2max} and changing intensities of molecular vibrational intensities) for thermal analytical techniques besides weight loss.

p.15385, ln.9-13: I would refer the authors to a recent article in ES&T (Fernandez et al. 2012 ES&T 46:8921) where we report on the coupling of TG-DSC with EGA by infrared gas analysis for CO2. This approach is similar in part to the one being proposed, and addresses some of the same issues.

This reference has been added to supporting literature as an example of EGA in the introduction.

p.15386, ln.12 & 16: Refrain from using "and/or". In terms of logic, "or" is not exclusive and therefore includes the possibility of "and". As such, using only "or" is sufficient.

This has been changed to use "or."

Section 2.1: Given that this work is method development, and that one of the major issues with thermal analysis is the role of the mineral matrix, I was somewhat disappointed by the limited number and range of soils used in the study. I understand the rationale of using multiple treatments or fractions to characterize SOM variability within a given soil, but I think the method development would have been much more robust by applying it to a much broader range of soils. Has the method been tested more extensively?

While not covering all soil types, we have included the analysis of different pure chemical compounds ($NaHCO_3$ as a standard and glucose, xylan, and tannic acid as examples of compounds found in soils) and long term fertilizer treatments which have resulted in different qualities of SOM and also different SOM fractions in which organic matter has varying degrees of association with the mineral matrix. In this way we have tried to show the application of these methods over a variety of stabilization mechanisms and also organic carbon contents that occur in all soils.

Given that the study includes a rather limited number of soils with limited variability in their properties, it is imperative to include a description of the mineralogy of these soils to partly address the issue of how the mineral matrix affects the results.

The bulk soil mineralogy and pH data have been added to table 1.

p.15387, ln.16: When was the bare fallow treatment initiated? That is, how long had the soil been bare before sampling?

The bare fallow treatment was initiated in early April, 2009 for the Kraichgau site early May for the Swabian Alb site.

p.15388, ln.1: Typo. Replace “3%” with “30%”.

This has been corrected in the text.

p.15388, ln.4-6: This sentence should be moved to the previous section as it describes pre-treatment of the soil in general rather than steps in the fractionation procedure.

This sentence has been moved to the previous section (2.1).

p.15388, ln.26: Is the term “rSOC” really necessary? Would hypochlorite-resistant C not be sufficient? I am reluctant to see new and unnecessary acronyms used.

We have followed the acronyms used in the Zimmermann et al., 2007 as their method is the specific procedure we have used to show that we have followed their methodology.

p.15388, ln.27: By “twice”, do the authors mean that two separate aliquots were fractionated to generate pseudo-replicates, rather than a single sampling between fractionated twice in sequence?

Two aliquots were fractionated separately. This has been clarified in the text.

p.15389, ln.2: I am not familiar with the “Scheibler method” and am not sure how well know it is in general. Please elaborate with one sentence to describe what the method entails.

This has been clarified in the text as the gasometric method by addition of HCl.

Section 2.3: I understand the rationale of the incubation experiment, but it should be stated more explicitly here. Much of the second paragraph can be omitted to reduce the emphasis on this experiment because many of the results are either not reported, or are not highly relevant to the study. For instance, I’m not convinced of the value of the microbial biomass and metabolic quotients. I’ll refer to this again in the discussion section. My recommendation would be to simplify this section to report how the incubation was performed, and then report only the cumulative amount respired as a proportion of initial C to give an indication of C loss during the incubation, and the thermal results (Fig 6).

We have added the carbon lost during the incubation experiment to table 1. As we are focusing on SOM, we would like to have these parameters in order to give an indication on the microbial biomass and what portion of the TOC it makes up.

p.15390, ln.26: Here and several other places in the manuscript, I would recommend reporting the data that is “not shown” in some way. As a methods development better, the results obtained under non-optimal conditions can be as useful as those that the authors have decided are indeed optimal. For this reason, I would like to see these data even if they are in some kind of supplemental file.

We have added figures on the effect of purge flow rate (Figure S1), heating rate (Figure S2) on CO_2 evolution, and a figure on the calibration range optimization (Figure S3) in a new supplementary file. Please see the end of this response (pages 20-26)

p.15391, ln.12 – p.15392, ln.2: This section reports on the post-processing of data acquired, and therefore I recommend that it be moved to and merged with section 2.4.2.

We agree with this suggestion as section 2.4.2 deals with spectral analysis and processing and better fits in 2.4.2.

p.15392, ln.3-7: Again, I would strongly recommend reporting these results in a figure showing how the curves differ by heating rate, similar to what we reported in Fernandez et al. (2011, JTAC).

We have added a supplementary figure (figure S3) which shows the effect of heating rate on the change in vibrational intensity of the peak at 1620 cm^{-1} (COO-/C=C vibrations). The larger increase and lower decrease upon reaching 700°C lends evidence to a greater production of secondary reaction products under the lower heating rate.

p.15392, ln.22-29: I would recommend separating this section out and moving it to a new section before 2.1 Soils. The analysis of model materials is an important first step in the method development, I would suggest that moving this paragraph would generate a better logical order to the methods, that would then be reflected in the order in which the results are reported.

We agree with this suggestion and have separated this out as a new section.

p.15392, ln.28: What was the rationale for the use of quartz as the inert material as opposed to the more frequently used calcinated kaolin?

Quartz was used as it is a dominant mineral in the soils studied and was not reactive when mixed with the pure organic substances and POM.

p.15394, ln.4: The Demyan et al. (2012) citation appears to be quite important. Unfortunately it is not listed in the references.

The reference has been added.
Demyan, M. S., Rasche, F., Schulz, E., Breulmann, M., Müller, T. and Cadisch, G.: Use of specific peaks obtained by diffuse reflectance Fourier transform mid-infrared spectroscopy to study the composition of organic matter in a Haplic Chernozem, Eur. J. Soil Sci., 63, 189-199, 2012.

Section 2.6: This is perhaps the most novel and important component of the work, but unfortunately, I found it difficult to follow. Perhaps it can be restructured and revised to improve clarity. My paraphrasing of this section is that DRIFTS data were used to determine the presence/absence of components within the CO2 evolution curve. These components (identified by changes in portions of the DRIFTS spectra) were used to guide the deconvolution of the CO2-EGA curves. Part of the confusion from the current structure is that the DRIFTS and FTIR-EGA are somewhat muddled together and it is difficult to tease them apart.

