

Dear Michael Weintraub,

We are pleased to upload our revised manuscript in response to the comments of the three reviewers. We have made a number of changes in the manuscript in order to address the concerns of the reviewers, which we found very constructive, objective and of high quality. In our initial response letters, we have included detailed answers to each concern including what we changed in the manuscript as a result. Therefore, we will summarize here the most important changes from our point of view.

As we understood it, the main concerns of Sander Bruun were, 1.1) whether the DRIFTS stability index (DSI) changes with type of mid-infrared spectrometer bench used (in our experience it slightly does), 1.2) why we used a statistical analysis of model error (mainly to interpret a temporal trend), 1.3) whether this Bayesian model calibration could be data limited (we rather think that it is due to model structure) and 1.4) if we could include graphs of the DSI change over time of the long-term experiments (we did so). To all these points we made changes in the text and added additional figures where necessary to further elaborate our point.

Additionally to some concerns shared with Sander Bruun, the main concerns of reviewer 2 were, 2.1) whether the DSI was a proxy supporting the hypothesis of resistance due to molecular properties of SOC only (to our understanding the DSI is also related to other forms of stabilization), and 2.2) whether the DSI might be also useful for models using microbial mineral models (to our understanding yes, as it correlates also well with size density fractionation) and 2.3) that we change the wording of some claims in the abstract, so that they are not misleading. To each of these concerns we made changes in the text to address them. The suggested spell and language checking was done.

As we understood it, the main concerns of Lauric Cécillon were: 3.1) whether the mineral interference of the 1620 cm^{-1} peak would mean that we only divide the 2930 cm^{-1} peak by some "artifact". By carefully selecting integration limits, hence the part of the 1620 cm^{-1} peak we use relates mostly to carbon. 3.2) Whether the DSI was more informative than the SOC content alone (the strong correlation to % of centennially persistent SOC across sites seems to indicate so) and 3.3) that we should discuss the shortcomings and the "known unknowns" of the DSI, due to mineral interference and other factors in more detail. We followed the advice by adding an additional figure (Figure S1 in updated manuscript – correlations with CPsoc), as well as adding a thorough discussion of the mineral, water and spectrometer interference that the DSI is subject to. We agree with you, that these concerns are likely shared by other readers and found the discussion with Lauric to be especially fruitful.

We thank you for handling the manuscript and are happy that it is considered to be of interest to the readers of Biogeosciences.

With kind regards on behalf of all coauthors,

Moritz Laub

Responses to Reviewers:

We would like to thank the editor for taking the time to handle our manuscript and for finding three very constructive reviewers. We also want to thank all reviewers for taking the time and reviewing our manuscript to help improve its quality. We are grateful for the honest and thorough feedback. The suggestions were highly useful and provided us with information, where misunderstandings could be possible and where we needed to make our message clearer and to discuss the limitations of the DSI in more detail. They helped to further improve the quality of this manuscript and we hope that we addressed concerns to a satisfying extent. Our comments to the reviewers in the following are in [blue color](#). We made use of the constructive criticism and altered the text of the manuscript, where applicable. We added screenshots of alterations in the text related to the comments. These are displayed in [green color](#).

1.1 Reviewer 1: Sander Bruun

General comments

The paper deals with initialization of pools in the soil organic matter model of Daisy. The paper is using unique datasets for long-term fallow treatments to test a new way of initializing the soil organic matter pools based on specific peaks in the DRIFTS spectra of the soils. Pool initialization of SOM model is an important issue that is still causing some difficulties with the currently used approaches. The paper is therefore very timely and presents an interesting approach that could be useful in many situations. The work is of a high quality and based on high quality data and the manuscript is well written.

Specific comments

Line 78. I agree that the DSI can be better than the steady-state assumption, but perhaps it is worth discussing this in a little more detail. If information about the history of the site is available then that method should work. This requires that the history is known for millennia, and that is rarely the case.

[We added one more sentence as suggested, at line 56.](#)

Line 118: Was soil samples from throughout the experimental period analyzed? Please specify.

[Yes, from throughout the period. We specified this more.](#)

Line 129: The spectra were not recorded in absorbance, but subsequently converted to absorbance units, right?

[Yes – wording changed](#)

Line 130: I wonder how much this way of determining the DSI is affected by the instrument i.e. if somebody took the same soils and did the measurement on another instrument would they get the same DSI and pool sizes. I am afraid that it would be quite much affected by that especially if you use other IR detection techniques. Maybe it would be worth addressing this in the discussion.

[Indeed, at least to our experience, there are some differences between the spectra of different spectrometers. We added a sentence addressing this in chapter 4.1. As we already tested different temperatures for drying, which we found to be the most dominant factor affecting DSI, it was beyond the scope of this publication to test the effect of the Spectrometer. We were first and foremost interested in, whether the DSI approach adds value in general to SOM initialization, which we think it does.](#)

Line 181: It says 84% and not 83% in Table 2. Please correct where appropriate.

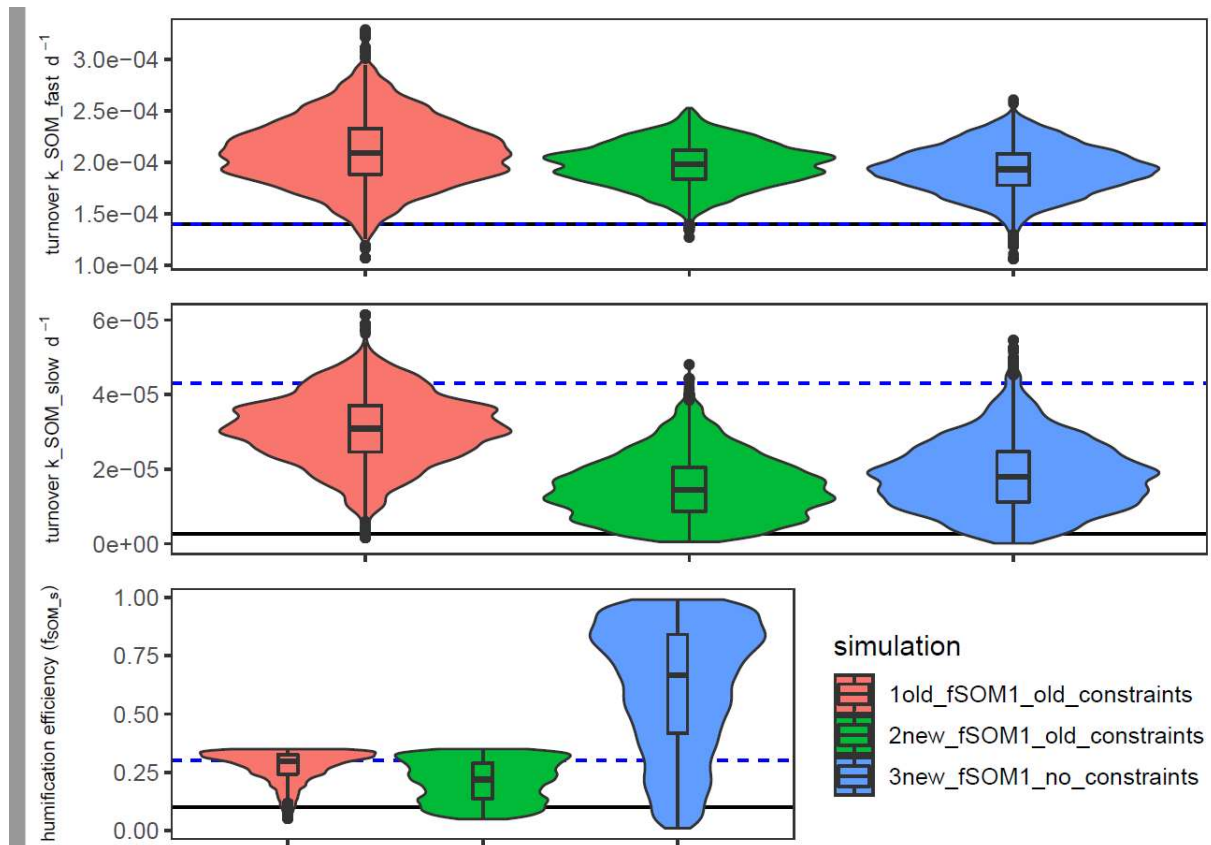
Done

Line 196 to 209: I am not entirely sure I understand what the point of analyzing the SMEx with a statistical model is. I think you should consider whether it add enough understanding to warrant inclusion. Alternatively explain the point a little better.

We wanted a more sophisticated analysis of the model error than and since in some experiments (Swabian Jura and Kraichgau) we had several fields, make use of the statistical power provided by the experimental design. The second advantage of a statistical analysis of model error was, that we could analyze for a time trend (increase with time) of the model error. Obviously, the results still only hold for the fields we analyzed.

Line 236-237. The necessity of constraints on the fSOM-Slow parameter is a little problematic. I cannot help thinking that it means that the data, which is used for calibration, is insufficient. With these restraints, I guess you are likely to end up with a value of 0.35 which is rather arbitrarily chosen by you.

We fully agree with this statement. Actually, we also found containing a bit problematic, but a humification of 95% or more also did also not seem realistic. For us, this is an indicator how model structure affect the results. This is why we came up with a possible alternative formulation of DAISY. Actually, we tested the new structure of DAISY and found, that with this fSOM_s does not run into the constraint anymore, even if we do not constrain it. See as an example the results of the new structure with (2) and without (3) the fSOM_s constraints compared to (1) the initial BC of this study:



Line 364-365. I agree that even though we have had the same management for a longtime the steady-state assumption is not valid. However, I believe that the reason for this has to do with

longer-term effects rather than the smaller effects that you mention i.e. variation in climate agricultural management. If you look at a longer terms, most sites would probably have been deforested within the last 2000 years. Because of the high inputs from the forest, this could have resulted in an unusually large fraction of resistant organic matter that has not been degraded from that period. Also it is very common with drained soils soil. This means that the soil at some time it its history has had a very high water table and perhaps even been inundated. We know that this can result in significant accumulation of organic matter. After the soil has been drained, this has led to a large residual of resistant C again. The same could happen if there has been a history of fires with inputs of charcoal. Perhaps this is worth discussing a bit more.

We agree and added these possibilities to the main text.

Line 373: I cannot help it thinking that it is somewhat of a coincidence that you get better model performance with the DSI as long as you have not recalibrated the model. Of course using more data as for example DSI to restrain the model should improve the model, but only after it has been recalibrated.

We interpreted the fact that SMB-C simulations were best when using the DSI as indicator that it is a proxy of generally utility, even if the turnover rates are unclear. As SMB-C is a much faster reacting pool than TOC, which did not change that much in our trials in Kraichgau and Swabian Jura. The DSI at 105°C was consistently lower in model error for simulated SMB-C than the steady state initialization, which we saw as an indicator that it is a useful proxy regardless of turnover rate, as long as there is a clear distinction between fast and slow pools.

It is not entirely clear what data were used for the calibrations based on DSI. As far as I understand, you measured DSI of all the soil samples and that means that you can compare the simulated distribution between fast_SOM1 and slow_SOM with the one measured and calculated using formula (2) and a similar formula for fast_SOM. Is this the case? And if it is why have you not shown the “measured” value of fast and slow SOM and compared it with the modelled?

