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.

Anonymous Referee #1
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Interactive comment on Biogeosciences Discuss., 9, 15381, 2012.
www.biogeosciences-discuss.net/9/C6219/2012/

General comments
This manuscript is a timely contribution to the research on soil organic matter, which has received renewed interest in the last decade because of the link between soil carbon stock and climate change. The advance in SOM research, however, is slow in terms of the development and use of new methodologies and techniques. The idea of combing FTIR-EGA system is novel, and the techniques the authors has developed are sound in principle. The manuscript would be publishable after some revisions.

We thank you very much for your input and suggestions and have addressed your points below.

As the authors correctly pointed out, methodologies are much needed to rapidly characterize the dynamics and stability of soil organic matter, for which CO2 max was proposed as an indicator. Does the value of CO2 max depend on the heating rate in thermal analysis? Could the authors provide an example of the dependence or independence of CO2 max on heating rate?

CO_{2max} does in fact depend on heating rate. In the supplemental files we have added a figure (Figure S2) from pretesting which shows dependence of CO_{2max} on heating rate. Standardisation is thus important when comparing different experiments.

Why did you hold samples for heating at 700oC for 10 minutes?
Was it for complete combustion of soil organic matter at 700oC or other purpose?

As shown by the thermograms of evolved CO_2 not all of the CO_2 evolution was finished upon reaching 700 ^{o}C and holding at this temperature for 10 minutes allowed for an excess of time to ensure all CO_2 was evolved.

Would it be a better choice to decrease the heating rate to half (34oC per min) and eliminate the holding time at 700oC? My own thermal analysis of a soil sample shows that the onset temperature of SOM decomposition changed from 221oC to 258oC, and peak maximum of heat flow curve increased from 295oC to 389oC when the heating rate was increased from 10oC to 60oC/min, although the shape of weight loss and heat flow curves was less affected by heating rate.

We chose a relatively high heating rate in order to minimize the formation of secondary compounds (evidence shown by an increase of COO^{-}/C=C vibrations in figure S3) during

thermal degradation. 68^{o}C min^{-1} was the upper limit of obtaining a linear heating rate, as higher heating rates would sometimes lead to an overshoot of the final set point temperature and non-linear temperature increases.

Have you compared the C content determined by your elemental analyzer with the data from thermal analysis (i.e., the weight loss from combustion, divided by a factor 1.724 for a conversion to C%)? These two values would be similar if you could determine the temperature at which SOM starts to decompose.

We have not compared weight loss of thermal analysis with the C concentrations from the elemental analyzer. As was pointed out in the introduction, TGA has the drawback of OM thermal degradation going on at the same time as weight losses from different types of sorbed and interlayer water.
For our purposes for the FTIR-EGA method we have taken 200°C to be the onset of the degradation of SOM as shown by the increase in evolved gas of CO_2.

p. 15390, line 24. (0.13 to 48%). Please specify which sample has a C content of 0.13%.

The rSOC samples had the lowest carbon contents, which was 0.13% by weight, while the highest OC content was tannic acid (48%). This has been clarified in the manuscript.

Technical corrections
There are several errors that the authors must correct during their revision of the paper. The below is an incomplete list of the errors:

• *P. 15388, lines 1-2. The clay contents in the sentence do not match with the numbers in Table 1a.*

This has been corrected in the text.

• *These references were cited in the text, but not listed in the references section:*

von Lützow et al., 2008 (p.15384); Demyan et al., 2012 (p.15394); Schulten, 2009 (p.15401); Dell'Abate et al., 2003 (p.15403); Schulten and Leinweber, 1999 (p.15405)

All references have been checked and omitted ones added in the reference list.

• *The reference of Schütt, 2010 was listed at the end, but not cited in the text.*

This reference has been deleted.

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.