The paraphrasing by the reviewer and interpretation are correct. In the revised manuscript the description of the processes and sequence has been adjusted to improve the clarity. First molecular vibration intensities were followed during the temperatures of OM degradation, which was between 200 and 700°C of the in $situ_T$ DRIFTS analysis. A decrease in the identified molecular vibrational peaks of the bulk soil during this period were assumed to coincide with the degradation of OM. Points of maximum decrease were identified by using 100% of the value at 200°C (start of thermal degradation of OM) and calculating the rate of change between each measurement point. These points of largest decrease were then taken as center points for the fitted components of the peak fitting procedure of the FTIR-EGA evolved CO_2 of the bulk soil.

p.15394, ln.13: Perhaps it is terminology, but it is not clear to how the Areawt output is used "for" curve fitting. Is it not more correct that the Areawt output is "subjected to" curve fitting/deconvolution? I am also not clear as to how the Areawt data forms a curve. Is Areawt not a single value for each sample? The FTIR-EGA curves reported in the figure are for Absorbance. Please clarify.

$Area_{wt}$ is the area of the integrated CO_2 peak (which is recorded every 4 sec^{-1}) divided by the sample weight. So in taking all values for one analytical run (300 readings), these values were then subject to curve fitting for one sample. This has been better clarified in the text.

p.15394, ln.16: When the authors refer to "a vibrational organic functional group", are they referring to "each", "any" or "all" groups? Please clarify.

This refers to when any of the C associated vibrational functional group (as defined in Demyan et al. (2012) was found to decrease. Then this formed the basis for the rational for that peak component to be placed at that temperature.

Section 3.1: I don't believe that the C concentration data of the soils and fractions are significant enough to warrant a separate results section, particularly since these samples come from well documented field experiments. Instead, my recommendation would be to fold the C concentration data into the background characterization of the soils in the methods section. Also, as noted above, I don't think the microbial biomass and metabolic quotient is relevant to the main story of the manuscript and should be omitted (also see comments below for p.15402 and Table 1).

We have consolidated the results of the C concentration data into one table. As mentioned above we have retained the microbial information in the table as part of the soil characterization. As this data has not previously been reported (for the Kraichgau and Swabian Alb sites) we think it is necessary to briefly characterize the C concentration and microbial information about the sites in the results. We have removed, though, the metabolic quotient information, as it does not add to the discussion in this manuscript.

Section 3.2 and 3.3: The titles for these sections do not appear to be completely appropriate. The title for Sec 3.2 should be limited to "organic substances" only and not include "soils", while the title for Sec 3.3 referring to "soils and fractions" is indeed appropriate. This structure for reporting the results for the model organic materials before the results for the soils and fractions is very good and should be reflected in the structure of the methods section as I noted above.

The title for section 3.2 has been changed to "organic substances." We have also modified the structure of the results in section 3.3 to follow the same format as 3.2

p.15396, ln.8: Again, I think these would be important data to show for method development.

We agree, hence the non-linear response of absorbances > 2.5 is shown in the supplemental figure S4.

p.15396, ln.25-28: This is a very important result and should be better highlighted. We reported similar incomplete yield of C in our IRGA-based EGA in our ES&T paper. We have been pursuing this line of investigation to determine the potential causes for incomplete recovery and to determine if the variability in the yield is systematic. Perhaps this is something the authors should elaborate on for their EGA method.

The possibilities cited in Fernandez et al. (2012) for incomplete yield of C (incomplete combustion leading to CO formation, liberation of volatile compounds at low temperatures, and condensation of gases before infrared analyzer) could also be possible explanations for incomplete yields found during our testing of diluted and undiluted organic substances (glucose, xylan, and tannic acid). It was seen during FTIR-EGA measurements that CO products were produced, but because the peak area was so small, it was not possible to quantify this gaseous product with the optimized setup, while simultaneously quantifying CO_2. Additionally, lack of a heated transfer line from the high temperature reaction chamber to the gas cell could have also resulted in some gases condensating in the transfer line and not being transferred and measured in the gas cell. As mentioned previously the optimized experimental conditions tried to minimize these effects via rapid heating rate, low residence time of gas by higher purge rate, and dilution of high C content substances (glucose, xylan, tannic acid, and POM).

p.15397, ln.1-11: I would suggest this paragraph is more appropriately located in the methods section and should be moved there.

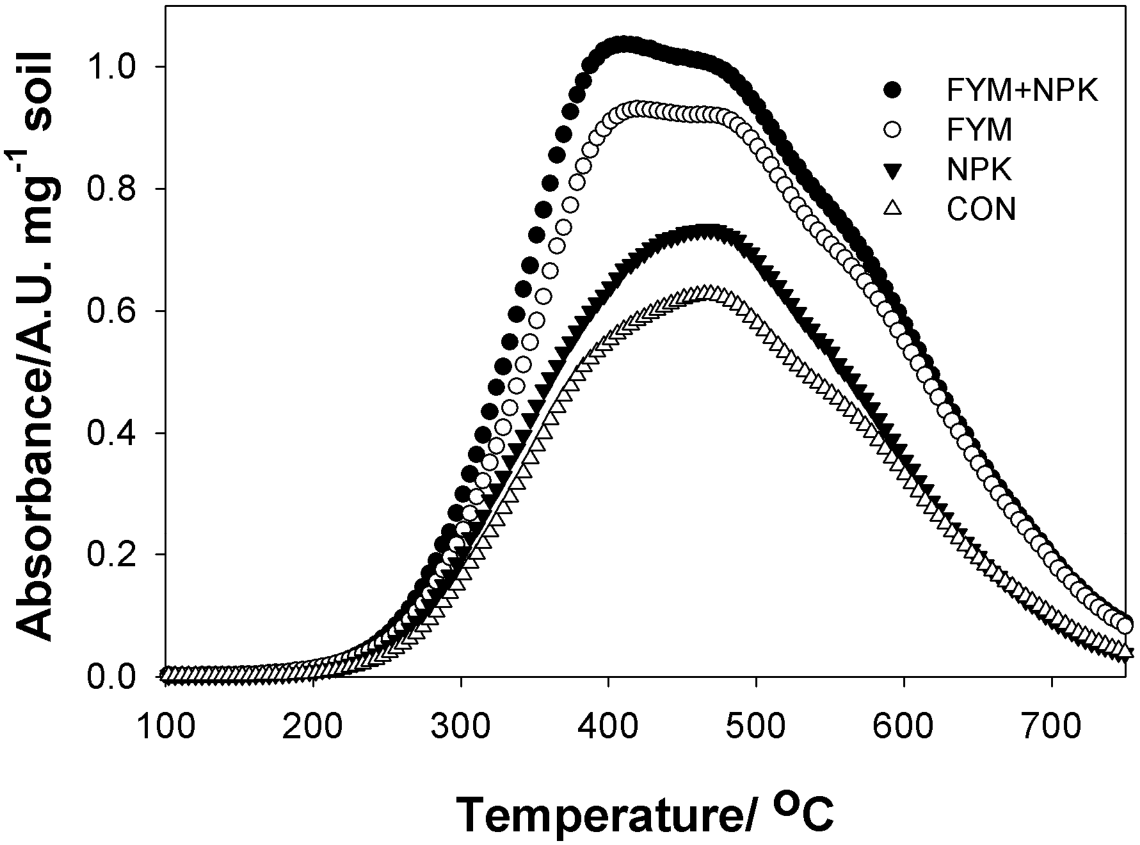
This paragraph has been moved to the materials and methods section.