You are correct, that we used the measured DSI throughout the simulation period for the Bayesian calibration. We are happy to provide the modelled vs measured DSI throughout the simulation period – we also added it to the manuscript as additional figure s7:

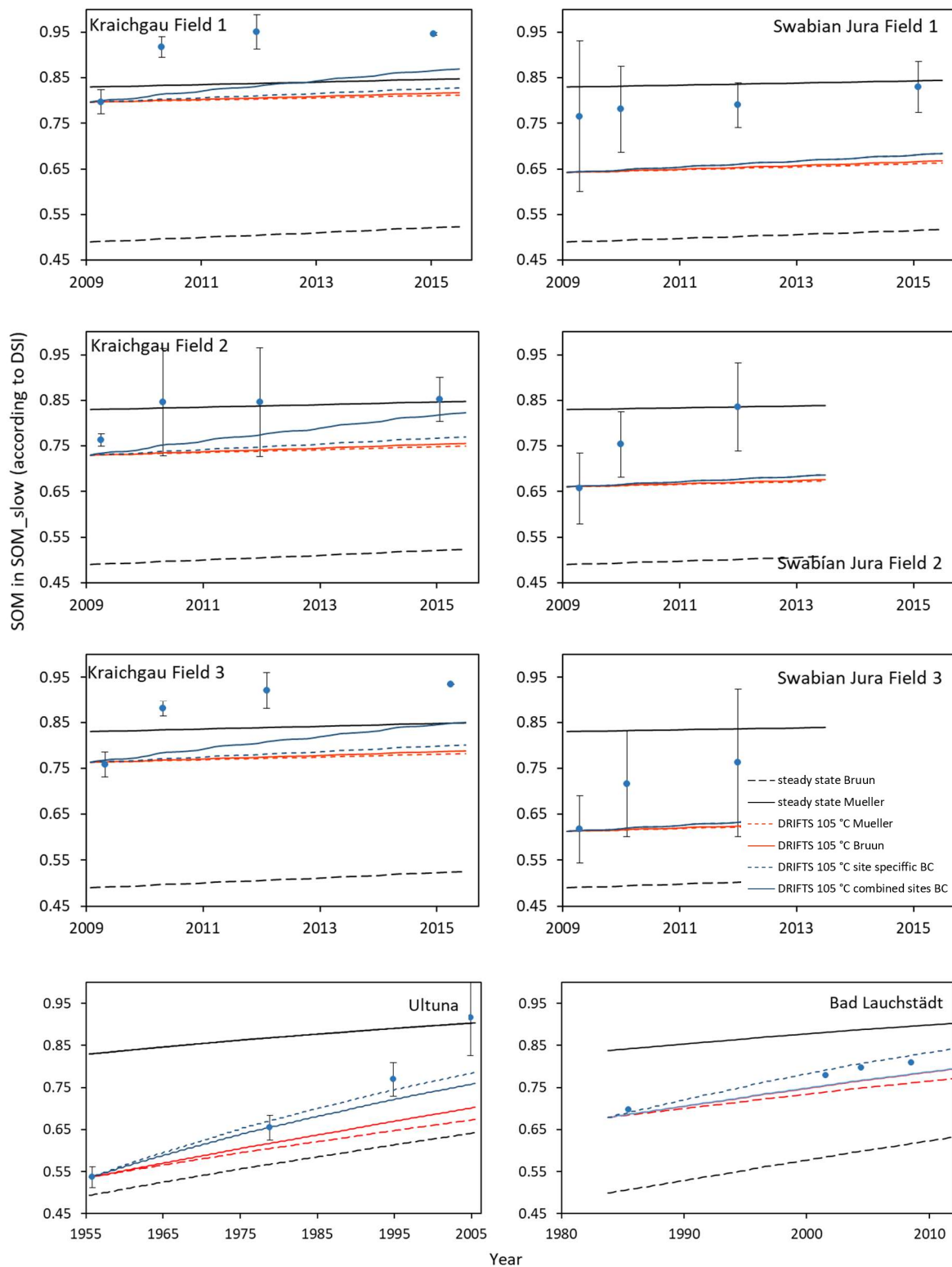


Figure S 1 Development of simulated vs observed SOM in the slow pool, according to DSI division throughout the simulation period (for brevity only for 105 °C). Bars indicate standard deviation of all plots per field.

Is it worth publishing the optimal parameters selected by the Bayesian calibration based on DSI?

While we think that the ideal way to use our results is using the posterior probability distributions of our parameters, we have mentioned the parameter set of the maximum likelihood from our

Bayesian calibration in chapter 3.3 (0.34 , $2.29 * 10^{-4}$, $3.25 * 10^{-5}$ for the original weight calibration and 0.06 , $9.58 * 10^{-5}$ and $5.54 * 10^{-5}$ for the calibration using original weights and no DSI).

1.2 Reviewer 2:

General comments

Laub and Colleagues present interesting ideas how DRIFTS spectra could be used to initialize and calibrate soil organic matter models. What warrants more discussion is that with their results we should put again more emphasis on the chemical recalcitrance hypothesis, i.e. that molecular properties determine the persistence of organic matter in soils. The literature seems to disagree (Schmidt et al., 2011). If we indeed assign the aromatic peak to slow cycling pools with a turnover time of 426 years and the aliphatic peak to a fast cycling pool with 47 to 90 years, the authors would contradict the synthesis of Schmidt et al. (2011) (their Figure 1, for example).

We do not think, that it contradicts Schmidt et al. (2011). Rather the DSI seems to point towards the same direction as other measures of SOM quality, such as the amount of SOM in different aggregate sizes and fractions. This was actually shown in our previous works (Demyan et al., 2012). We have to keep in mind that the DSI is still only a proxy and dividing the whole continuum of SOM quality into two “qualities” is a strong simplification of the real world. However, we think it seems to be a valid one, especially when two pools SOM models are to be used, which anyway divide SOM into two pools.

In my opinion, it would be interesting if the authors could at least discuss how their DRIFTS peaks could be useful for the new class of microbial-mineral models such as Tang and Riley (2015) or Sulman et al., (2014)

We think that DRIFTS could also be useful for those models, because of a good correlation of the DSI to size density fractionation (Demyan et al., 2012), which is thought more representative of structural protection mechanisms. We added one sentence about this in the discussion. As Tang and Riley (2015) stated, it is not likely that CUE and Q10 are static (or the same for different complexities of SOM), which to our opinion points to the need of reliable pool partitioning proxies. As we already addressed this issue in the manuscript (line 528ff), we did not add anything new.

Specific comments

The authors state that “the DRIFTS initialization of SOM pools significantly reduced model errors of poor performing model runs assuming steady state, irrespective of the turnover rates used, but the faster turnover parameter set fit better to all sites except Bad Lauchstädt. This suggests that soils under long-term agricultural use were not necessarily at steady state.” In my opinion this statement is not backed up by their results. The Bruun parameters with steady state assumption perform better at Ultuna and Kraichgau + Swabian Jura (Table 4) for SOC stocks.

We agree that it was a bit oversimplified, so we altered the wording. For this statement we placed more weight on the Kraichgau + Swabian Jura sites than Ultuna, because those consisted of six fields. What we saw there was a significant improvement of the sensitive SMB-C, for both turnover rates, while for SOC stocks, there were only significant differences in model error between turnover rates but not between initializations.

The authors also state that “[...] two approaches [...] significantly reduced parameter uncertainty and equifinality”. One of the approaches was the inclusion of DRIFTS. But looking at the violin plots in Figure 5, only the humification efficiency seems to be better constrained. I suggest modifying the statement towards this direction.

It is true, that humification efficiency was the parameter most seriously constrained by the DSI, also the turnover of the slow carbon pool was stronger constrained (standard deviation of $9.3 * 10^{-6}$ with DSI vs $12.3 * 10^{-6}$ without DSI). We altered the wording in the sentence, to be more accurate.

I agree with the other reviewer, Sander Bruun, that analyzing the squared model errors with a statistical model should at least be better explained.

This was done, see the comment to Sander Bruun, above.

The manuscript would benefit from a thorough spell and language check.

This will be done on the final reviewed version manuscript.

Comments of Reviewer 3: Lauric Cécillon

"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.

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 $<1000 \text{ cm}^{-1}$ 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 $>1.8 \text{ g cm}^{-3}$ fractions) to labile C (amount of C in the $<1.8 \text{ g cm}^{-3}$ 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).

We originally stated (line 369ff) that the peaks were selected in order to have limited mineral interference (e.g. Demyan et al., 2012). In their original publication only soils from the same field experiment with the same texture and mineral background were taken as additional measure of caution. As this approach showed potential for the site at Bad Lauchstädt, we hypothesized that this could justify evaluating the use of the DRIFTS 1620:2930 ratio as a more general stability index. We are aware of the mineral signal in the vicinity of the 1620 cm^{-1} peak and this fact was also acknowledged in the original publication of Demyan et al. (2012). By carefully selecting the integration limits, it was possible to minimize the mineral interference and get a general applicable stability index (see evidence below). In the current study, we aimed to combine several sites with differing textures and mineralogies to have several test cases. The reason for the statistical analysis of the model error was exactly that we wanted to test whether the DSI is a useful proxy across a range of sites. We state some further reasoning below why we think the

1620 cm⁻¹ peak and the specific peak limits that we have used (1660 – 1580 cm⁻¹) is representative of aromatic carbon and what was changed in the main text.

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).

It is not correct that we claimed an “exclusive” assignment of the 1620 cm⁻¹ peak to SOM functional groups, but rather that by carefully selected integration limits, the delimited area of the 1620 cm⁻¹ is mostly representative of those organic groups.

In fact, the different spectra of soils before and after ashing or pyrolysis (as the example below taken from the supplementary material of Nkwain et al. (2018)) demonstrate that a considerable part of the delimited 1620 cm⁻¹ peak is lost. Demyan et al. (2013) found a decrease in absorbance intensity at 1620 cm⁻¹ with maximum losses occurring between 400-500°C (Figure S8, Left) for bulk soils. In the same study separated fractions were also analyzed, with a similar 1620 cm⁻¹ peak loss found for particulate organic matter (POM) that was assumed to be mineral free. These consistent findings of the organic contribution to the 1620 cm⁻¹ peak from both rapid pyrolysis and in situ thermal monitoring of soil samples up to 700 °C were also found when pretreating bulk soil or fractions with NaOCl (Yeasmin et al., 2017).

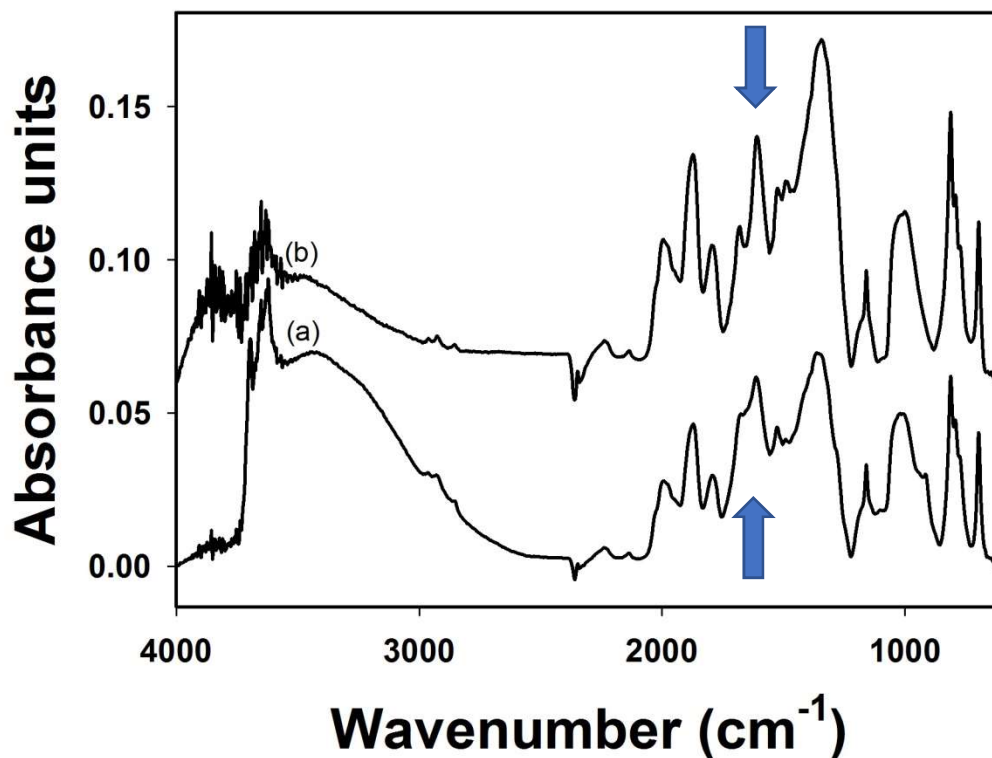


Figure S7. DRIFTS spectra of (a) unpyrolyzed soil and (b) pyrolyzed soil from Bad Lauchstädt (FYM). From (Nkwain et al., 2018)

