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Interactive comment on "DRIFTS peaks as measured pool size proxy to reduce parameter uncertainty of soil organic matter models" *by* Moritz Laub et al.

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"Reservation on the rationale of the DRIFTS stability index of soil organic matter (SOM) in mineral soil, and its use for partitioning the C kinetic pools of SOM dynamics models"

This draft by Laub and colleagues describes a method to divide soil organic matter (SOM) into fast and slow cycling C pools in the soil organic module of the DAISY model. This method is based on the characterization of bulk mineral soil samples using mid-infrared diffuse reflectance spectroscopy (DRIFTS). DRIFTS spectra of bulk mineral soils are used to compute the "DRIFTS stability index" of SOM, defined as the ratio of aliphatic C-H (2930 cm-1) to aromatic C=C (1620 cm-1) stretching vibrations.

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Discussion paper

The DRIFTS stability index was previously published by Demyan et al. (2012) in the European Journal of Soil Science.

The development of routine and operational method to initialize the relative size of C kinetic pools from SOM dynamics models is a very important and timely topic. Indeed, the accuracy of the simulations of SOM evolution in mineral soils by current models is strongly questioned, notably because a poor initialization of the size of C kinetic pools.

The method proposed by Laub and colleagues, using the DRIFTS stability index to divide soil organic matter (SOM) into fast and slow cycling C pools in the soil organic module of the DAISY model is original and very interesting, and their draft is well structured and written.

However, I have a major concern regarding the rationale of the DRIFTS stability index of SOM in mineral soil, and its use for partitioning the C kinetic pools of SOM dynamics models. In this review, I will only discuss this concern, though this stimulating and timely work would deserve many other comments, as highlighted by the two other reviewers of this draft.

First, I would like to come back on the justification of the DRIFTS stability index by Demyan and colleagues in their 2012 paper. Demyan et al. (2012) searched for information related to SOM in DRIFTS spectra of bulk mineral soils, and its link to SOM stability as assessed by a SOM density fractionation scheme. In their search for SOM information in DRIFTS spectra of bulk mineral soils, they discarded "wavenumbers of functional groups associated with non-organic compounds such as silicates and alumino-iron oxides". For them, "these criteria removed the peaks <1000 cm−1 and the peaks at 1980, 1870, 1792 and 1390 cm−1", but not the 1620 cm−1 peak. For them, "the [DRIFTS] peak at 1620 cm−1 was assigned to predominately aromatic C = C stretching and/or asymmetric–COO− stretching but possibly also C = O vibrations".

Demyan et al. (2012) show that "a positive relationship was found between the ratio of the peaks at 1620 and 2930 cm−1 (1620:2930) and the ratio of stable C (sum of

C contained in clay and >1.8 g cm−3 fractions) to labile C (amount of C in the <1.8 g cm−3 fraction) (R^2 = 0.62, P = 0.012).” For the authors, this result justifies that the DRIFTS stability index can reliably be “taken as an indicator of SOM stability” (Demyan et al., 2012).

However, a short look at the literature on DRIFTS of soils show that the 1620 cm-1 peak in bulk mineral soils cannot be exclusively assigned to absorption from SOM functional groups (C = C or C = O) as claimed by Demyan et al. 2012. I will only cite two important papers: Nguyen et al. (1991) and Reeves (2012).

Nguyen and colleagues, based on DRIFTS spectra of pure mineral compounds and various soil samples demonstrated that “The DRIFT spectra of soils containing organic matter show considerable overlap of the silicate combination bands in the 2000-1600 cm-1 region”. I provide here the Figure 1 modified from Nguyen et al. (1991) showing the DRIFTS spectra of quartz (pure or diluted in KBr), highlighting the strong absorption of quartz at 1620 cm-1 (for the DRIFT spectra of pure quartz). They suggested that “Spectral subtraction techniques or prior chemical treatment may thus be required to resolve these peaks.” (Nguyen et al., 1991). Reeves (2012) based on works similar than Nguyen et al. (1991), concluded that “With the exception of the bands at 2930 and 2850 cm−1 due to aliphatic CH [when the soil does not contain carbonates, added by me] and the large OH band spanning most of the region between 2700 and 3500 cm−1, there is little that is obviously due to OM in the soil spectra”. Regarding the 1620 cm-1 DRIFTS peak, he suggested, following Nguyen et al. (1991) that “the region between 1750–1600 cm−1 can be interpreted, despite the presence of strong silica bands, because silica can be ash subtracted quite well”. But he also concluded his paper with this warning regarding spectral subtraction: “It will detect not only whether your sample is changed by 0.1% at some point in time, but will also seem to detect the phases of the moon and the mood you were in while you were measuring the data.” (Hirschfeld, 1984; cited by Reeves, 2012).