p.15397, ln.8: Why was the pre-heating treatment of the sand performed up to 600°C instead of 700°C like the samples or hotter?

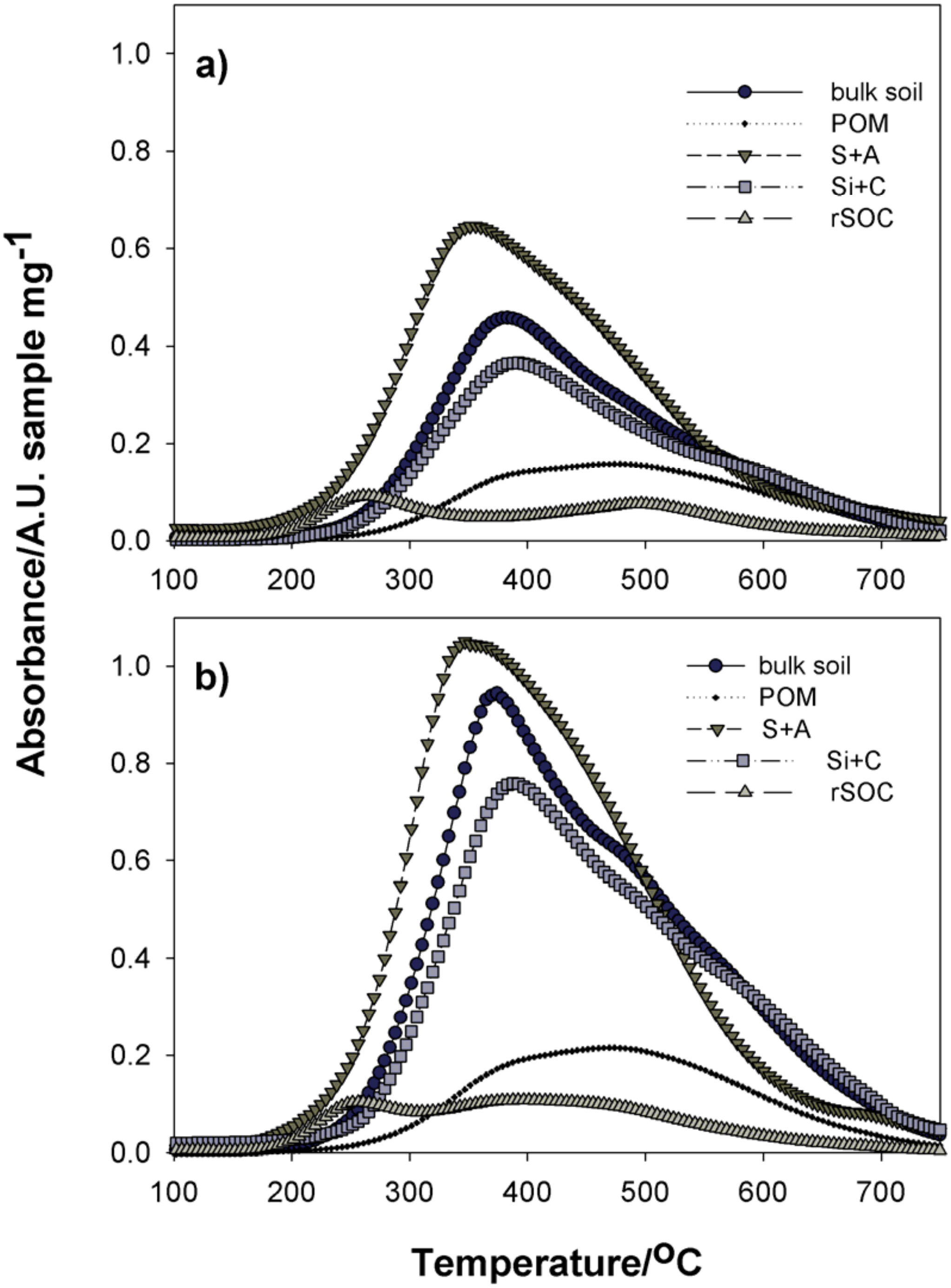
The main purpose of the pre-heatings was to drive off any organic carbon contamination from the quartz sand in a muffle furnace. Since the sand was held at 600°C for several hours (a much longer time then the FTIR-EGA analysis) this was deemed sufficient to drive off any organic carbon contamination.

Section 3.3: The structure of this section should be revised to parallel the previous section on the model organic materials by describing the curve shapes and C yield, then CO2max. For instance, what was the C yield for the soil samples, and how did it compare to the model organic materials? It would also improve the structure and clarity to separate the results from each soil in separate paragraphs. In addition, it is essential that the various FTIR-EGA curves be reported as figures. These are some of the most important results to be reported. See additional comments below concerning Table 2 & 3 and Fig 5. Lastly, it does not appear that the results of the various "thermal characteristics" described in Sec2.4.2 are actually reported.