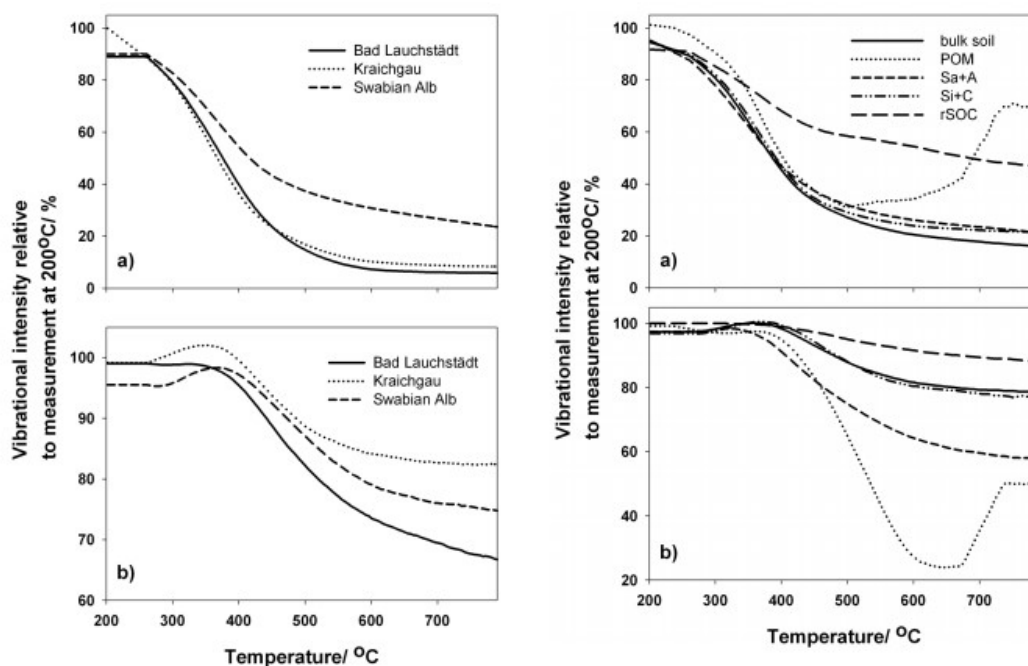
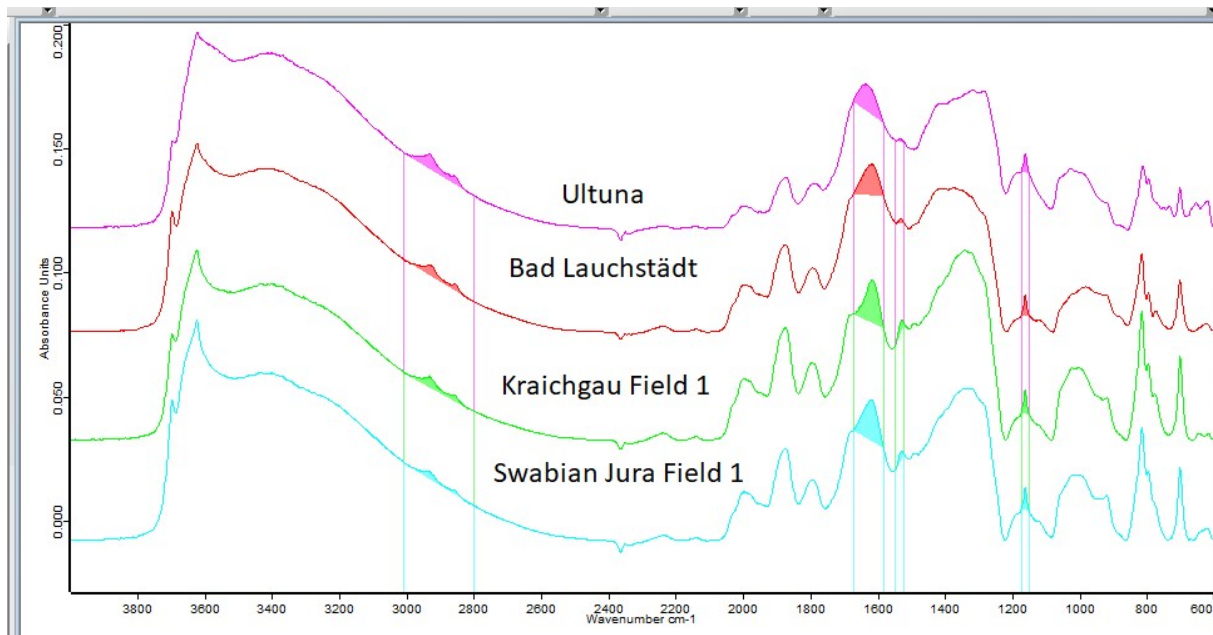


Figure S8 Left: (a) Change of C-H (2930 cm^{-1}) and (b) C = O/C = C (1620 cm^{-1}) vibrations with heating as measured by in situ DRIFTS of bulk soil samples from Bad Lauchstädt, Kraichgau, and Swabian Alb. Right: (a) Change of C-H (2930 cm^{-1}) and (b) C = O/C = C (1620 cm^{-1}) vibrations measured in bulk soil and fractions of soils from Kraichgau and Swabian Alb (Demyan et al., 2013). *POM-particulate organic matter, Sa+A-sand and stable aggregates, Si+C-silt and clay, rSOC-resistant soil organic carbon.

We would like to draw the attention to the fact that by a careful selection of the integration limits, we only take the top of the larger 1620 cm^{-1} peak (which in our samples made up 15 to 33% of the whole peak area). As the three examples above demonstrate, this is mostly the part,

which is removed by burning, pyrolyzing or NaOCl treatment. This is the same principle as used for the aliphatic peak area at 2930 cm^{-1} , which is on top of a larger OH peak and to our knowledge, there is little debate about using this approach for the 2930 cm^{-1} . See the picture below for typical peak areas from our samples.



While we certainly do not claim that we can completely eliminate mineral interference, we think that the specifically delimited 1620 cm^{-1} peak that we use mostly consists of aromatic carbon i.e. the part of the peak that is selected is the part that disappears with the mentioned methods of SOC destruction. The finding, that it really is a meaningful proxy for carbon quality or stability is corroborated by the strong correlation (0.84) between the DSI and the percent of CPSoc, as was suggested to be computed by Lauric (new Figure S1 and comment below). As we recently demonstrated (Laub et al., 2019), and further found in the current study, the 2930 cm^{-1} peak is also subject to interference even in non-carbonate containing soils. This is mostly by water, which can partly be removed by higher drying temperatures. So, in summary we believe that there is sufficient evidence that, even though there is noise in the DSI at both peaks, DSI is still a meaningful and useful proxy, which is highly correlated to other measures of SOC composition but has the advantage of being cost/time effective to measure.

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.

The result is strongly affected by the delineation of the peak area. We thus agree if the whole 1620 cm^{-1} peak area (ca. $1755\text{--}1555\text{ cm}^{-1}$) is taken results may not be reliable.

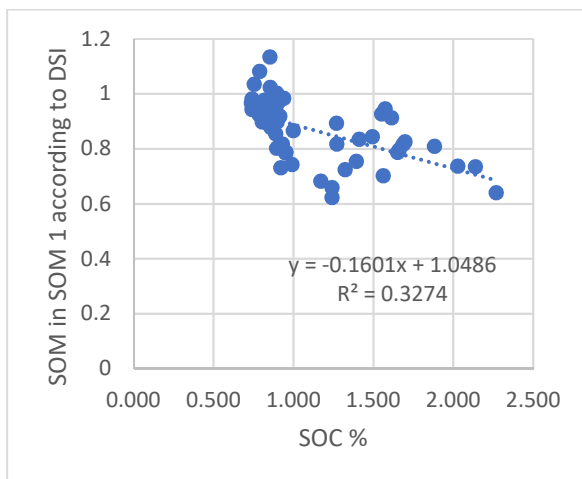
My interpretation is that this index is dividing a quantity that is highly correlated to SOC concentration (the 2900 cm⁻¹ spectral region), by a quantity that is weakly changing when SOC concentration is modified (the 1620 cm⁻¹ spectral region, provided a similar mineral composition). The DRIFTS stability 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.

We agree with the interpretation that the DSI is “dividing a quantity that is highly correlated to SOC concentration by a quantity that is weakly changing when SOC concentration is modified”, and as we demonstrate above, both quantities are linked to forms of SOC. The fact that the selected subregion of the 1620 cm⁻¹ peak does not change strongly with SOC content, while, as destructive techniques demonstrate, it is still consisting mostly of aromatic carbon compounds (according to our integration limits), is exactly the reason why it is a very suitable proxy for slow turnover SOC.

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 and colleagues?

We calculated the Pearson’s correlation coefficient -0.57 and Spearman’s rank correlation coefficient to be -0.68 between OC content and the DSI (as in formula 2) for the whole dataset (n=50). See the plot below



We think, that the nonlinearity of the relationship between the DSI and the SOC content, as indicated by a higher rank correlation coefficient, points towards the possibility, that as SOC increases, most of the carbon is added to the fast turnover pool and that this could potentially be lost rather fast again.

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.

Dilution with KBr (1:3 and 1:100) had been tested by Demyan et al. (2012), mainly to determine whether there was specular reflectance in the 1159 cm^{-1} region, but was not found to yield better performances for deriving the DSI. Using neat samples avoids hygroscopic KBr which would have the potential to absorb water interfering with the 2930 cm^{-1} and 1620 cm^{-1} peaks and other non-desired interactions with the sample. We think that the major advantage of the DSI and DRIFTS PLSR is that it is possible to use undiluted bulk soil samples, and that it is nondestructive (cost effective and other analysis can be done with the same samples). We see the major advantage also in large scale applications, such as regional simulations, where other techniques are either too expensive or time consuming.

Indeed, MIR-ATR is a technique where the 1620 cm^{-1} peak region seems to be much less affected by quartz and other minerals than neat DRIFT signal, as illustrated in Figure 3 (Cécillon, Unpublished data).

From our understanding, the issue with ATR usually is that the signal throughput to the detector is weaker, thus the overall spectral features stand out less and are dominated by the silica vibrations at $<1500 \text{ cm}^{-1}$, which is also shown in Figure 3 of Lauric Cécillon's comment. The maximum absorbance in the DSI wavenumbers is almost an order of magnitude lower as compared to DRIFTS. If you zoom in on the figure, you can also see a small peak probably around 1620 cm^{-1} in the silica sample, so it seems not to be free of mineral interference.

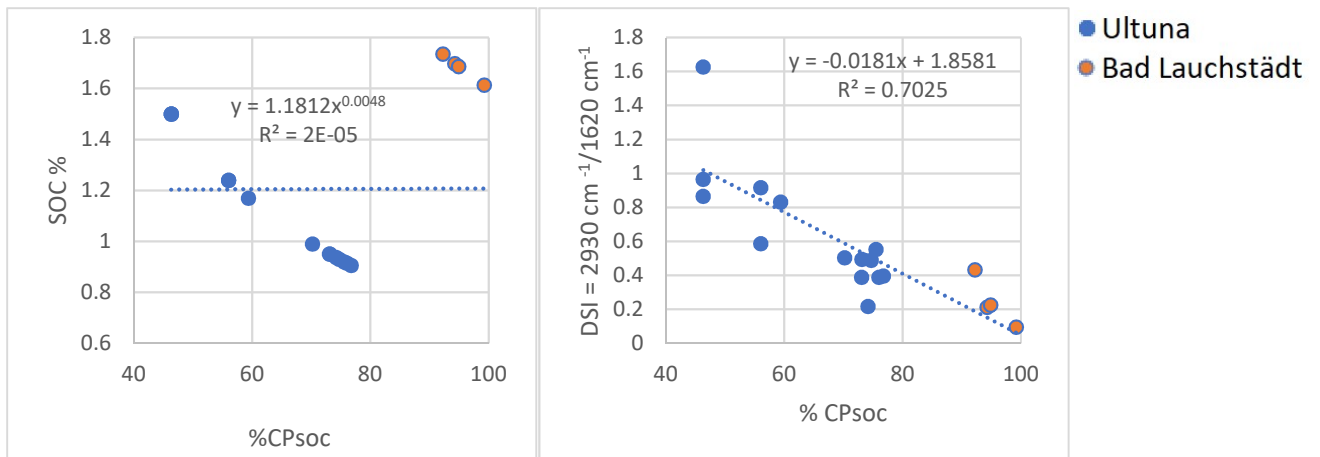
It might be possible that MIR-ATR is an alternative to DRIFTS, if it can reduce mineral interference at the 1620 cm^{-1} , but given the less strong signal of organic peaks it might be of limited use in low C soils. It could be worthwhile to do further research towards that direction and we think that this could be the content of another future publication.

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 CP-soc, would suggest an added value of the index compared to SOC concentration, in its current state.