I deduce from this short literature survey that in their 2012 paper, Demyan et al. incorrectly assigned to SOM compounds (C = C, C = O) exclusively the 1620 cm-1 DRIFTS peak of bulk mineral soils, as this peak is also due to mineral compounds such as quartz (but also to water in some phyllosilicates).

To further illustrate how the 1620 cm-1 DRIFTS peak of bulk mineral soil is poorly related to SOM compounds, I provide the Figure 2 based on published and unpublished data from the paper of Barré et al. (2016) in Biogeochemistry showing the non-parametric Spearman's Rho coefficient of DRIFTS spectra from soils coming from the Ultuna Fame trial, one site that was used in this reviewed work by Laub and colleagues, with SOC concentration. In Figure 2, we clearly see the strong and positive Rho coefficient of the 2900 cm-1 spectral region with SOC concentration while the 1620 cm-1 spectral region show a Rho coefficient with SOC concentration close to 0, suggesting (though not demonstrating) that other compounds that organic matter absorb energy in the 1620 cm-1 spectral region of DRIFTS spectra, when scanning bulk mineral soils.

From the above-mentioned information, I therefore question the rationale of the DRIFTS stability index of soil organic matter (SOM) in mineral soil samples.

My interpretation is that this index is dividing a quantity that is highly correlated to SOC concentration (the 2900 cm-1 spectral region), by a quantity that is weakly changing when SOC concentration is modified (the 1620 cm-1 spectral region, provided a similar mineral composition). The DRIFTS stability index may thus show an increased SOC lability when SOC concentration is increased. I thus hypothesize that the DRIFTS stability index, as proposed by Demyan et al. (2012) and Laub and colleagues in this reviewed draft, may provide some information that is basically the same (though with added noise) than a variable much simpler than their index: total SOC concentration. It is well documented that an increase in SOC concentration is associated with an increased in the labile/stable SOC ratio, and all proposed indicators of SOM stability should be compared to SOC concentration, the most simple and straightforward indicator of SOM stability (though not very accurate). What is the Spearman's Rho coefficient of the DRIFTS stability index with SOC concentration in the dataset of Laub

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and colleagues?

I suggest that the authors (rather than using the spectral subtraction technique suggested by Nguyen et al., 1991 or Reeves, 2012), (i) test a soil dilution in KBr to reduce mineral artifacts in the 1620 cm-1 spectral region of neat DRIFTS, (ii) or test attenuated total reflectance mid-infrared spectroscopy (MIR-ATR) as an alternative technique. Inded, MIR-ATR is a technique where the 1620 cm-1 peak region seems to be much less affected by quartz and other minerals that neat DRIFT signal, as illustrated in Figure 3 (Cécillon, Unpublished data).

Finally, as Laub and colleagues benefit from soil samples from two long-term bare fallow sites in Europe, I suggest that they compute the Spearman's Rho coefficient of their DRIFTS stability index with the proportion of centennially persistent soil organic carbon (CPsoc), that may be derived from the SOC evolution in the bare fallow plots, as shown by Cécillon et al. (2018). A higher Spearman's rho coefficient of the DRIFTS stability index with CPsoc than the Spearman's rho coefficient of SOC concentration with CPsoc, would suggest an added value of the index compared to SOC concentration, in its current state.