We have reorganized section 3.3 (soils) to provide a consistent reporting of the results following the format of section 3.2 (standards). We have added information on the calculated C yield versus actual.
We have added additional figures (please see new figures 5 and 6 below) for the FTIR-EGA curves of the various soils and fractions, and treatments of the long term experiment.
Not all of thermal characteristics are reported separately, but we felt that it was important to show the calculated steps in how we arrived at the values we did report (CO_{2max}).



New figure 5. FTIR-EGA evolved CO_2 thermograms of bulk soil from the Static Fertilization Experiment, Bad Lauchstädt heating from 25 to 700°C at 68°C min^{-1} under synthetic air purge. Treatments: FYM+NPK (farmyard manure and mineral fertilizer), FYM (farmyard manure), NPK (mineral fertilizer), Control (no fertilizer inputs).

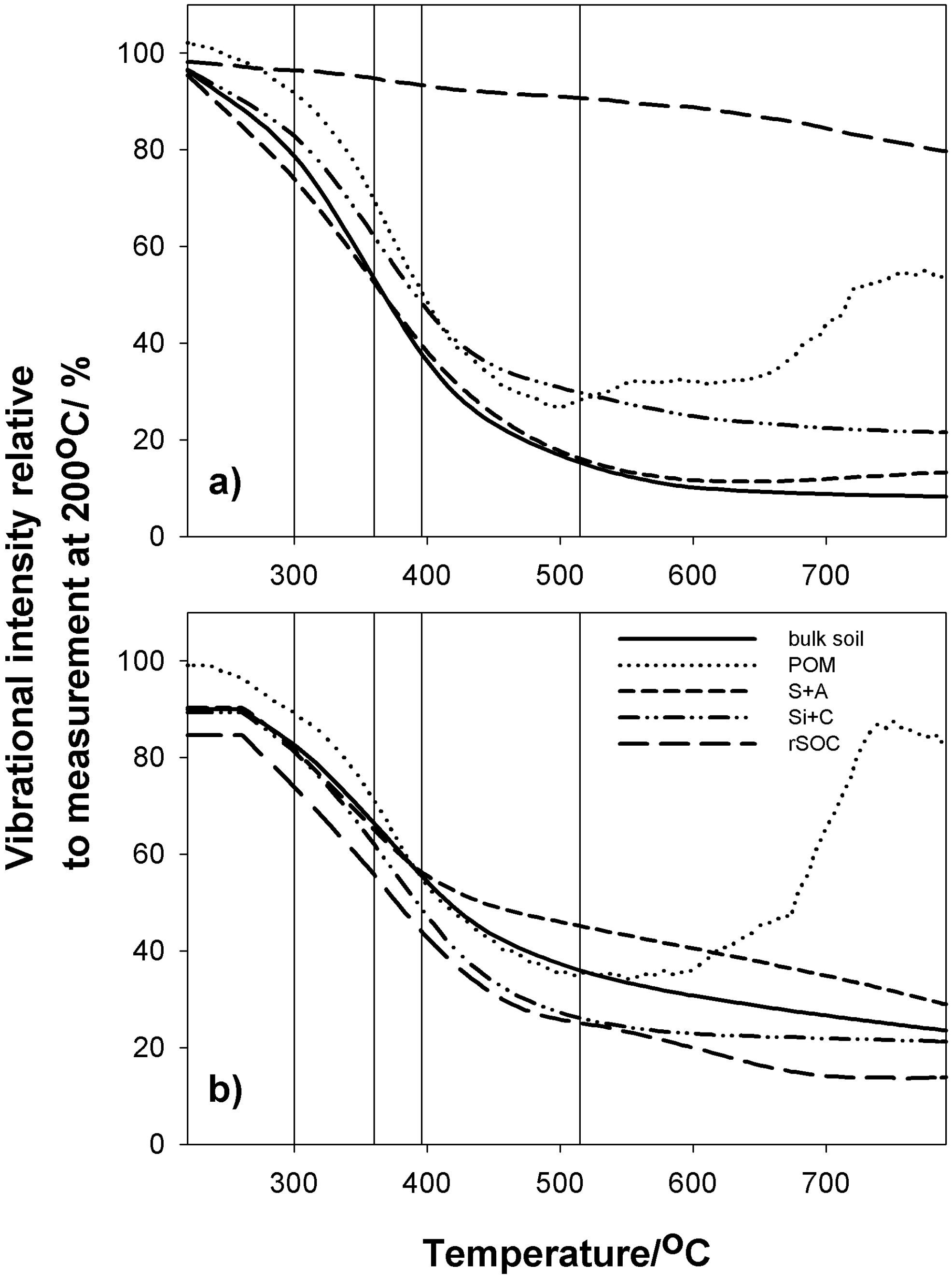


New figure 6. FTIR-EGA evolved CO_2 thermograms of bulk soil and fractions heating from 25 to 700°C at 68°C min^{-1} under synthetic air purge. - Bulk soil <2 mm, POM-sand fraction < 1.8 g cm^{-3}, S+A sand fraction > 1.8 g cm $^{-3}$, silt+clay < 63 µm, rSOC < 63 µm treated with hot sodium hypochlorite *p.15398, ln.9-14: The results of the cumulative CO2 evolved (perhaps as a proportion of initial C) should be reported here along with the comparison of the pre- and post-incubation thermograms. I would also recommend moving this paragraph ahead of the previous one to keep all the results of bulk soils together first, before moving on to the results of the fractions.*

