

Authors' Response to:

Biogeosciences Discuss., 9, C6890–C6893, 2012

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.

S. Sleutel (Referee)

steven.sleutel@UGent.be

Received and published: 27 December 2012

<http://www.biogeosciences-discuss.net/9/C6890/2012/bgd-9-C6890-2012.pdf>

This is a high quality study, and the introduced technique, a coupling of FTIR-EGA and in situ DRIFT seems to hold potential to rapidly assess SOM quality. Most importantly, it holds promise to provide us with information on the strength of bonding of SOM constituents. I support publication of the present paper but I do have some ideas for its improvement. Most importantly, a further elucidation of the observed evolution of the DRIFT spectra with temperature is needed. To really get this new approach accepted an important requirement is that more than two samples are investigated. Other elements like a soil incubation experiment, the assessment of the effect of chemical oxidation, and a strictly statistical deconvolution of the coupled data FTIR-EGA DRIFT are of lesser importance.

We thank S. Sleutel for the input and suggestions on the improvement of this manuscript. We do agree that the in situ_T DRIFTS method can give us additional information during thermal analytical analysis. As is addressed below, we have added additional examples of in situ_T DRIFTS data of the individual treatments of the Bad Lauchstädt long-term experiment, and the bulk soil and fractions at each site that will give more of an idea of the dynamics during heating and differences between the fractions and bulk soils.

The authors here present an alternative technique to gather temperature resolved information on SOM composition. Over the past 40 years HR Schulten and P Leinweber have thoroughly developed pyrolysis field-ionization MS, i.e. temperature resolved analytical pyrolysis with soft ionization. This technique has amply been used to study the thermal stability of specific individual (soil) OM molecular markers and these efforts have resulted in the formulation of a conceptual model linking SOM biochemistry to thermal stability and biodegradability. This wealth of information cannot be overlooked.

We do acknowledge the extensive work by Schulten and Leinweber and have referred to their work when possible and drawn parallels when appropriate. (i.e. p15400 L10, p15401 L20, p15403 L20 (similar heating rate of 70°C min⁻¹) & L25, P15405 L6 (thermal stability of aliphatic and aromatic compounds). As noted below we have also included additional references in the discussion section.

To better interpret the FTIR-EGA in situ DRIFT data (4.2), more analogies could be made to previous findings. (e.g. P15386. & Table 2: In fact Py-FIMS has been applied on clay fractions

originating from two treatments of the Static Fertilization experiment at Bad Lauchstadt - Mertz et al., 2005 Organic Geochemistry).

We have now included this reference in the discussion to relate our findings. Indeed their findings in the analysis of the coarse and fine clay fractions found a general increase of thermal stability of compounds in the coarse clay after 98 years of fertilizer deprivation compared to the full fertilized treatment (Mertz, et al., 2005) which would complement our results of increased thermal stability of the bulk soil in the CON treatment relative to the FYM+NPK treatment.

Mertz, C., Kleber, M. and Jahn, R.: Soil organic matter stabilization pathways in clay sub-fractions from a time series of fertilizer deprivation, *Org. Geochem.*, 36, 1311-1322, 2005.

Py-FIMS analysis of soils has revealed general trends in organic compound class distribution. Phenols and lignin monomers increase in relative abundance with progressing decomposition stage, while the contributions of lignin dimers and alkyl aromatics decrease. Labile N-containing compounds and carbohydrates, representing products of microbial synthesis (Leinweber and Schulten, 1995), are enriched in clay size separates. This model should be referred to in the discussion.

In the revised manuscript, we have tried to refer to this overall model, but it is a difficult comparison as the molecular vibrations as measured by in situ_T DRIFTS can be associated with several different classes of organic compounds. Therefore at this point, we only make some generalizations as to what the compounds are referring to.

The DRIFT technique yields an overall, yet coarse picture on C-speciation – not a detailed recording of ion intensities of individual SOM components (lignin monomers, peptides, pentose- and hexose units, fatty acids, sterols, : : :). This is a limitation of the technique and should be recognized in the text. On the other hand this may be compensated for by a (low?) cost of analysis and a (high?) sample throughput. Could the authors make a comparison with Py-FIMS?

With the oxidizing environment that we use, it is not possible to make a direct comparison with Py-FIMS. Additionally with DRIFTS, the measurements are of fundamental molecular vibrations which generally are not unique to single SOM components, although they may be put into general classes (Demyan, et al., 2012)

P 15386 Thermal stability cannot be seen independently from the soil mineral phase. It is the intimate association of SOM with soil minerals which primarily affects thermal stability. Clay% and contents of Feox and Alox are of importance. This should also be made clear in the introduction.