Thanks for the discussion on this comment. We have now computed %CPsoc with the value of 6.95 g kg^{-1} CPsoc from Ultuna derived by Cécillon et al. (2018) and 16.0 g kg^{-1} CPsoc from Franko and Merbach (2017) for the bare fallow data we have available. As shown below, when combining the two datasets of Bad Lauchstädt and Ultuna the correlation between SOC and CPsoc across sites is poor. This shows that SOC alone is not a sufficient indicator for SOC quality. The correlation between the DSI and CPsoc on the other hand is quite strong (0.84), which according to Lauric's comment is a strong indicator of its added value.

We think that it would be highly interesting to test this for other long-term bare fallows, where CPsoc could be mathematically derived (needing probably 30+ years of fallow) and this might help to optimize the DSI further. We think that a future publication could go into this direction and are excited about this finding.



As the reasoning behind CPsoc comes from RothC type models, which assume that there is only one actively decomposing SOC pool and another passive or inert SOC pool which is NOT subject to decomposition, this could mean that the DSI might also be useful for these types of models. In this study, we worked with DAISY, which is a CENTURY type model, that has a fast and slow SOC pool, both subjected to decomposition. We think that this is in agreement with the principle behind DRIFTS, and that microorganisms primarily target high energy aliphatic SOC, but aromatic SOC is also decomposed at a much slower rate, probably as a byproduct of enzyme release.

Overall, we very much acknowledge the issue of mineral interference addressed by the reviewer (see line 369 in the original manuscript) and the new addition:

85 information on SOM quality (Giacometti et al., 2013; Margenot et al., 2015). Demyan et al. (2012) While both peaks are subject to interference (2930 cm⁻¹ mainly from water and 1620 cm⁻¹ mainly from minerals (Nguyen et al., 1991)), it should be possible to limit the interference using subregions of the peaks with carefully selected integration limits, only selecting the specific peak area of interest. Indeed, Demyan et al. (2012) found aliphatic aliphatic compounds to be enriched under long-term farmyard manure application and depleted in mineral fertilizer or control treatments, and showed that the ratio of the 2930 cm⁻¹ to 1620 cm⁻¹ peaks had a significant positive correlation with the ratio of labile to stable SOM obtained by size and density fractionation. Hence, we hypothesised ratios of the 1620 cm⁻¹ to 2930 cm⁻¹ peak had a significant positive correlation with the
 90 ratio of stable to labile SOM obtained by size and density fractionation. It was further corroborated that the specific integration limits of the peaks they used, which mainly selected the top subregion of the peak areas, are lost during combustion (Demyan et al., 2013). Hence, we hypothesized that the ratio of the aliphatic to aromatic DRIFTS

We have addressed this issue mainly by carefully delimiting the integration area and now have more clearly pointed to this in the methods:

160 peak areas of the four subsamples averaged after that. The local baselines were drawn between the intersection of the spectra and a vertical line at the integration limits (3010 – 2800 cm⁻¹ for the aliphatic C-H stretching, 1660 – 1580 cm⁻¹ for aromatic C=C stretching vibrations), stretching, 1660 – 1580 cm⁻¹ for aromatic C=C stretching vibrations). Example spectra and integrated peak areas are displayed in Figure S 1. These carefully selected integration limits were critical to reducing signal interference from water and minerals. Particularly, the mineral interference close to the 1620 cm⁻¹ peak makes accurate selection of integration limits necessary, so that only its top part (assumed to consist mostly of aromatic carbon) is selected. In the case of our samples, the selected specific

165 peak area of the 1620 cm⁻¹ peak accounted for approximately 10 to 30 % of the total peak area (ca. 1755-1555 cm⁻¹), and roughly corresponds to the peak portion that is lost with combustion or chemical oxidation (Demyan et al., 2013; Yeasmin et al., 2017). A strong correlation between the DSI and the percentage of centennially persistent SOC ($r = 0.84$) from the combined long term experiments used in this study (using values of centennially persistent SOC from Cécillon et al., 2018; and Franko and Merbach, 2017), showed that the DSI selected in this manner did

170 in fact explain a large portion of the SOC quality change across sites (Figure S 2).

We have further added a more detailed discussion on open questions of the DSI in the new manuscript version and finalize the section with the limitation that DSI should be tested before used with different soil types.

Compared with the other proxies for SOM quality discussed above, the measurements by DRIFTS are inexpensive, relatively simple, and the equipment of the same manufacturer is standardized. This should also constrain

485 variability between different laboratories and be attractive for large-scale applications with large sample size, for example to initialize simulations at the regional scale. However, for standardization of the DSI for model initialization one needs to address how the type of spectrometer (e.g. detector type) influences the spectra, if water and mineral interferences (Nguyen et al., 1991) in the spectra can be further reduced and if a mathematical standardization of the spectra and DSI (across instruments and water contents) is possible. While a complete elimination of mineral interference is not possible, a careful selection of integration limits and the use of a local baseline minimizes mineral interference of DRIFTS spectra from bulk soils. This mostly selects the top part of the 1620 cm⁻¹ peak, which corresponds to the part that is reduced or completely lost when SOC is destroyed (Demyan et al., 2013; Yeasmin et al., 2017). Other approaches such as spectral subtraction of ashed samples or HF destruction of minerals prior DRIFTS analysis have been developed

490 in the attempt to obtain spectra of pure SOC. All are rather labor intensive and still produce artifacts, as it is not possible to destroy only the minerals or only the SOC without altering the respective other fraction (Yeasmin et al., 2017). Hence, we think that the selected integration limits might represent at this point the most feasible option for obtaining a robust and cost-effective proxy of SOC quality for modeling. The strong correlation of DSI and centennially persistent SOC as well as the model results of this study seem to corroborate this. The method of DSI estimation might be improved by a study of the best integration limits optimizing the fit of the DSI and centennially persistent SOC, which would require more bare fallow experiments than in this study. It could be worthwhile to use a purely mineral peak to correct for the mineral interference at 1620 cm⁻¹ similar to what was done to correct for carbonates in the 2930 cm⁻¹ peak by Mirzaeitalarposhti et al. (2016). The recent coupling of pyrolysis with

495 in the attempt to obtain spectra of pure SOC. All are rather labor intensive and still produce artifacts, as it is not possible to destroy only the minerals or only the SOC without altering the respective other fraction (Yeasmin et al., 2017). Hence, we think that the selected integration limits might represent at this point the most feasible option for obtaining a robust and cost-effective proxy of SOC quality for modeling. The strong correlation of DSI and centennially persistent SOC as well as the model results of this study seem to corroborate this. The method of DSI estimation might be improved by a study of the best integration limits optimizing the fit of the DSI and centennially persistent SOC, which would require more bare fallow experiments than in this study. It could be worthwhile to use a purely mineral peak to correct for the mineral interference at 1620 cm⁻¹ similar to what was done to correct for carbonates in the 2930 cm⁻¹ peak by Mirzaeitalarposhti et al. (2016). The recent coupling of pyrolysis with

500 in the attempt to obtain spectra of pure SOC. All are rather labor intensive and still produce artifacts, as it is not possible to destroy only the minerals or only the SOC without altering the respective other fraction (Yeasmin et al., 2017). Hence, we think that the selected integration limits might represent at this point the most feasible option for obtaining a robust and cost-effective proxy of SOC quality for modeling. The strong correlation of DSI and centennially persistent SOC as well as the model results of this study seem to corroborate this. The method of DSI estimation might be improved by a study of the best integration limits optimizing the fit of the DSI and centennially persistent SOC, which would require more bare fallow experiments than in this study. It could be worthwhile to use a purely mineral peak to correct for the mineral interference at 1620 cm⁻¹ similar to what was done to correct for carbonates in the 2930 cm⁻¹ peak by Mirzaeitalarposhti et al. (2016). The recent coupling of pyrolysis with

In the quest to find measurable fractions for model pools, we think that the DSI is a useful proxy (carefully selected integration limits, nonlinear relation with SOC, evidence that our 1620 cm⁻¹ is mostly from carbon, drying at 105 °C to reduce water interference at 2930 cm⁻¹). We first and foremost consider the DSI as a potential proxy to help initializing two pool SOM models, and our

question was, whether it was useful for this purpose or not, compared to steady state initializations. We think the value of this publication is to establish that the DSI has the potential to be a measurable fraction as a model pool proxy and thereby reducing model uncertainty, and show this to the scientific community. As any research this opens new questions which could lead to further development and refinement of the DSI. We think, that our study could demonstrate the DSI's usefulness and that it might be worthwhile to put further efforts and research towards its validation, use or optimization, especially because of its ease of use and inexpensive nature.

References:

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(2), 189–199, doi:10.1111/j.1365-2389.2011.01420.x, 2012.

Demyan, M. S., Rasche, F., Schütt, M., Smirnova, N., Schulz, E. and Cadisch, G.: Combining a coupled FTIR-EGA system and in situ DRIFTS for studying soil organic matter in arable soils, *Biogeosciences*, 10(5), 2897–2913, doi:10.5194/bg-10-2897-2013, 2013.

Franko, U. and Merbach, I.: Modelling soil organic matter dynamics on a bare fallow Chernozem soil in Central Germany, *Geoderma*, 303(May), 93–98, doi:10.1016/j.geoderma.2017.05.013, 2017.

Laub, M., Blagodatsky, S., Nkwain, Y. F. and Cadisch, G.: Soil sample drying temperature affects specific organic mid-DRIFTS peaks and quality indices, *Geoderma*, 355, 113897, doi:10.1016/j.geoderma.2019.113897, 2019.

Nkwain, F. N., Demyan, M. S., Rasche, F., Dignac, M.-F., Schulz, E., Kätterer, T., Müller, T. and Cadisch, G.: Coupling pyrolysis with mid-infrared spectroscopy (Py-MIRS) to fingerprint soil organic matter bulk chemistry, *J. Anal. Appl. Pyrolysis*, 133(April 2017), 176–184, doi:10.1016/j.jaap.2018.04.004, 2018.

Yeasmin, S., Singh, B., Johnston, C. T. and Sparks, D. L.: Evaluation of pre-treatment procedures for improved interpretation of mid infrared spectra of soil organic matter, *Geoderma*, 304, 83–92, doi:10.1016/j.geoderma.2016.04.008, 2017.

DRIFTS peaks as measured pool size proxy to reduce parameter uncertainty of soil organic matter models

Moritz Laub¹, Michael Scott Demyan², Yvonne Funkuin Nkwain¹, Sergey Blagodatsky¹,
Thomas Kätterer³, Hans-Peter Piepho⁴, Georg Cadisch^{4,3},

Thomas Kätterer⁴, Hans-Peter Piepho⁵, Georg Cadisch¹

5 ¹ Institute of Agricultural Sciences in the Tropics (Hans-Ruthenberg-Institute), University of Hohenheim, 70599 Stuttgart, Garbenstrasse 13, Germany

² School of Environment and Natural Resources, The Ohio State University, Columbus, 2021 Coffey Rd., OH, USA, 43210

10 ^{3,3} Institute of Physicochemical and Biological Problems in Soil Science, Russian Academy of Sciences, 142290 Pushchino, Russia

⁴ Department of Ecology, Swedish University of Agricultural Sciences, Uppsala, Ulls Väg 16, Sweden

^{4,5} Institute of Biostatistics, University of Hohenheim, 70599 Stuttgart, Fruwirthstr. 23, Germany

15 *Correspondence to:* Moritz Laub (moritz.laub@uni-hohenheim.de) and Georg Cadisch (Georg.cadisch@uni-hohenheim.de)

20 *Abbreviations:* soil organic matter (SOM), Diffuse reflectance mid infrared Fourier transform spectroscopy (DRIFTS), DRIFTS stability index (DSI), soil microbial biomass carbon (SMB-C), squared model error (SME), soil organic carbon (SOC)