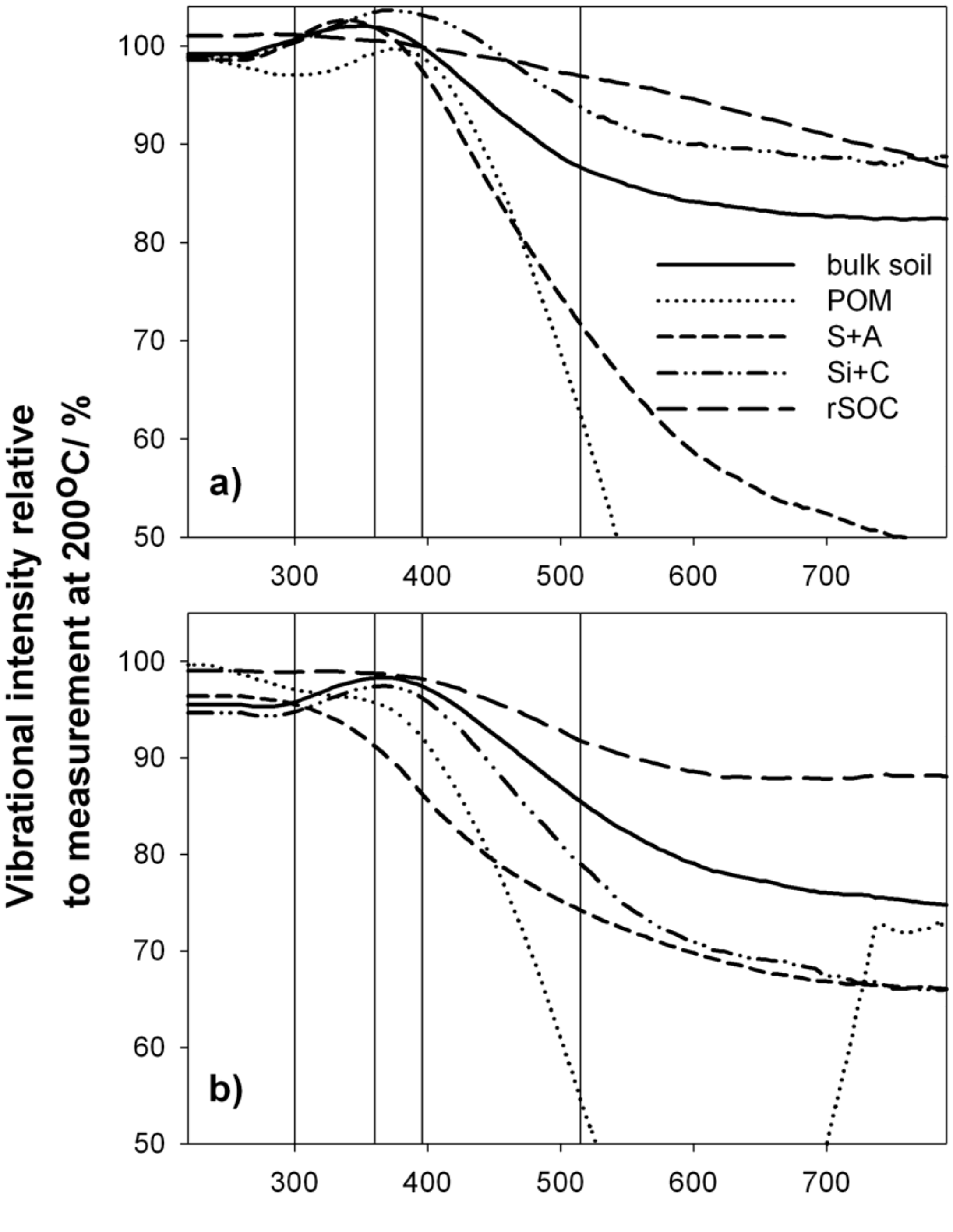
We agree with these suggestions and have moved the results of the incubation FTIR-EGA thermograms together with the soils and kept the fractions after this paragraph.

Section 3.4: These results are the most novel part of the study, and therefore warrant better reporting. Again, instead of "data not shown", I would strongly recommend reporting these results in some form or another. The authors need to show more of these results to demonstrate the diversity of results among samples. See comment below in reference to Fig 7.

We have included several figures (figures 8 and 9) of the bulk soils and fractions of the in $situ_T$ DRIFTS from two of the contrasting vibrational wavenumbers that were of interest (2930 and 1620 cm^{-1}). We have also added to the description in the results of the additional figures.



New figure 8. In situ$_T$ DRIFTS of C-H (2930 cm^{-1}) vibrations of bulk soil and fractions of a) Kraichgau site and b) Swabian Alb site. Reference lines indicate the temperature used for fitting components to the FTIR-EGA CO_2 results.


Vibrational intensity relative to measurement at 200^{o}C/ %
a)
b)
100
90
80
70
60
50
300
400
500
600
700
bulk soil
POM
S+A
Si+C
rSOC
Temperature/^{o}C

New figure 9. In situ$_T$ DRIFTS of C=O/C=C (1620 cm^{-1}) vibrations of bulk soil and fractions of a) Kraichgau site and b) Swabian Alb site. Reference lines indicate the temperature used for fitting components to the FTIR-EGA CO_2 results.

Section 3.5: It is not clear to me why the peak-fitting appears to only have been performed on two soils/samples. The authors should consider a different comparison. Comparing the SOM composition/stability in two different soils is not a straight-forward exercise because of the large number of confounding variables that might affect the results of the thermal analysis such as mineralogy. Instead, I strongly recommend that the authors expand the analysis to the other samples and consider alternative comparisons. Better comparisons would be among treatments or fractions within a soil. Or has the method not proven to be sufficient sensitive to detect these differences? See also the comment below in reference to Table 4.

We have further applied the peak-fitting method to the four treatments of the Bad Lauchstädt long-term experiment which shows the sensitivity of the method to different fertilizer types (farmyard manure and mineral fertilizer).

p.15401, ln.12-28: This is great and really hits right at the heart of the underlying assumptions for using thermal analysis for SOM characterization. The distinction between results of the model organic materials, litter, and POM fractions, and the results of mineral-associated C fraction is very important has not yet been properly highlighted in the literature. We have unpublished data that show similar trends that the authors report here. I recommend this finding be better highlighted, and better placed in the context of previously published results on litter, compost and soils (e.g., papers by Rovira, DellAbatte, etc.).