We agree and have added in the introduction a sentence regarding issue. A sentence has been added after the sentence (p15384 L.3) “Thermal degradation of organic molecules is affected by the arrangement of the molecules in the larger macromolecule and likewise influenced by interactions with mineral surfaces (Blumstein, 1965).” Organo-mineral interactions such as

ligand exchange, cation ion bridging, and complexation are influenced by the clay, and Fe- and Al-oxide content and type of the soil. (von Lützow et al., 2006)

von Lützow, M., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B. & Flessa, H. Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions- a review. *European Journal of Soil Science*, **57**, 426-445, 2006.

P15391 L4 'Synthetic air was used as the purge and carrier gas of the system'. Just what is synthetic air? This is a crucial point which needs to be specified. Does this gas contain any oxygen – this would be a major drawback because in that case combustion of the OM cannot be excluded – unlike in pyrolysis, which occurs in the absence of oxygen. While it seems acceptable to postulate that bonding strength may relate to thermal energy required for cleavage in an atmosphere absent of oxygen, I don't know whether this assumption still holds in the case of combustion. It should be made very clear to the reader that this important difference exists with temperature resolved pyrolysis. I'm not familiar with EGA so I may be wrong, just like other readers could be. So please explain if this possibility of combustion is realistic or not.

Synthetic air is atmospheric air which has had water and hydrocarbons removed, and so contains strictly nitrogen and oxygen. Indeed, in evolved gas analysis one of the goals is the complete decomposition/combustion of organic compounds in the sample to measure the total amount of OC. As we are not only interested in the quantity of organic matter, but also the quality, this is why we have coupled the in situ_T DRIFTS analysis to the FTIR-EGA analysis. As is seen in the in situ_T DRIFTS results, there is not a single reaction pathway and we see that some vibration intensities increase during heating before finally decreasing indicating that we have not only thermal decomposition but also combustion, part of which seems to form intermediate products before final decomposition. This is a tradeoff when analyzing in the presence of oxygen. Likewise when analyzing in the absence of oxygen, combustion is absent, but then there is a certain proportion of the OM that is not pyrolyzed (e.g. in Leinweber and Schulten, 1995 where they found 50 to 70% of the C was accounted for during Py-FIMS under nitrogen atmosphere) precludes characterization of the total SOM. We have now clarified these aspects and pointed to the difference between pyrolysis under inert atmosphere and combustion under an oxidizing atmosphere.

Leinweber, P. and Schulten, H. -: Composition, stability and turnover of soil organic matter: investigations by off-line pyrolysis and direct pyrolysis-mass spectrometry, *J. Anal. Appl. Pyrolysis*, **32**, 91-110, 1995.

P15400 L3-5 This seems a bold statement to start the discussion with. At this point it has not been demonstrated yet that the technique is sensitive to changes in the quality and composition of organic matter.

This statement has been moved to the end of the discussion.

P15401 L25 Lignin is always thermostable in case of Py-FIMS (around 550_C) – bound or unbound to minerals – occluded in aggregates or free. Thermal stability of bulk SOM therefore can strongly depend on its proportion of lignin, which is strongly depending on the nature of OM inputs (lignin-rich woody materials vs green above ground plant materials). Thermal stability of a bulk soil rich in lignin therefore tells little about the bonding strength of SOM constituents or on their proneness to microbial decomposition.

We agree that results of pure organic compounds do not directly relate to the bonding strength of other SOM constituents other than that of POM which has little interaction with mineral components. Our results nevertheless indicate the potential of the approach to relate to the relationship between known chemical structure and their degradability.

The purpose of using pure substances (glucose, xylan, and tannic acid) was to show a.) the effect of dilution vs non-diluted samples on the outputs of the FTIR-EGA analysis; and b.) how thermal stability was related to the SOM fractions. We have taken the large changes in FTIR-EGA thermograms of the pure substances to be due to changes in decomposition during heating and not because of an interaction with the quartz sand. It is possible that the increased thermal conductivity of the sample could have changed the position of the peaks by a few degrees, but not by the large shifts that we found. So in the POM, where we have found relatively high thermal stability, we have hypothesized that there is a relative enrichment in lignin relative to other compounds as the mineral content of this fraction was very low. In the in situ_T DRIFTS results, we can see a slight trend in the sand and stable aggregates fraction (S+A) compared to the silt and clay fraction (Si+C) in that decreases of COO- /C=C and C=C functional groups decreased at a lower temperature in the S+A fraction compared to the Si+C. This could lend evidence to greater thermal protection within the Si+C fraction.