Abstract. The initialization of soil organic matter (SOM) turnover models has been a challenge for decades. Instead of using laborious and error prone size-density fractionation for SOM pool partitioning, we propose the inexpensive cost effective, rapid, and non-destructive Diffuse reflectance mid infrared Fourier transform spectroscopy (DRIFTS) technique on bulk soil samples to gain information on SOM pool partitioning from the infrared spectra. Specifically, the DRIFTS stability index, defined as the ratio of aliphatic C-H (2930 cm⁻¹) to aromatic C=C (1620 cm⁻¹) stretching vibrations, was used to divide SOM into fast and slow cycling pools in the soil organic module of the DAISY model. Long-term bare fallow plots from Bad Lauchstädt (Chernozem, 25 years) and the Ultuna frame trial in Sweden (Cambisol, 50 years) were combined with bare fallow plots of 7 years duration from the Kraichgau and Swabian Jura region in Southwest Germany (Luvisols). All fields had been in agricultural use for centuries before fallow establishment, so classical theory would suggest an initial steady state of SOM, which was hence used to compare the performance of DAISY initializations against the newly established DRIFTS stability index. The test was done using two different published parameter sets (2.7 * 10⁻⁶ d⁻¹, 1.4 * 10⁻⁴ d⁻¹, 0.1 compared to 4.3 * 10⁻⁵ d⁻¹, 1.4 * 10⁻⁴ d⁻¹, 0.3 for the turnover rates of slow pool, and fast pool turnover rates and humification efficiency, respectively). The DRIFTS initialization of SOM pools significantly reduced DAISY model errors of poor performing model runs (for soil total organic and microbial carbon) for cases where assuming steady state, led to poor model performance. This was irrespective of the turnover rates used, but the faster turnover parameter set fitted better to all sites except Bad Lauchstädt. This, which suggests that soils under long-term agricultural use were not necessarily at steady state. A Bayesian calibration was applied

hat formatiert: Hochgestellt

Formatiert: Zeilenabstand: Mehrere 1.08 ze

40 in a next step to identify the best-fitting turnover rates for the DRIFTS stability index in DAISY, both for each site individually and for a combination of all sites. The two approaches which significantly reduced parameter uncertainty and equifinality were: 1) the addition of the ~~physico-chemically-based~~ physicochemical DRIFTS stability index, ~~(for humification and slow SOM turnover)~~, and 2) combining several sites into one Bayesian calibration, as derived turnover rates can be strongly site specific. The combination of all four sites showed that
45 SOM is likely lost at relatively fast turnover rates with the 95 % credibility intervals of the half-life of slow SOM pools ~~half-life~~ ranging from 278 to 1095 years, with 426 years as a value of highest probability density. The credibility intervals of this study were consistent with several recently published Bayesian calibrations of similar two-pool SOM models, i.e. all turnover rates were considerably faster than earlier models ~~model calibrations~~ suggested. It is therefore likely that published turnover rates ~~underestimate~~ underestimate the potential loss of SOM.

50 1 Introduction

Process-based models of plant-soil ecosystems are used from plot to ~~regional and~~ global scales as tools of research and to support policy decisions (Campbell and Paustian, 2015). ~~The~~ In soil organic matter (SOM) ~~in such models,~~ SOM is traditionally divided into several pools, representing fast, and slow ~~and for some models cycling or~~ even inert SOM (Hansen et al., 1990; Parton et al., 1993). Common methods of SOM pool initialization ~~assume~~ require
55 that one assumes steady state conditions or ~~perform~~ includes a model spin-up run. In ~~the~~ a model spin-up run the user attempts to simulate ~~the~~ SOM dynamics according to history and carbon inputs for the decades to several millennia prior to the period of actual interest (~~eg. O'Leary et al., 2016~~) (e.g. O'Leary et al., 2016). Theoretically if the SOM pools are at steady state, models can be initialized, i.e. pool sizes calculated, either by simple equations (~~eg. DAISY, S. Hansen et al., 2012~~) or by inverse modelling (RothC—(e.g. DAISY, Hansen et al., 2012) or by
60 inverse modeling (RothC, Coleman and Jenkinson, 1996). In ~~both~~ most cases, data is insufficient to guarantee that the assumptions of SOM steady state or long-term ~~knowledge of~~ land use history and inputs are correct, given the lack of data of residue/manure input and weather data variability for the required long-term timescales (> 200 years) to millennia). Hence, ~~while the approach should work in theory, the history of a site is usually not sufficiently known for the timescales that SOM needs to equilibrate.~~ Therefore, the simulation of past carbon
65 inputs and the assumption of steady state are a rough approximation at best. ~~Hence, it is therefore~~ critical to find measurable proxies such as soil size density fractionation or infrared spectra, that can provide information on the quality of SOM and hence help in SOM pool initialization (Sohi et al., 2001).

As was shown by Zimmermann et al. (2007), and recently confirmed by Herbst et al. (2018), a link exists between soil fractions obtained by size ~~and~~ density fractionation and fast and slow cycling SOM pools. However, Poeplau et al. (2013) showed, that the same fractionation protocol led to considerably different results at six different laboratories which regularly applied the technique (coefficient of variation from 14 to 138 %). The resulting differences in the model initializations for simulated SOM loss after 40 years of fallow, lead ~~led~~ to differences in SOM losses that were up to 30 % of initial SOM. Hence there is a need for a reproducible proxy for SOM pool initiation.

75 We ~~hypothesised~~ hypothesized that such a proxy could be ~~obtained~~ obtained from inexpensive, high-throughput Diffuse reflectance mid infrared Fourier transform spectroscopy (DRIFTS). DRIFTS can provide information on SOM quality, but also on texture and even mineralogy (Nocita et al., 2015; Tinti et al., 2015). The interaction of

mid-infrared energy with molecular bonds in soil produce typical vibrational peaks of absorbance at distinct wavelengths, which. These can be linked to different bonds of carbon, nitrogen, silicon and other elements. The vibrational peaks which relate to carbon of different complexities, such as the aliphatic C-H stretching peak around 2930 cm⁻¹ and the aromatic C=C stretching peak at 1620 cm⁻¹, provide information on SOM quality (Giacometti et al., 2013; Margenot et al., 2015). Demyan et al. (2012) While both peaks are subject to interference (2930 cm⁻¹ mainly from water and 1620 cm⁻¹ mainly from minerals (Nguyen et al., 1991)), it should be possible to limit the interference using subregions of the peaks with carefully selected integration limits, only selecting the specific peak area of interest. Indeed, Demyan et al. (2012) found aliphatic compounds to be enriched under long-term farmyard manure application and depleted in mineral fertilizer or control treatments, and showed that the ratio of the 2930 cm⁻¹ to 1620 cm⁻¹ peaks had a significant positive correlation with the ratio of labile to stable SOM obtained by size and density fractionation. Hence, we hypothesized ratios of the 1620 cm⁻¹ to 2930 cm⁻¹ peak had a significant positive correlation with the ratio of stable to labile SOM obtained by size and density fractionation. It was further corroborated that the specific integration limits of the peaks they used, which mainly selected the top subregion of the peak areas, are lost during combustion (Demyan et al., 2013). Hence, we hypothesized that the ratio of the aliphatic to aromatic DRIFTS peaks can be used as proxy for SOM pool initialization, thus providing a major improvement over assuming steady state SOM. This ratio of aliphatic to aromatic peaks, will be called referred to as the DRIFTS stability index (DSI) hereafter. Testing, improvement and proper use of the DSI was the central topic of this study. Recent findings have highlighted that the residual water content in bulk soil samples after drying at different temperatures affects the DSI considerably. Water has both an absorbance reducing impact on affects significant parts of the whole mid-infrared spectra and it does overshadow particularly influences the 2930 and 1620 cm⁻¹ peak peaks (Laub et al., 2019). For this reason, we also tested how the drying temperature prior to DRIFTS measurements affects the use of the DSI proxy, using 32, 65 and 105°C as pretreatment temperatures.

To test our hypotheses about DSI performance, we used the DAISY SOM model (Hansen et al., 2012) to test our hypotheses about the DSI performance. DAISY is a commonly used SOM model (Campbell and Paustian, 2015) with a typical multi-pool structure, which includes two soil microbial biomass pools, as well as two SOM pools (fast and slow). With first-order turnover kinetics and a humification efficiency values parameter (Figure 1 Fehler! Verweisquelle konnte nicht gefunden werden.), the DAISY structure is similar to other widely used SOM models such as CENTURY (Parton et al., 1993) or ICBM (Andrén and Kätterer, 1997). In the current study only Model SOM pool initialization using the DSI was compared to initialization via a steady state assumption with different published turnover rates. For this comparison bare fallow experiments from a range of different sites and time scales from one to five decades were included. Bare fallow experiments were used to avoid the complication added complexity caused by the conversion of different plant compounds into SOM of different varying stabilities while being recycled at several stages. A range of different sites and time scales from one to five decades were included, and the SOM pool initialization by the use of the DSI was compared to initialization by assuming steady state with different published turnover rates during decomposition.

As SOM pool sizes and turnover rates are closely linked, it could also be necessary to recalibrate DAISY parameters for the use of the DSI. Therefore, a Bayesian calibration of turnover rates was done in order used to adjust DAISY turnover rates to the pool division by the DSI and the change time dynamics of the measured DSI throughout the fallow period. Thus, the DAISY parameterization was evaluated with respect to equifinality and

uncertainty as well as dependence on model structure ~~was evaluated~~. The final hypothesis was, that through a Bayesian calibration using the DSI, DAISY pools will correspond to measured, i.e. physiochemically meaningful fractions thus reducing uncertainty. The posterior credibility intervals and optima of turnover rates should correspond to the results of other Bayesian calibrations done for ~~models with similar~~ similarly structured two-pool ~~structures for relatively stable SOM pools~~ models. If such relations could be confirmed, this would point towards fundamental insights about the intrinsic ~~speed of~~ SOM turnover in temperate agroecosystems.

2 Material and Methods

2.1 Study sites and data used for ~~modelling~~ modeling

~~We used datasets~~ Datasets originating from bare fallow ~~plot~~ treatments of four different sites with different ~~observational~~ experimental durations and measurement frequencies. ~~Samples of the~~ were used in this study. Topsoil (0-20 cm topsoil) samples were available from the long-term experiments of (a) the Ultuna Frame trial (established in 1956, with additional data from 1979, 1995 and 2005; (Kätterer et al., 2011), four replicates), and (b) the Bad Lauchstädt Extreme Farmyard Manure Experiment (established in 1983, with additional data from 2001, 2004 and 2008, two replicates) (<https://www.ufz.de/index.php?de=37008> (<https://www.ufz.de/index.php?de=37008>, date accessed 10.01.2019). Additional ~~data from two~~ medium-term experiments (2009 until 2016) from ~~two~~ Southwest German regions were available, i.e. of (c) the Kraichgau and (d) the Swabian Jura, representing different climatic and geological conditions. The bare fallow plots (~~of~~ 5 x 5 m size) in the Southwest Germany experiments were established within agricultural fields (Ali et al., 2015) and had monthly to yearly measurement frequencies of ~~samplings of the top soil samples taken from 0-30 cm~~. In both regions, three replicates of bare fallow plots were established in each of three different fields. Further details on all the sites can be found in **Table 1**. All sites had been under cultivation for at least several hundred years prior to establishing the bare fallow plots, which would suggest that steady state could be assumed.

Bulk soil samples from the start and throughout the simulation period of all experiments were analyzed for total organic carbon and DRIFTS spectra; samples from the Kraichgau and Swabian Jura sites were additionally ~~analysed~~ analyzed for soil microbial biomass carbon (SMB-C). After sampling, all bulk soil samples (except for SMB-C) were passed through a 2 mm sieve, then air dried, ball milled (for two minutes) to powder and stored until further analysis. ~~Their soil~~ Soil organic carbon (SOC) content was analyzed with a Vario Max CNS (Elementar Analysensysteme GmbH, Hanau, Germany). Soil samples for DRIFTS analysis were obtained after 24 hr drying at 32, 65 and 105°C. The dried samples were kept in a desiccator until measurement. DRIFTS spectra of bulk soil samples ~~were obtained (with 4 repeated measurements~~ four subsamples per sample) ~~after 24 hr drying at 32, 65 and 105°C~~ were obtained using an HTS-XT microplate extension, mounted to a Tensor-27 spectrometer using the processing software OPUS 7.5 (equipment and software from Bruker Optik GmbH, Ettlingen, Germany). ~~The details: a~~ A potassium bromide (KBr) beam splitter with a nitrogen cooled HTS-XT reflection detector was used to record spectra in the mid infrared range (4000 – 400 cm^{-1}); ~~each~~. Each spectrum was a combination of 16 co-added scans with a 4 cm^{-1} resolution ~~4 cm^{-1}~~ . Spectra were recorded ~~in~~ and then converted to absorbance units (AU); the acquisition mode “double-sided, forward-backward” and the apodization function Blackman-Harris-3 were used. ~~The dried samples were kept in a desiccator until measurements.~~ After a baseline correction and a vector normalization of the spectra, peak areas of interest were obtained ~~as the integral on top of~~ by integration

160 using a local baseline with the integration limits of Demyan et al. (2012) and integrated
peak areas of the four subsamples averaged after that. The local baselines were drawn between the intersection of
the spectra and a vertical line at the integration limits (3010 – 2800 cm⁻¹ for the aliphatic C-H stretching, 1660 –
1580 cm⁻¹ for aromatic C=C stretching vibrations), stretching, 1660 – 1580 cm⁻¹ for aromatic C=C stretching
vibrations). Example spectra and integrated peak areas are displayed in Figure S 1. These carefully selected
integration limits were critical to reducing signal interference from water and minerals. Particularly, the mineral
interference close to the 1620 cm⁻¹ peak makes accurate selection of integration limits necessary, so that only its
top part (assumed to consist mostly of aromatic carbon) is selected. In the case of our samples, the selected specific
165 peak area of the 1620 cm⁻¹ peak accounted for approximately 10 to 30 % of the total peak area (ca. 1755-1555 cm⁻¹
) and roughly corresponds to the peak portion that is lost with combustion or chemical oxidation (Demyan et al.,
2013; Yeasmin et al., 2017). A strong correlation between the DSI and the percentage of centennially persistent
SOC ($r = 0.84$) from the combined long term experiments used in this study (using values of centennially persistent
SOC from Cécillon et al., 2018; and Franko and Merbach, 2017), showed that the DSI selected in this manner did
170 in fact explain a large portion of the SOC quality change across sites (Figure S 2).