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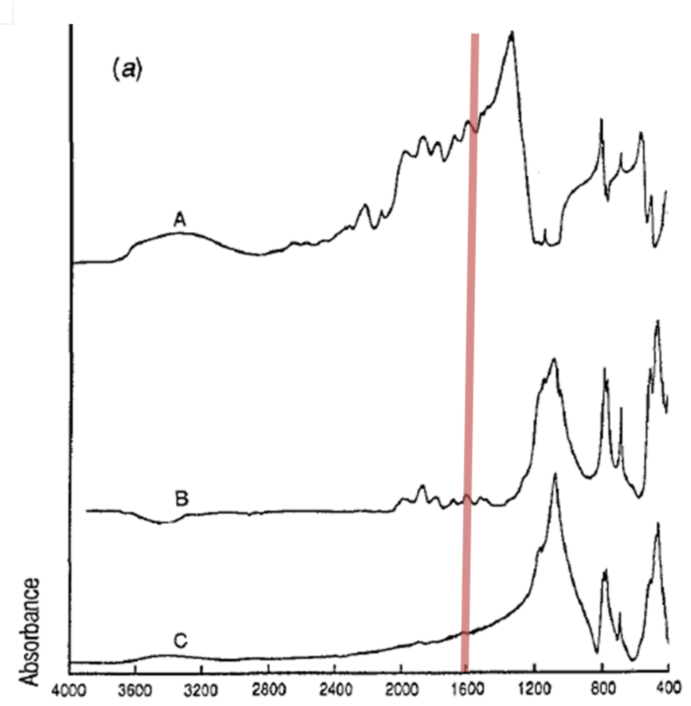

Infrared spectra of powdered quartz

A: neat DRIFT; B: 3% in KBr DRIFT; C: 0.3% in KBr disc
(Figure modified from Nguyen et al., 1991)

Fig. 1.

Spearman's Rho of DRIFTS spectra with SOC concentration at Ultuna Frame trial (n=34)

Information on soil samples & DRIFTS data acquisition and treatment is described in Barré et al., 2016.

Fig. 2.

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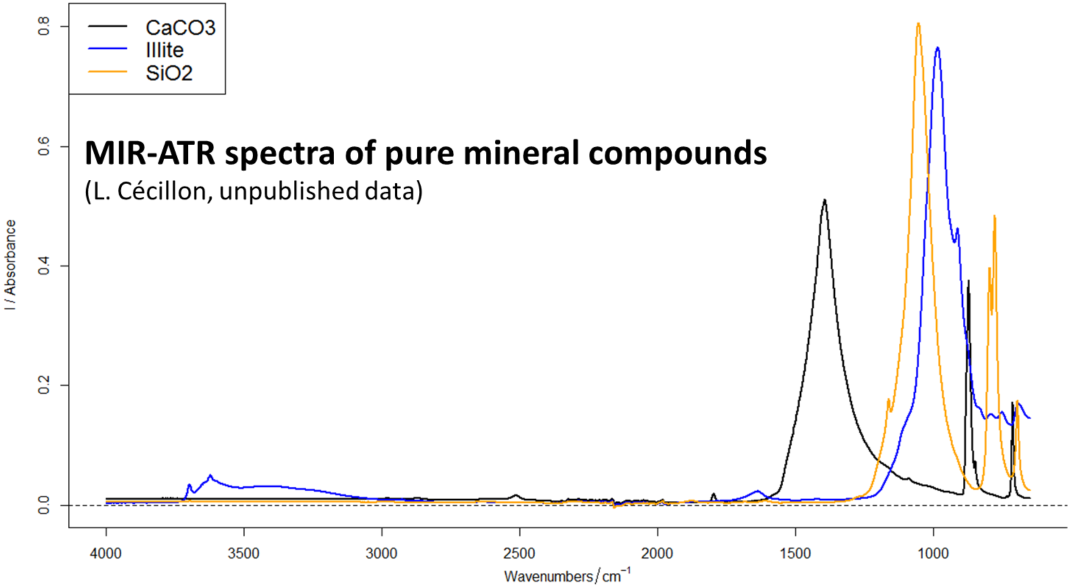
CaCO3
Illite
SiO2
MIR-ATR spectra of pure mineral compounds
(L. Cécillon, unpublished data)
I / Absorbance
0.0
0.2
0.4
0.6
0.8
4000
3500
3000
2500
2000
1500
1000
Wavenumbers / cm^{-1}

Fig. 3.