We agree and have added to this section to include results from Dell'Abate et al. (2000) whom found via DSC and TG measurements of compost during a 56 day experiment a decrease of the exotherms of both the first and second peaks (around 300 and 450°C respectively) and an increase in the proportion of the 2nd peak relative to the first indicating an enrichment in more thermally stabile humic substances. Also Rovira et al. (2008) found a general increase in the temperature of 50% of thermal weight loss and a decrease in the temperature of 50% of energy loss by DSC of four different residue types. Rovira et al. (2000) cited mineral interferences in the change of thermal stability of pure residues compared with residues mixed with red earth even after subtracting the DSC curves of the unamended red earth from the DSC curves of the red earth mixed with residues.

Dell'Abate, M. T., Benedetti, A. and Sequi, P.: Thermal methods of organic matter maturation monitoring during a composting process, J Therm Anal Calor, 61, 389-396, 2000.

Rovira, P. and Vallejo, V. R.: Examination of thermal and acid hydrolysis procedures in characterization of soil organic matter, Commun. Soil Sci. Plant Anal., 31, 81-100, 2000.

Rovira, P., Kurz-Besson, C., Coûteaux, M. and Ramón Vallejo, V.: Changes in litter properties during decomposition: A study by differential thermogravimetry and scanning calorimetry, Soil Biol. Biochem., 40, 172-185, 2008.

p.15401, ln.14: Should "but CO2" refer instead to CO2max?

This has been corrected to CO_{2max}.

p.15402, ln.6-8: This sentence is not necessary in the discussion. It should instead be in the methods or results.

This information has been given in the materials and methods, thus has been deleted.

p.15402, ln.21-26: I am not at all convinced that the differences in microbial biomass are sufficient to be expressed in the thermal analysis. Biomass was reported to be 0.6 mgC/g, which represents approximately 3% of the total organic C in the bulk soil (which is reported to be 19.4 mgC/g). I believe this is a red herring unless there is substantial supporting evidence. My recommendation, as I have noted above, is to omit the microbial biomass and metabolic quotient components of the experiments, and limit the incubation study results to the total cumulative CO2 respired as an index of C loss during the incubation. More important to the discussion, however, is to highlight that the newly developed coupled FTIR-EGA and DRIFTS method provides a mechanistic/concrete foundation for the deconvolution of the thermogram. I previously published some peak deconvolution of DSC data (Plante et al. 2005 Geoderma 129:186), but have become highly reluctant to continue to do so become of the problem of attribution. Peak deconvolution is strictly a statistical method that has no theoretical or mechanistic foundation with other data to guide it. The authors have provided some of the first data using their DRIFTs analysis that can provide this guidance. This, in my opinion, is the most important outcome of the new method, and should be highlighted.

We agree with the notion of the reviewer that the use of in $situ_T$ DRIFTs is a major step forward in underlying deconvolution approaches. We thus reinforced this important aspect and have reduced the focus on microbial biomass aspects, e.g. that is the sentence has been changed to make the link this component is related more to labile OM matter rather than microbial biomass.

Section 4.4: I am not sure this is the best position for this section. It does not provide the best bookend for the discussion, which should instead end with the broadest implications for the study. I would recommend moving this section between 4.1 and 4.2, or perhaps even merging it with Sec4.1.

This section has been added into 4.2.

Conclusions: The impact of the conclusion can be greatly improved by shortening it. The conclusion section can be easily shortened by omitting much of the summary or repetition of the results and discussion. Rather than a summary, the conclusions should instead highlight the most salient outcomes of the study and provide guidance about future developments and applications of the method.

The conclusion has been shortened to include less summary information but rather the major points from the findings such as:

The amount and shape of evolved CO_2 under an oxidizing atmosphere evolved from 25 to 700°C depends on chemical structure (e.g. single chain C-C and C=C aromatic structures), type of soil (e.g. Chernozem v. Cambisol) and also fraction of soil investigated (e.g. silt and clay fraction v. bulk soil v. POM). Temperature dependant changes in the intensity of mid-infrared molecular vibrations also indicated different OM compounds decomposing at different temperatures. The combined setup offers a rather simple analysis without expensive absorption columns and relatively straightforward interpretation of results. The combined use of FTIR-EGA and in $situ_T$ DRIFTS provides a theoretical molecular basis and a major step forward for the fitting of different components to the evolved gas thermogram.

Table 1a: Which treatment(s) are represented in the TOC data? Is it the mean of all treatments? I would actually recommend omitting the TOC data from this table, and limiting this table to basic characterization data. For instance, in addition to %clay, pH and mineralogy could be reported.

Table 1a has been modified to include mineralogical data on the soils and pH, while TOC data has been combined in table 1b.

Tables 1b and 2: Instead of reporting the TOC concentrations in Table 1a, I would recommend creating a new, merged table that reports only the TOC concentrations for all soils, treatments/years and fractions. As it is now, the TOC data is spread over three different data, and I do find that do be very effective. It would be a better presentation of the background information about C concentrations it were all compiled into a single table.
Table 1b: Why are TN data reported? How are they relevant? If the authors consider them important, they need to be explained in the methods and described in the results text. I would recommend that they be omitted as they have little bearing on the central issues of the study.

We have removed the N data from this table and have included all C concentration data here.

Table 2: Why are the TOC data reported as the mean of the three years? Did the C concentration not change through time? My guess would be that they did not actually change much because the standard errors appear to be quite low. In any case, this should be explained in the results. Also, as I described above, I recommend a single table to report the TOC data. However, the authors might elect to report peak temperatures along with the TOC data or as a separate, similarly-structured table reporting only peak temperatures.

Table 2 has been deleted, as the TOC data is now reported in table 1b and the FTIR-EGA thermograms are now reported in a new figure. The TOC data from the Bad Lauchstädt experiment was reported as the average of the three years sampled, as it did not change statistically significantly over the sampling dates.

Table 3: I strong recommend that the authors replace this table with a figure showing the shapes of the thermograms. This would be much more impactful for the reader. It is difficult to imagine the shape of the thermograms based on a listing of peak and shoulder temperatures.

We have now included a figure of the bulk soils and the fractions (please see new figures 5 and 6 above).

Table 4: Was peak deconvolution performed only for these two samples? I found this to be a rather weak comparison, and as I noted in a comment above, I recommend that this table be expanded to include more samples provide a better comparison (i.e., among treatments or fractions within a soil). Or is the method not sufficiently sensitive to detect these differences?

We have now included the four treatments from the Bad Lauchstädt experiment.