Additionally, soils from the experiments in Kraichgau and Swabian Jura were analyzed for SMB-C using the
chloroform fumigation extraction method (Joergensen and Mueller, 1996). Briefly, field moist samples were
transported to the lab in a cooler, with extractions beginning the next day within 24 hours after field sampling and
the final SMB-C values corrected to an oven-dried (105° C) basis. The SMB-C was measured two to four times
175 throughout the whole year. Stocks of SOC and SMB-C for the modelled layers 0-30 cm were calculated by
multiplying the percentage of SOC and SMB-C with the bulk density and depth of the modelled sampled layer
thickness (Table 1), respectively. Bulk density was assumed constant for Bad Lauchstädt, Kraichgau and
Swabian Jura, while for Ultuna the initial 1.44 tMg m⁻³ (Kirchmann et al., 2004) in the beginning was used for all
but the last measurement, where 1.43 Mg m⁻³ (Kätterer et al., 2011) was used. Due to low stone coarse fragment
180 contents (< 5 % for Swabian Jura 3, < 2 % for Swabian Jura 1 and < 1 % for the other six sites), and because
changes in stone content throughout the simulation periods are unlikely, no correction for stone coarse fragment
content was done.

2.2 Description of the simulation model: DAISY Expert-N 5.0

All simulations were conducted using the DAISY SOM model (Hansen et al., 2012) integrated into the Expert-N
185 5.0 modelling framework. Expert-N 5.0 is a flexible modelling framework, which allows a wide range
of soil, plant and water models to be combined and interchanged (Heinlein et al., 2017; Klein et al., 2017; Klein,
2018). Expert-N can be compiled both for Windows and Linux systems. A detailed description of the DAISY
SOM submodule as it was implemented into the Expert-N 5.0 framework can be found in Mueller et al. (1997). A
graphical representation of the DAISY pools considered in this study is shown in Figure 1. The additional modules
190 available for selection in the Expert-N 5.0 framework are from consist of a range selection of established models
for all simulated processes in the soil-plant continuum. The evaporation, ground heat, net radiation, and emissivity
were simulated according to the Penman-Monteith equation (Monteith, 1976). Water flow through the soil profile
was simulated by the Hydrus-flow module (van Genuchten, 1982) with the hydraulic functions according to
Muallem (1976). Heat transfer through the soil profile was simulated with the DAISY heat module (Hansen et al.,
195 1990). In the first step of the DSI evaluation, simulations were conducted with two established parameter sets for

DAISY SOM. The first set was from Mueller et al. (1997) and was a modification of the original parameter set of turnover rates in Jensen et al. (1997) reported by Jensen et al. (1997). The second set was established after calibrations made by Bruun et al. (2003) using the Askov Long-Term Experiments and, in which they introduced considerable changes into the turnover rates of the slow pool and the humification efficiency. An equation developed by Bruun and Jensen (2002) was used to compute the sizes proportions of the slow and fast cycling SOM pools at steady state for both parameter sets at steady state (see next section). All the parameters Parameters of both sets are displayed given in Table 2.

Climatic driving variables For simulating soil temperature and moisture in Expert-N, daily averages of radiation, temperature, precipitation, relative humidity and wind speed, are needed for Expert-N simulations. For the long-term experiments they were extracted from the nearest weather station with complete data (Ultuna source: Swedish Agricultural University (SLU), ECA Station ID #5506, Elevation: 15 m, Lat: 59.8100 N, Long: 17.6500 E; Bad Lauchstädt source: Deutsche Wetter Dienst (DWD) Station #2932, Elevation: 131 m, Lat: 51.4348 N, Long: 12.2396 E, Locality name: Leipzig/Halle). For the fields of the Kraichgau and Swabian Jura, the driving variables were measured by weather stations installed next to eddy covariance stations located at the center of each field. Details on the measurements, instrumentation as well as gap filling methods of those eddy covariance weather stations are described by in Wizemann et al. (2015).

2.3 SOM pool initializations with the DRIFTS stability index and at steady state

Measured SMB-C was divided into the slow and fast cycling microbial pools, with 10 % in the fast (8 % in Mueller et al., 1998) and 90 % in the slow pool. The remaining part of carbon (difference between total SOC and SMB-C) was divided either by the DRIFTS stability index (DSI), or according to the steady state assumption. For runs with the using a steady state assumption, the equation of Bruun and Jensen (2002) was used, which directly computes estimates the fraction of SOM in the slow pool at steady state from the model parameters:

$$\text{slow SOM fraction} = \frac{1}{1 + \frac{k_{SOM_slow}}{f_{SOM_slow} * k_{SOM_fast}}} \quad (1)$$

with k_{SOM_slow} and k_{SOM_fast} representing the turnover (per day) of the slow and fast SOM pools respectively, and f_{SOM_slow} representing the amount fraction of fast SOM directed towards the slow SOM pool at turnover of fast SOM (humification efficiency). This resulted in 83 % of SOM being in the slow pool for the original DAISY turnover rates and 49 % in the slow pool for the Bruun et al. (2003) turnover rates (Table 2). For the DSI initialization, the amount fraction of SOM in the slow pool was calculated with the formula

$$\text{slow SOM fraction} = \frac{A_{1620} \text{cm}^{-1}}{A_{1620} \text{cm}^{-1} + A_{2930} \text{cm}^{-1}} \quad (2)$$

With $A_{2930} \text{cm}^{-1}$ and $A_{1620} \text{cm}^{-1}$ being the extracted peak areas specific peak area of the aliphatic and aromatic peaks (described in section 2.1). The remaining carbon was allocated to the fast pool. As was mentioned before, three different data inputs for the DSI were used, with obtained at drying temperatures of 32, 65 and 105°C, in order to test which drying temperature is derived the best proxy for modelling modeling. An example of the change of DRIFTS spectra occurring after several years of bare fallow can be found in Figure 2. Each of the three All DSI model initializations was were then run with both published sets of model parameters. Steady state

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

initializations using **Equation 1** were only conducted with the corresponding parameter set from which they were calculated.

2.4 Statistical evaluation of model performance

Statistical analysis was performed with SAS version 9.4 (SAS Institute Inc., Cary, NC, USA). To compare different model initializations, a statistical analysis of squared model errors (SME) was conducted:

$$SME_x = (obs_x - pred_x)^2 \quad (3)$$

with obs_x being the observed value, $pred_x$ the predicted value and x the simulated variable of interest. A linear mixed model with SME_x as response was then used to test for significant differences between initialization methods. This approach allowed us to make use of the statistical power of the three Kraichgau and Swabian Jura fields to analyze which initialization was most accurate and to evaluate the trend of the model error with increasing simulation time. In some cases, SME_x was transformed to ensure a normal distribution of residuals (square root transformation for Ultuna SOC and Kraichgau/Swabian Jura SMB-C and fourth root for Kraichgau/Swabian Jura SOC), which was checked by a visual inspection of the normal QQ plots and histograms of residuals (Kozak and Piepho, 2018). Random effects were included to account for temporal autocorrelation of SME_x within (a) the same field and (b) the same simulation. The model reads as follows:

$$y_{ijkl} = \phi_0 + \alpha_{0i} + \beta_{0j} + \gamma_{0ij} + \phi_1 t_k + \alpha_{1i} t_k + \beta_{1j} t_k + \gamma_{1ij} t_k + u_{kl} + u_{ijkl} \quad (4)$$

where y_{ijkl} is the SME_x of the simulation using the i th initialization with the j th parameter set, at the k th time on the l th field, ϕ_0 is an overall intercept, α_{0i} is the main effect of the i th initialization, β_{0j} is the main effect j th parameter set, γ_{0ij} is the ij th interaction effect of initialization x parameter set, ϕ_1 is the slope of the time variable t_k , $\alpha_{1i} t_k$ is the interaction of the i th initialization with time, $\beta_{1j} t_k$ is the interaction of the j th parameter set with time, $\gamma_{1ij} t_k$ is the ij th interaction effect of initialization x parameter set x time, u_{kl} is the autocorrelated random deviation on the k th time in the l th field and u_{ijkl} is the autocorrelated residual error term corresponding to y_{ijkl} .

The detailed SAS code can be found in the supplementary material. For Ultuna and Bad Lauchstädt, the u_{kl} term was left out, as both trials only had one field. As the Kraichgau and Swabian Jura had the exact same experimental setup and time frames/durations, these sites were jointly analyzed in the statistic model, but due to completely different setups and time frames/durations, this was not possible for Bad Lauchstädt and Ultuna. The full models with all fixed effects were used to compare different correlation structures for the random effects including (i) temporal autocorrelation (exponential, spherical, Gaussian), (ii) compound symmetry, (iii) a simple random effect for each different field and simulation, (iv) a random intercept and slope of the time variable (with allowed covariance between both) for each field and initialization method. A residual maximum likelihood estimation of model parameters was used and the best fitting random effect structure for this model was selected using the Akaike Information Criterion as specified by Piepho et al. (2004). Then a stepwise model reduction was conducted until only the significant effects ($p < 0.05$) remained in the final statistical model. Because a mixed model was used, the Kenward-Roger method was used/applied for estimating the degrees of freedom (Piepho et al., 2004) and to compute post hoc Tukey-Kramer pairwise comparisons of means.

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Schriftart: Kursiv

hat formatiert: Schriftart: Kursiv

hat formatiert: Schriftart: Kursiv

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Schriftart: Kursiv

hat formatiert: Schriftart: 10 Pt.

hat formatiert: Schriftart: 10 Pt.

hat formatiert: Schriftart: 10 Pt.

2.5 Model optimization and observation weighting for Bayesian calibration

The optimization with Bayesian calibration was done for Optimization of parameters k_{SOM_slow} , k_{SOM_fast} and the humification efficiency (f_{SOM_slow}) was performed using a Bayesian calibration approach. These parameters were chosen as only these three parameters they have a considerable impact on the rate of native SOM loss (we provide a detailed explanation why this is the case see further details in the supplementary material chapter S 12.2). The Bayesian calibration method uses an iterative process to simulate what the distribution of parameters would be, given the data and the model would be, combining. It combines a random walk through the parameter space with a probabilistic approach on parameter selection.

The Differential Evolution Adaptive Metropolis algorithm (Vrugt, 2016) implemented in UCODE_2014 (Lu et al., 2014; Poeter et al., 2014) was used for the Bayesian calibration in this study. As no Bayesian calibration of DAISY SOM parameters has been done before, we used noninformative priors were used. The main drawback of noninformative priors is that they can have longer computing times, but as was shown by Lu et al. (2012) with enough sufficient data and long enough running periods simulation durations, the posterior distributions are very similar to using informed priors. Ranges were set far beyond published parameters with $1.4 * 10^{-2}$ to $1.4 * 10^{-6}$ d^{-1} for k_{SOM_fast} and $1.4 * 10^{-3}$ to $5 * 10^{-7}$ d^{-1} for k_{SOM_slow} . The parameter f_{SOM_slow} had to be more strongly constrained as without constraints it tended to run into unreasonable values up to 99 % humification. The limits were therefore set to 0.05 to 0.35 for, which is +/- 5 % of the two published parameter sets and also represents the upper boundaries of other similar models (eg. Ahrens et al., 2014). As convergence criteria the (e.g. Ahrens et al., 2014). The default UCODE_2014 Gelman-Rubin criterion (Gelman and Rubin, 1992) with a value of 1.2 was chosen for the convergence criteria. A total of 15 chains were run in parallel with a timestep of 0.09 days in Expert-N 5.0 (this was the largest timestep and fastest computation, where the simulation results of water flow, temperature and hence SOM pools was unaltered compared to smaller timesteps). It was ensured that at least 300 runs per chain were done after the convergence criterion was satisfied.