P15398 L 26 The decrease of C-H signals between 220 and 300_C may originate from the loss of 'free' fatty acids.

From the in situ_T DRIFTS there were two different periods of decreases in C-H signals that may indicate two different classes or sources of the C-H compounds, but it is difficult to speculate if they are from free fatty acids or not. It would seem since it is at a relatively low temperature they are relatively labile, but is difficult to assign to the fatty acid group.

P15402 Fig 7 & Table 4 I'm not in favor of attempting to deconvolute the DRIFTS peak into artificial components. Interpretation of these components may always remain speculative and I would myself choose to omit this exercise from the present paper. If the authors stay with their convoluted components, more than two soils should be included to make general statements of distinct SOM pools. At least, I would ask to make an analogy to the conceptual model by Schulten & Leinweber, 1999, Eur J SoilSci 50) These authors found that volatilization of mineral bound OM requires higher temperatures than unbound OM to enable thermal bond cleavage. They identified three thermal classes: i) unbound undecomposed plant fragments relatively rich in aliphatics; ii) a thermally labile fraction containing N-containing compounds and carbohydrates associated with humified OM and iii) thermally stable mineral bound OM.

As also emphasized by reviewer 2, we believe that the use of in situ_T DRIFTS is a major step forward in underlying deconvolution approaches as up to now most peak deconvolution exercises were strictly statistical based that had no theoretical or mechanistic foundation with other data to guide it'. We thus have included the peak fitting exercise in order to show that a molecular vibrational basis can be the template for guiding the peak fitting, instead strictly a mathematical basis. As was shown with the FTIR-EGA thermograms, the evolved CO₂ does not contain evident peaks (in the case of bulk soil) besides the main one, which shows that different compounds are being evolved at overlapping temperatures forming a continuum. Using the information from the in situ_T DRIFTS, we can see via decreasing of different molecular vibrations, that different classes of compounds (e.g. C-O, C-H, C=O, C=C) are being evolved at different temperatures, which then gives the justification for the peak temperature of a fitted component. It is not possible to say that one fitted component is 100% evolved from one source, but that there is evidence that part of it is evolved from a certain source.

In the revised manuscript we mention alternative approaches such as the conceptual model by Schulten & Leinweber (1999).

P15402 l20 I don't think the microbial biomass is large enough to explain differences in component 1. l24-28 Speculative, delete

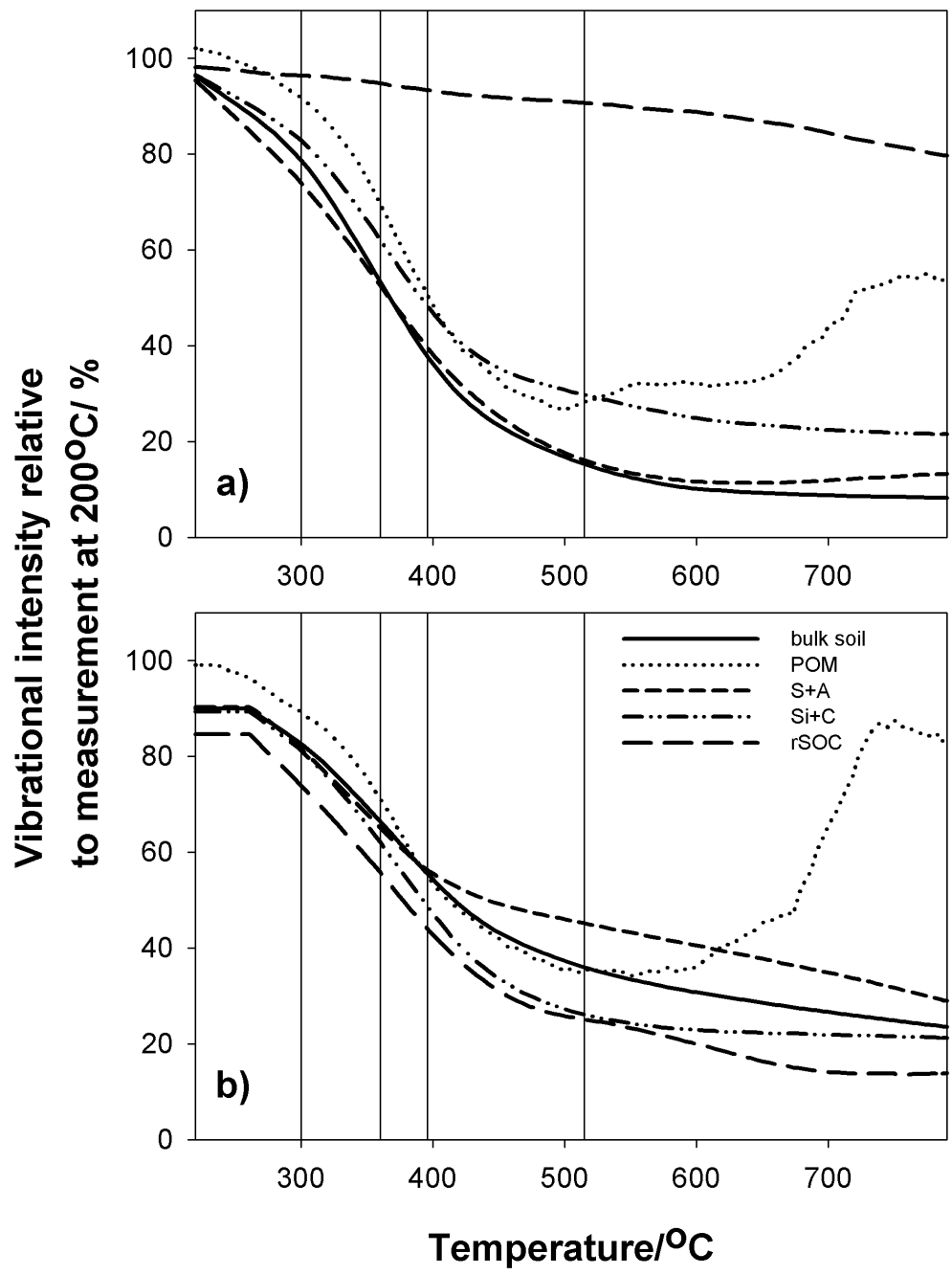
This has been changed to reflect the fact of different proportions of labile compounds available for decomposition and not directly related to microbial biomass.