Figure 5: Which treatments are represented here? As noted above, I strongly recommend that this figure be expanded to illustrate the thermograms of many more of the soils, treatments and fractions analyzed.

This figure has been separated into two parts, new figure 5 contains the thermograms for the four treatments of the Bad Lauchstädt experiment and new figure 6 has the thermograms for the bulk soils and fractions from the Kraichgau and Swabian Alb sites (please see above).

Figure 6: Rather than a three-panel figure, I would suggest that the figure would be more effective if the difference curves for each soil were included in each of panels A and B. Having the third panel as is suggests that the comparison of the difference curves between the two soils is important. I'm not convinced that a comparison between the soils is intended or meaningful.

As we would like to characterize each of the sites and the comparison of the difference curve between the two sites shows these differences, we think it is valid to have the third panel.

Figure 7: As noted above, the figure illustrating the DRIFTS data needs to be expanded to include more samples.

We have now included figures of bulk soil and the fractions. (please see new figures 8-9 above).

Supplementary information

Combining a coupled FTIR-EGA system and in situ DRIFTS for studying soil organic matter in arable soils

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For the optimization of the FTIR-EGA and in $situ_T$ DRIFTS systems, purge rate, heating rate, and calibration range were investigated in order to obtain the optimal operating conditions. Figure S1 shows the effect of purge rate of the heating chamber and gas cell. At low purge rate the CO_2 concentration is more than twice as high and the residence time of the gas in the system is much longer, as seen by the lack of a decrease of the curve upon reaching the end of the programmed heating at 700°C. The change in heating rate from 10 to 68°C also produced a marked change in the evolved gas profile (Figure S2). An increase in both the peak temperature of maximum CO_2 evolution was found and also an increase in the absorbance values. Figure S3 shows the effect of the two extreme heating rates on the change in relative intensity of the mid-infrared peak at 1620 cm^{-1} (COO=/C=C). The lower heating rate seems to produce a greater overall increase in this peak area and likewise at the end of the programmed heating increase, the intensity of the peak has not declined as much as compared to 68°C min^{-1} possibly indicating the formation and retention of more thermal recalcitrant C which justified our use of the higher heating rate. Figure S4 shows the linear range of the FTIR-EGA gas cell calibration with $NaHCO_3$ and also shows the “overflow” or non-linear area where the absorbance values no-longer respond linearly to an increase in C content of the sample. Additionally if any of the variables are changed in the experimental setup (heating rate, purge rate, purge gas), then a new calibration must be developed.

Figure S1. Effect of flow rate (synthetic air) on evolved gas profile of CO_2 as measured by FTIR-EGA of bulk soil from Kraichgau site. Sample was heated from 25 to 700°C at 68°C min^{-1} under synthetic air purge.

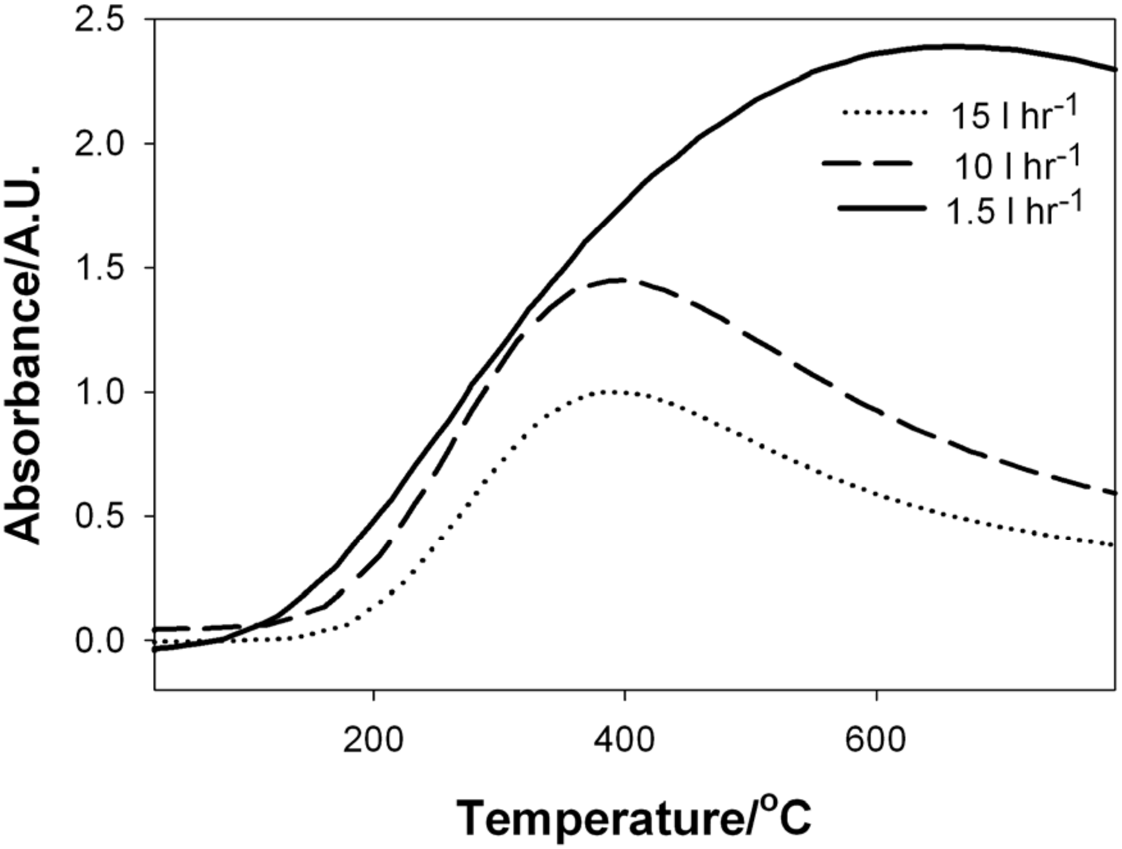

Figure S2. Effect of heating rate on evolved gas profile of CO_2 as measured by FTIR-EGA of bulk soil from Kraichgau site heated from 25 to 700 °C under synthetic air purge.