In Bayesian calibration, a proper weighting of observations is needed in order to achieve a diagonal weight matrix of residuals (proportional to the inverse of the variance covariance matrix), and to ensure that residuals are in the same units (Poeter et al., 2005, p18 ff). This included several steps. A differencing removed autocorrelation in the individual errors in each model run of the Bayesian calibration itself (the first measurement of each kind of data at each field was taken as raw data, for any repeated measurement the difference from this first measurement was taken instead of the raw data). Details on differencing are provided in chapter 3 of the UCODE_2005 manual (Poeter et al., 2005). To account for different varying levels of heterogeneity of different fields in the weighting, a mixed linear model was used to separate the variance of observations from different fields originating from natural field heterogeneity from the variance originating from measurement error. To do so, a linear mixed model with random slope and intercept of the time effect for each experimental plot was fitted to the SOC, SMB-C and DSI data for each field individually:

$$y_{kl} = \phi_0 + \phi_1 t_k + u_l + u_k + u_{kl} \quad (5)$$

where y_{kl} is the modelled variable at the k th time on the l th plot, ϕ_0 is the intercept, ϕ_1 is the slope of the time variable t_k , u_l is the random intercept, u_k is the autocorrelated random deviation of the slope and u_{kl} is the autocorrelated residual error term corresponding to y_{kl} .

hat formatiert: Englisch (Vereinigte Staaten)

The error variance of each type of measurement (DSI, SMC-C, SOC) at each field $\sigma_{fM}^2 = \sigma_{u_k}^2 + \sigma_{u_{kl}}^2$ was then used for weighting of observations, excluding the field variance $\sigma_{u_l}^2$ from the weighting scheme. This error variance was used in UCODE_2014 to compute weighted model residuals for each observation as follows:

$$w_SME_x = \frac{(obs_x - pred_x)^2}{\sigma_{fM}^2} \quad (6)$$

where w_SME_x is the weighted squared model residual, obs_x is the observed value, $pred_x$ is the predicted value and σ_{fM}^2 is the error variance of the M th type of measurement at each field. All w_SME_x are combined to the sum of squared weighted residuals, which is the objective function used in UCODE_2014 (Poeter et al., 2014). By this procedure, observations with higher measurement errors have a lower influence in the Bayesian calibration.

Since the medium-term experiments had a much higher measurement frequency, it was also tested if giving each experiment the same weight would improve the results of the Bayesian calibration (equal weight calibration). In this case an additional group weighting term was introduced for groups of observations, representing different datasets at the different sites. This weighting term is internally multiplied with each w_SME_x in UCODE_2014 and was calculated as

$$w_G_x = \frac{1}{(n_{obs} * n_{par} * n_f)} \quad (7)$$

where w_G_x is the weight multiplier for each observation, n_{obs} is the number of observations per parameter, n_{par} is the number of parameters per field, and n_f is the number of fields per site. This weighing assures that with the exact same percentage of errors, each site would have the exact weight of 1.

The influence of several factors was assessed in this Bayesian calibration: the use of individual sites compared to combining sites, including an equal weight (as described above) vs weighting only by error variance, and the effect of in/excluding the DSI in the Bayesian calibration. Therefore, seven Bayesian calibrations were conducted in total: four for each individual site with original weight and DSI, i.e., 1) Ultuna, 2) Bad Lauchstädt, 3) Kraichgau, 4) and Swabian Jura, 5) equal weight calibration for all sites combined with equal weighting using DSI, 6) original weight calibration for all sites combined without using DSI in the Bayesian calibration (only for initial pool partitioning) and finally 7) original weight calibration for all sites combined using the DSI and original weight. The comparison of these seven Bayesian calibrations was designed to assess the effect of the site on the calibration, as well as the effect of the DSI and of user weighting decisions.

3 Results

3.1 Dynamics of SOC, SMB-C and DRIFTS during bare fallows

All bare fallow plots lost SOC over time with the severity of SOC loss varying between soils and climates at the different sites. The Bad Lauchstädt site experienced the slowest carbon loss (7% of initial SOC in 26 years), while SOC at Ultuna and Kraichgau was lost at much faster rates (Ultuna - 39% of initial SOC in 50 years, Kraichgau on average 9% of initial SOC in 7 years) (Table 3). In the Swabian Jura field 1 the SOC loss was comparable to that of the Kraichgau (about 10% of initial SOC in 7 years), but was much less in fields 2 and 3. Some miscommunications with the field owner's contractors led to unwanted manure addition and fields ploughing

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Schriftart: Kursiv

hat formatiert: Schriftart: Kursiv

hat formatiert: Schriftart: Kursiv

hat formatiert: Englisch (Vereinigte Staaten)

in Swabian Jura field 2 and 3 in 2013, hence results of these two fields after the incident in 2013 were excluded. The DRIFTS spectra revealed that the aliphatic peak area (2930 cm⁻¹) decreased rather fast after the establishment of the bare fallow plots while the aromatic peak area (1620 cm⁻¹) had only minor changes and no consistent trend (Figure 2). The resulting amount fraction of SOC in the slow pool according to the computed DSI changed from the initial range of 54 to 80 % to the range of 76 to 99% at the end of the observational period. (Table 3, Figure S 3). The SMB-C reacted even more rapidly to the establishment of fallows and halved on average for all fields within 7 years duration. (Table 3).

3.2 Comparison of the different model initializations

The observed trend of SOC loss with ongoing bare fallow duration was also found in all simulations (Figure 3) and Figure S 4). For Ultuna, simulated SOC loss in all cases underestimated measured loss, while for Bad Lauchstädt, simulated SOC losses consistently overestimated measured losses. At Kraichgau sites SOC loss was underestimated by the models, but using with the Bruun (2003) parameter set yielded yielding simulated values closer to what was measured actual measurements. In the Swabian Jura, both parameter sets underestimated SOC loss. The decline of SMB-C in the Kraichgau and Swabian Jura (Figure 4) occurred more rapidly than that of SOC, though SMB-C had higher variability of measurements. The parameter sets with steady state assumptions marked the upper and lower boundaries of the SMB-C simulations but the DRIFTS stability index (DSI) initializations were closer to the measured values (with exception of Swabian Jura field 3). For brevity only simulations of field 1 for Kraichgau and Swabian Jura are displayed here shown. Simulation results for fields 2 and 3 are found in the supplemental material (Figure S 5 for SOC simulations and Figure S 6 for SMB-C).

The statistical analysis of the model error revealed a site dependency of the effect of the parameter set. The three-way interaction of initialization, parameter set and time $\gamma_{1ij}t_k$ was significant for all but Bad Lauchstädt SOC, where only the parameter set had a significant effect. In the case of Bad Lauchstädt, the model error was significantly lower with the slower Mueller (1997) SOM turnover parameter set, while for the rest of tested cases, the faster Bruun (2003) set performed significantly better (Table 4). For Ultuna and for Kraichgau + Swabian Jura SOC, the steady state assumption with Mueller (1997) parameters had the highest model error, while the steady state assumption with Bruun (2003) parameters had the lowest model error of all simulations, but there was only a statistical significant difference to the DRIFTS initialization of DSI using 105°C drying temperature was only significant for to DSI using other 32°C and 65°C for the Ultuna and not for the other sites site. For the SMB-C simulations in at the Kraichgau + Swabian Jura sites, however, the errors were lowest for the DRIFTS DSI initialization using the 105° C drying temperature with Bruun (2003) parameters and significantly lower than both steady state initializations. Of the DRIFTS DSI initializations using different drying temperatures, the model error was always lowest when using the 105°C drying temperature initialization compared to 32°C and 65°C (significant for Ultuna, as well as for Kraichgau + Swabian Jura SMB-C using Mueller (1997) parameters). As initializations with DRIFTS DSI using 105°C drying temperature consistently performed the best of all three DRIFTS DSI initializations, it was chosen to continue only with DRIFTS DSI spectra of soils dried at 105°C were used for the Bayesian calibration.

3.3 Informed turnover rates of the Bayesian calibration

The posterior distribution of parameters from the Bayesian calibration differed considerably between the different calibrations for individual sites, but there were also differences between different weighting schemes and to or

when performing the Bayesian calibration without DSI when using all sites the DSI (Figure 5). The highest probability turnover of the fast SOM pool (k_{SOM_fast}) was 1.5 and 3 times faster for Ultuna and Kraichgau, respectively, when compared to initial rates ($1.4 * 10^{-4} d^{-1}$ for both parameters sets), which fitted well for Bad Lauchstädt and Swabian Jura. For the slow SOM pools (k_{SOM_slow}) the Bad Lauchstädt, Kraichgau and Swabian Jura site calibrations were in between the two published parameter sets, but tended towards the slower rates ($2.7 * 10^{-6} d^{-1}$ by Mueller (1997)), while the optimum for Ultuna was exactly at the fast rates of Bruun (2003) ($4.3 * 10^{-5} d^{-1}$). The humification efficiency (f_{SOM_slow}) was not strongly constrained in the Bayesian calibration, except for the Kraichgau site, where it ran into the upper boundary of 0.35. This trend towards higher humification existed also for the other sites, but with much less strength to a lesser extent than for Kraichgau.

The different calibrations of the combination of all sites under different weightings and with or without the DSI also led to considerable differences in the posteriors. When combining the sites with the artificial equal weighting, the posterior distribution of all three parameters was the widest, basically covering the range of all four sites calibrations. With the original weighting scheme, only informed by the variance of the data, the posteriors were much more narrow for all parameters, with the optima of k_{SOM_fast} being slightly faster than the two (similar) published rates. The optima of k_{SOM_slow} were slightly slower than that of Bruun (2003) but much faster than that of Mueller (1997) and f_{SOM_slow} was even above the higher Bruun (2003) value of 0.3 by Bruun (2003). The use of the original weighting scheme but without the use of the DSI in the Bayesian calibration did not constrain the f_{SOM_slow} at all and had faster k_{SOM_slow} and slower k_{SOM_fast} than the one using the DSI. Both these Bayesian calibrations using the original weighting (with and without DSI) showed a trend towards slightly faster turnover than was suggested by Bruun (2003).

There was a strong negative correlation between k_{SOM_fast} and k_{SOM_slow} parameters for all but the Bad Lauchstädt calibration (Figure S 7). When DSI was not included in the Bayesian calibration, this negative correlation was stronger than when it was included in the Bayesian calibration (Figure 6). The parameters k_{SOM_fast} and f_{SOM_slow} were always positively correlated, most strongly for Kraichgau (0.49) and Swabian Jura (0.38), but only weakly for the long-term sites. The correlations between the parameters k_{SOM_slow} and f_{SOM_slow} were generally low and both positive and negative. The parameters with the highest probability density of the calibrations combining all sites for f_{SOM_slow} , k_{SOM_fast} and k_{SOM_slow} in that order were 0.34, $2.29 * 10^{-4}$, $3.25 * 10^{-5}$ for the original weight calibration and 0.06, $9.58 * 10^{-5}$ and $5.54 * 10^{-5}$ for the calibration using original weights and no DSI, showing. These results suggest that turnover rates of k_{SOM_slow} of very could be similar magnitude as or faster than k_{SOM_fast} were possible without the use of the DSI. About 10 % of simulations of the Bayesian calibration without DSI had even a faster k_{SOM_slow} than k_{SOM_fast} .