4.4 This section is out of focus and I suggest to delete this entire part. Why should we at all be interested in the effect of hypochlorite on thermal stability? Other parts of the present study are far more important.

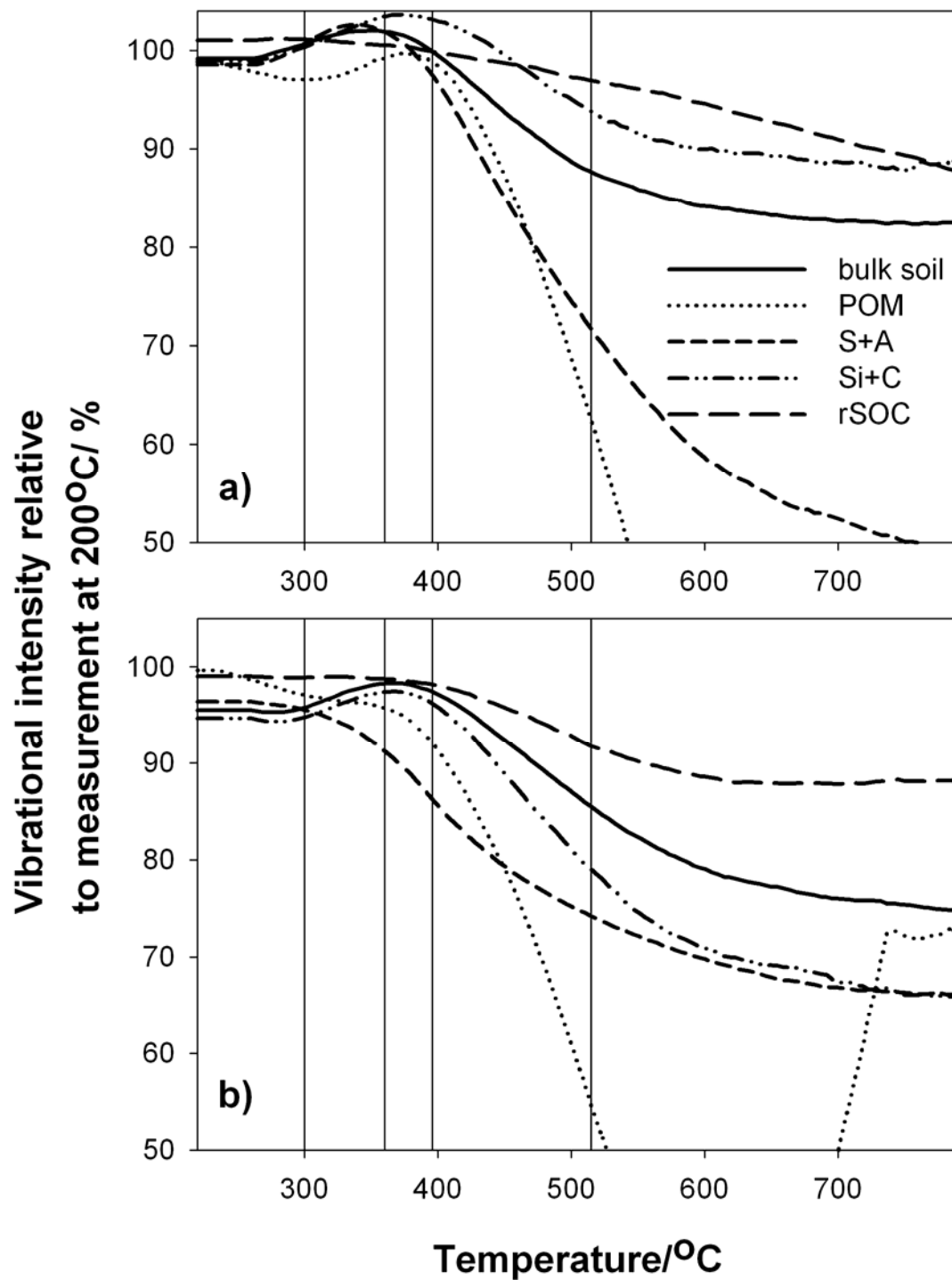
This section has been moved into section 4.1 as it is more relevant there. We would like to include this in the findings as it confirms what has been previously found that sodium hypochlorite has not only destroyed OM but has changed the nature of the remaining OM possibly by the saturation of Na on the exchange complex, which has rendered the remaining OM thermally labile, which shows a protection in association with clay particles in the non-oxidized silt and clay fraction.