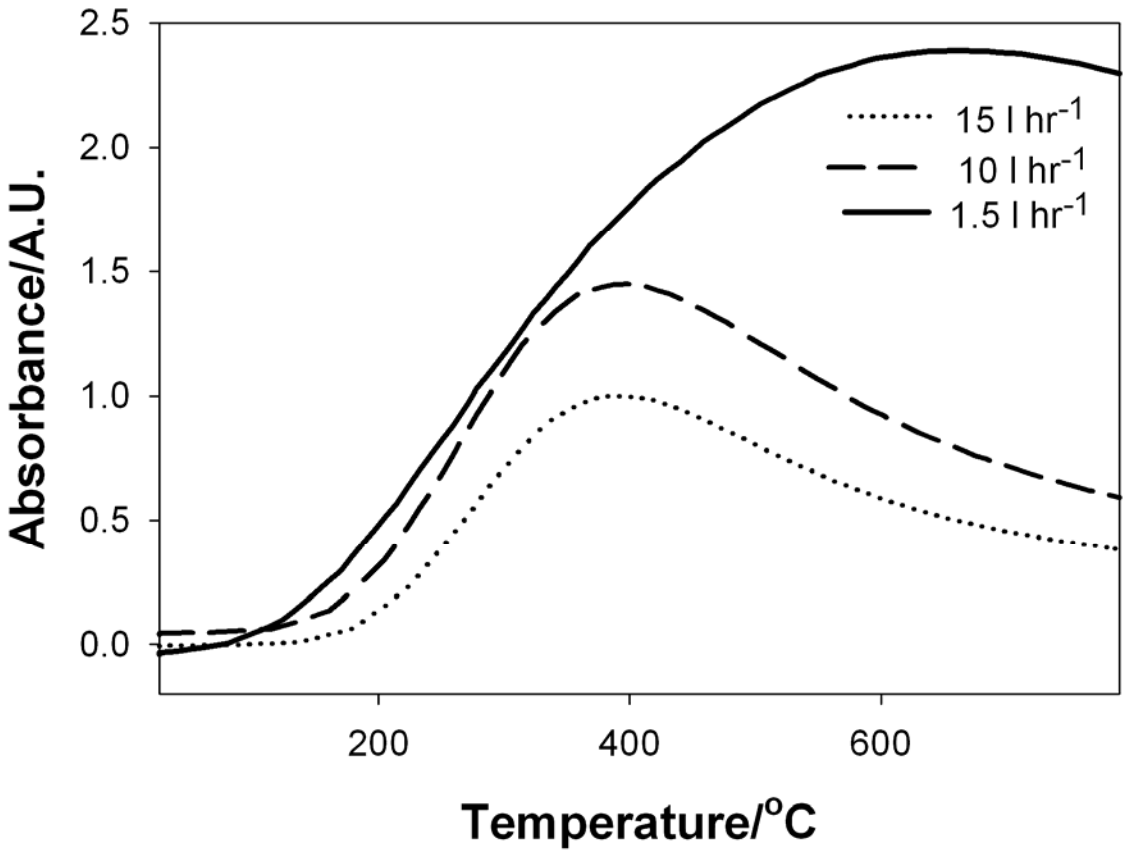

Figure S2. Effect of heating rate on evolved gas profile of CO_2 as measured by FTIR-EGA of bulk soil from Kraichgau site heated from 25 to 700 °C under synthetic air purge.