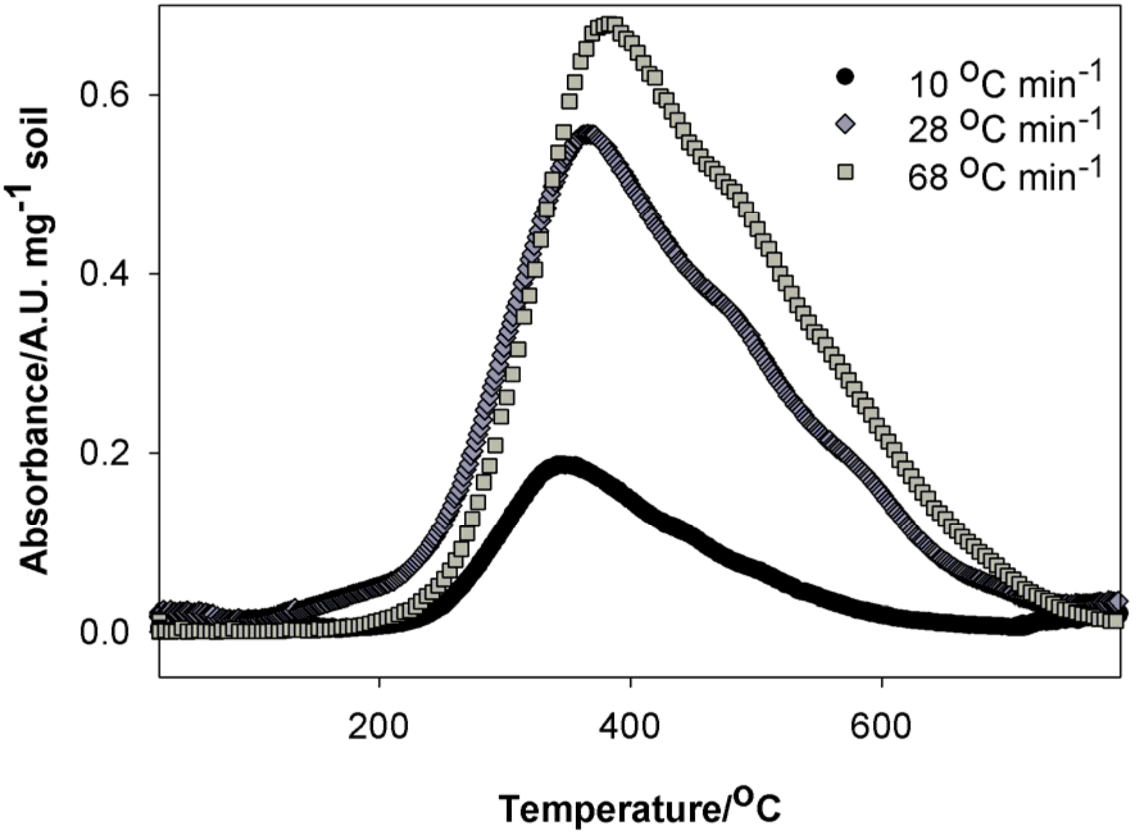

Figure S3. In situ$_T$ DRIFTS of effect of heating rate on vibrational intensity change of peak at 1620 cm^{-1} (COO-/C=C) of bulk soil samples heated from 25 to 700°C under synthetic air purge.

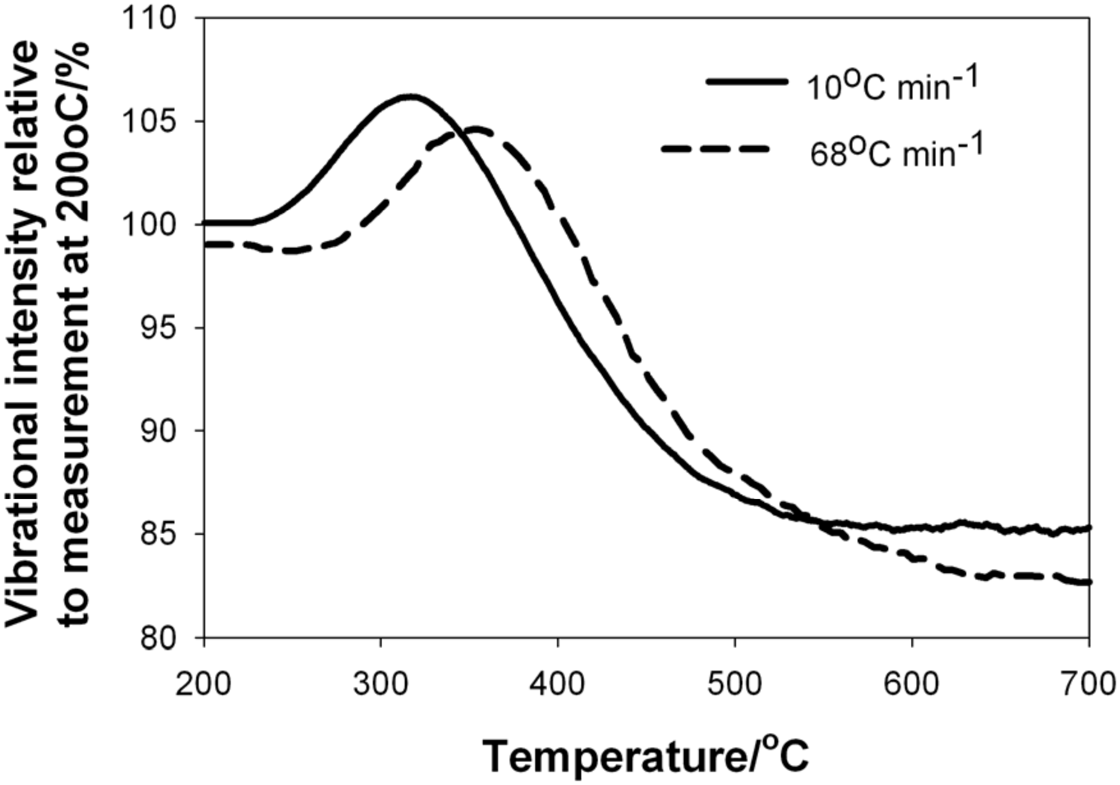

Figure S4. Extended range of $NaHCO_3$ standard showing no-linear response with increasing C content under synthetic air purge.