The complete data received by coupled FTIR-EGA and DRIFTS on two soils needs to be further investigated. The paper would have really been stronger if more samples were analyzed by coupled FTIR-EGA and DRIFTS and it is not clear why so few samples were included.

We have included further figures (see new figures 9 and 10) of the bulk soils and fractions of two of the investigated vibrational groups during in situ_T DRIFTS analysis as examples of contrasting behavior during heating of the bulk soils and fractions.



New figure 9. 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 CO₂ results.



New figure 10. In situ_T DRIFTS of COO⁻/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 CO₂ results.

I would ask to expand the analysis made in 4.2. You need to attempt to better explain (Fig 7a) the temperature patterns in the DRIFT spectra. A statement like 'which lends evidence to different organic compounds being decomposed at different temperatures.' (lines 13-14) is insufficient.

Section 4.2 has been expanded to include an explanation of the results of the general trends of the bulk soils and fractions of the in situ_T DRIFTS results.

Three main trends were seen in the changing vibrational intensities over the heating experiment. First, at relatively low temperatures (200-300°C) a decrease in intensity was found for the C-O and C-H vibrations. This was evidence for the breakdown of aliphatic groups and also carbohydrates. Secondly, at a slightly higher temperatures the rapid decrease of C-H groups indicated the cracking of longer chained aliphatic with an almost simultaneously increase in both C=O/C=C and C=C intensities. This could have indicated the formation of neoproducts such as more condensed aromatic structures which has also been found during the heating of brown coal, although under an inert atmosphere (Murakami et al., 1997). Thirdly, the final decrease of both the C=O/C=C and C=C peaks at <400°C. The lower temperature decrease of the C=O/C=C peak relative to the C=C peak seems to indicate decarboxylation happening before the breakdown of the aromatic structures which was also found by Lu et al. (1997) via FTIR emission spectroscopy of humic substances. In the case of the increase in the "C-O" group at 2226 cm⁻¹, this may indicate the formation of nitriles as has been found in humic acid salts (Woelki and Salzer, 1995), as C≡N vibrations can also be present in this mid-infrared range.

Lu, X. Q., Vassallo, A. M. and Johnson, W. D.: Thermal stability of humic substances and their metal forms: An investigation using FTIR emission spectroscopy, *J. Anal. Appl. Pyrolysis*, 43, 103-114, 1997.

Murakami, K., Shirato, H. and Nishiyama, Y.: In situ infrared spectroscopic study of the effects of exchanged cations on thermal decomposition of a brown coal, *Fuel*, 76, 655-661, 1997.

Woelki, G. and Salzer, R.: Thermal investigations of the structure of two humic acid salts by in situ FTIR spectroscopy, *Fresenius J. Anal. Chem.*, 352, 529-531, 1995.

15383 L 9-14, very long sentence

This sentence has been split into two separate sentences.