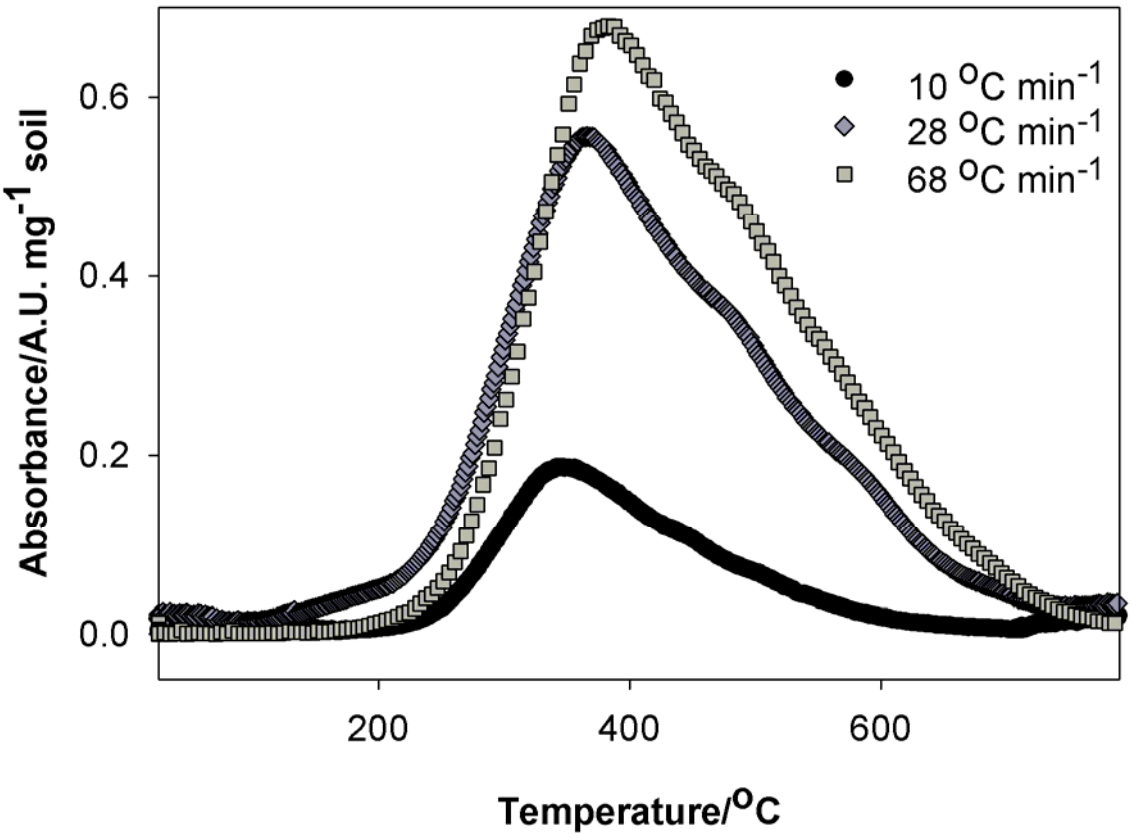

Figure S3. In situ$_T$ DRIFTS of effect of heating rate on vibrational intensity change of peak at 1620 cm^{-1} (COO-/C=C) of bulk soil samples heated from 25 to 700°C under synthetic air purge.

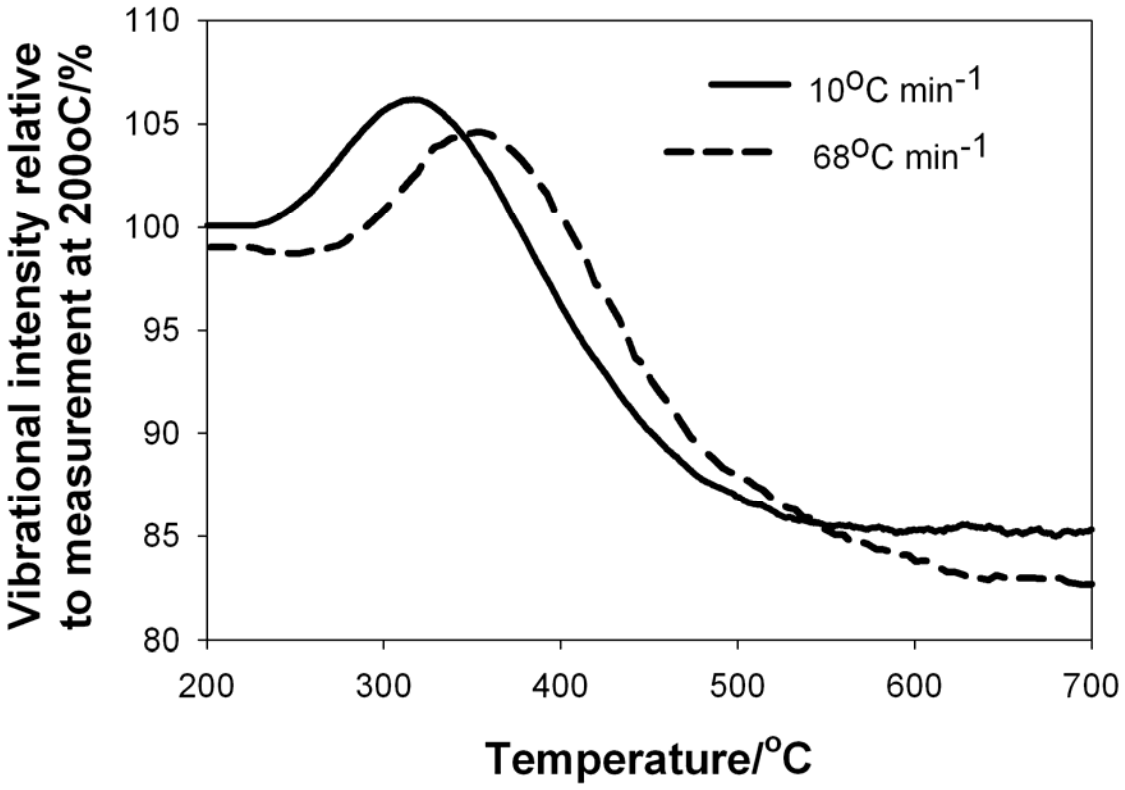

Figure S4. Extended range of $NaHCO_3$ standard showing no-linear response with increasing C content under synthetic air purge.