4 Discussion

4.1 How useful is the DRIFTS stability index?

The results of this study confirm the hypothesized usefulness of the DRIFTS stability index for SOM pool partitioning for a number of soils across Europe. The DSI therefore is a proxy of the current state of SOM in a particular field. This is particularly relevant, given that the changes in genotypes of crops, agricultural management, crop rotations and the rise of average temperatures in recent decades probably have affected the past quality and quantity of carbon inputs to soil. Consequently, the steady state assumption for model initialization is

~~not likely to be valid.~~ A search for suitable proxies for SOM pool partitioning into SOM model pools that correspond to measurable and ~~physiochemically~~~~physicochemical~~ meaningful quantities is ~~therefore~~ of high interest (Abramoff et al., 2018; Bailey et al., 2018; Segoli et al., 2013). ~~The results of this study confirm the hypothesized usefulness of the DSI proxy assessing the current state of SOM for pool partitioning to model SOC for several soils across Europe. This is particularly relevant, given that changes in crop genotype and rotation, agricultural management, and the rise of average temperatures in recent decades as well as land use changes, such as draining of soils or deforestation, in recent centuries have altered the quality and quantity of carbon inputs to soil. Consequently, the steady state assumption for model initialization is not likely to be valid. Despite the acknowledged mineral interference of the DSI,~~ Demyan et al. (2012) showed that with a careful selection of peak integration limits, the DSI ~~through identifying organic contributions in DRIFTS spectra~~ is a sensitive indicator of SOM stability if mineralogy is similar. ~~With (despite acknowledged mineral interference). Combined with a higher temperature (105 °C) for soil drying prior to DRIFTS analysis, a strong correlation between the results~~ portion of centennially persistent SOC and the DSI (Figure S 2) was found which supports the hypothesis that it might be of general applicability across sites. ~~Results from our study we could not reject the hypothesized modeling corroborated the~~ usefulness of the DSI for SOM pool partitioning for soils of different properties across Europe. The statistical analysis of the model error ~~for both SOC and SMB-C~~ showed clearly that the DSI ~~does~~ can improve poor model performance, especially with the slower turnover rates of Mueller (1997). When model performance is already satisfactory, the natural variability of the DSI can make model performance worse, as in the case of Ultuna SOC with Bruun (2003) parameters, but this reduction was minor compared to the improvement the DSI had over steady state assumptions at Ultuna with Mueller (1997) rates. The better results for Ultuna with the Bruun (2003) steady state might also just be an effect of turnover times still being too slow and hence the more SOC in the fast pool, the faster ~~the turnover is in general~~ turnover and the lower the model error. This was also indicated by faster optima by the Bayesian calibration compared to both published turnover rates. ~~Also in~~ In the case of Bad Lauchstädt, ~~only~~ turnover rates had a ~~high~~ influence on model performance. The properties of ~~the~~ Chernozem were generally not well captured with ~~both~~ either parameter ~~sets~~ set, and it ~~has~~ probably has a slower overall SOM decomposition ~~as~~ than many other agricultural soils. Nevertheless, the use of DSI also was suitable for Bad Lauchstädt, as it did ~~also~~ not reduce model performance.

~~The results for SMB-C, typically the pool that reacts fastest to changes of input, corroborated the evidence that the DSI initialization is a more realistic estimation of SOM pools than the steady state assumption.~~ The range of different sites, soils, and climatic conditions of Europe represented within this study suggest ~~the~~ robustness of the DSI ~~as a~~ proxy for SOM quality and SOM pool division for a large environmental gradient. Hence, it would be an improvement over assuming steady state of SOM wherever there is a lack of detailed information of carbon inputs and climatic conditions. Considering the timescales at which SOM develops, this is almost anywhere, as detailed data is available at best for <200 years, which is not even one half-life of the slow SOM pool.

So far, studies that assessed SOM quality and pool division proxies, either using thermal stability of SOM (Cécillon et al., 2018) or size-density fractionation (Zimmermann et al., 2007), only indirectly related the proxies to inversely ~~modelled~~~~modeled~~ SOM pool distributions, using machine learning and rank correlations. In contrast, our study showed that the DSI is a proxy which can be directly used for pool initialization. ~~As for other proxies such as thermal stability (Demyan et al., 2013) and size density fractionation (Puttaso et al., 2013), the relationship between SOM quality and the DSI is only indirect as e.g. determined by comparing high/low SOM treatments in~~

manipulation experiments. However, the DSI also makes sense from the perspective of energy content of the molecules that create the peaks of absorption, as microorganisms can obtain more energy from the breakdown of aliphatics compared to aromatics. The DSI also makes sense from the perspective of energy content, as microorganisms can obtain more energy from the breakdown of aliphatic than aromatic compounds (e.g. Good and Smith, 1969), and therefore aliphatic compounds are primarily targeted by microorganisms (hence have faster turnover) as previously shown for bare fallows (Barré et al., 2016).

The two distinct peaks for aliphatic and aromatic carbon bonds of the DSI fit well to the two SOM pool structure of DAISY and the simulation of carbon flow through the soil in DAISY is very similar to several established SOM models such as SoilN, ICBM and CENTURY. It is therefore likely that with calibration, the DSI could be used as a general proxy for SOM models with two SOM pools and a humification efficiency (f_{SOM_slow} in DAISY). The parameter correlations between k_{SOM_slow} , k_{SOM_fast} and f_{SOM_slow} according to the Bayesian calibrations also showed clearly that, as suggested that without a pool partitioning proxy, modifying any one parameter can lead to similar results in terms of SOC and SMB-C simulation. A clear distinction between fast and slow pools needs a pool partitioning proxy as can be seen by faster k_{SOM_slow} than k_{SOM_fast} for some of the simulations of the Bayesian calibration without using DSI. Assigning the DSI to DAISY reduced parameter correlations and led to clear distinction between fast and slow pools.

The aliphatic molecular vibrational peak of DRIFTS is most resolved when applying a 105°C drying temperature to samples prior to analysis. Bruun and Jensen (2002) postulated, the three parameters are strongly related, and without the DSI modifying anyone of them can lead to the same results in terms of SOC and SMB-C simulation. Without the DSI, no clear distinction between fast and slow pools in the calibration was given as can be seen by sometimes faster k_{SOM_slow} than k_{SOM_fast} . Assigning the DSI to DAISY not only reduced the correlations, but also made this clear distinction between fast and slow pool in the Bayesian calibration. The aliphatic carbon peak of DRIFTS is most resolved when applying a 105°C drying temperature (Laub et al., 2019). The current study's modeling results from modelling corroborated the finding that the DSI should be obtained from measurements after drying at 105 °C with the performance of the DRIFTS initializations being always in the order 105°C > 65°C > 32°C drying temperature (differences being sometimes but not always significant).

Compared with the other proxies for SOM quality discussed above, the measurements by DRIFTS are inexpensive, relatively simple, and the equipment of the same manufacturer is standardized. This should also constrain variability between different laboratories and be attractive for large-scale applications with large sample size, for example to initialize simulations at the regional scale. However, for standardization of the DSI for model initialization one needs to address how the type of spectrometer (e.g. detector type) influences the spectra, if water and mineral interferences (Nguyen et al., 1991) in the spectra can be further reduced and if a mathematical standardization of the spectra and DSI (across instruments and water contents) is possible. While a complete elimination of mineral interference is not possible, a careful selection of integration limits and the use of a local baseline minimizes mineral interference of DRIFTS spectra from bulk soils. This mostly selects the top part of the 1620 cm⁻¹ peak, which corresponds to the part that is reduced or completely lost when SOC is destroyed (Demyan et al., 2013; Yeasmin et al., 2017). Other approaches such as spectral subtraction of ashed samples or HF destruction of minerals prior DRIFTS analysis have been developed

495 in the attempt to obtain spectra of pure SOC. All are rather labor intensive and still produce artifacts, as it is not
possible to destroy only the minerals or only the SOC without altering the respective other fraction (Yeasmin et
al., 2017). Hence, we think that the selected integration limits might represent at this point the most feasible option
for obtaining a robust and cost-effective proxy of SOC quality for modeling. The strong correlation of DSI and
500 centennially persistent SOC as well as the model results of this study seem to corroborate this. The method of DSI
estimation might be improved by a study of the best integration limits optimizing the fit of the DSI and centennially
persistent SOC, which would require more bare fallow experiments than in this study. It could be worthwhile to
use a purely mineral peak to correct for the mineral interference at 1620 cm⁻¹ similar to what was done to correct
for carbonates in the 2930 cm⁻¹ peak by Mirzaeitalarposhti et al. (2016). The recent coupling of pyrolysis with
505 DRIFTS (Nkwain et al., 2018) might be a further analytical advancement of the DSI, as it overcomes mineral
interferences in the spectra. However, this technique is more complex due to a larger number of visible organic
peaks, including CO₂ that develops from the pyrolysis, which makes it not easily applicable to established two-
pool models such as DAISY. In addition, a considerable portion (30–40 %) of SOM is not pyrolyzed and therefore
not recorded in the spectra. In summary, it was found that the DSI can be directly used to distribute SOM between
510 pools in two pool models, though there is some mineral interference. Furthermore, DSI was suitable for a wide
range of soils and improved model performance. Hence, DSI seems to be a more robust proxy for pool initialization
then methods such as steady state or long-term spin-up runs which rely on strong assumptions to which they are
very sensitive though there is very limited data to prove them. In summary, even despite of the acknowledged
shortcomings, the DSI was useful to partition SOM between pools. It seems more robust than steady state or
515 long-term spin-up runs which rely on strong assumptions. Further tests are needed before using the DSI for
mineralogy that differs considerably from the soils of this study. Finally, the DSI is not purely related to chemical
recalcitrance of SOM, as it also correlates with the level of SOC protected by aggregation (Demyan et al., 2012).
Hence, it is likely that aggregation and chemical recalcitrance are related.

4.2 Parameter uncertainty as estimated with Bayesian calibration

520 According to our Bayesian calibrations, a wide range of parameter values are possible for DAISY going far beyond
the initial published parameter sets. By combining various sites and including meaningful proxies, such as the DSI,
the parameter uncertainty and equifinality could be reduced and the credibility intervals narrowed. The predictions
of mechanistic models usually fail to account for the three main statistical uncertainties of (1) inputs, (2) scientific
judgments resulting in different model setups and (3) driving data (Wattenbach et al., 2006). However, with a
Bayesian calibration framework such as implemented in UCODE 2014, almost any model can be made
525 probabilistic. ~~Then the, so~~ uncertainties of parameters and outputs can be assessed, even for projections into the
future (Clifford et al., 2014). As this study focused on Bayesian calibration and we used an established model, we
mainly address ~~mainly the~~ parameter uncertainty, although input uncertainty was also included through the
weighting process. We clearly demonstrated an effect of the individual site used for Bayesian calibration on the
resulting model parameters and uncertainties. Similarly diverging site specific turnover rates were also found by
530 Ahrens et al. (2014) in a study of soil carbon in forests. Diverging results for different sites generally point towards
a need for a better understanding of the ~~modeled~~ modeled system and model improvements (Poeter et al., 2005),
but this often requires a deeper understanding of the system and new measurements – hence it is not always
feasible. A Bayesian calibration asks the question: “What would be the probability distribution of parameters,
given that the measured data should be represented by the selected model^{24,??}”. Hence, if only one site is used, it

535 can only answer this question for that specific site. As this study showed, the parameter set could then be highly
biased for other sites. For a more robust calibration, several sites should be combined to obtain posterior
distributions of parameters for a gradient of sites, though this might reduce model performance for individual sites.
The introduction of the equal weighting scheme, which gave similar weights to the different sites, highlights how
540 the highest uncertainties and it appears as if the Ultuna site had by far the strongest influence. In contrast to that,
the combination of all four sites with the original weights based on the error variances or measurements led to a
very clear reduction of parameter uncertainty and the narrowest parameter credibility intervals (**Figure 6 a**
compared to **b** and **c**).

The results of the statistical analysis of model errors (**Table 4**) suggests that the DSI is suitable for pool
545 initialization. This was corroborated by the Bayesian calibration, as the inclusion of the DSI narrowed credibility
intervals for the slow SOM pool turnover and humification efficiency and reduced the correlation between fast
and slow SOM turnover compared to the simulation without the DSI as constraint. Especially the clear distinction
between k_{SOM_slow} and k_{SOM_fast} shows the advantage of attaching a physiochemical meaning to the pools that was
not given before. Finding new and meaningful proxies is therefore crucial in addressing the equifinality originating
550 from the complex model structures and hence to reduce model uncertainty. While we demonstrated this with the
DSI, it is a general principle which others have used in similarly effective approaches, for example within a time
series of ^{14}C data (Ahrens et al., 2014) and the combination of several meaningful proxies would likely lead to the
best. Especially in the case of the clear differentiation between k_{SOM_slow} and k_{SOM_fast} , our results show the advantage
of attaching a physiochemical meaning to the pools that was not provided before. Other effective approaches, such
555 as time series of ^{14}C data could be combined with the DSI for better results.

Of all three parameters, the humification efficiency (f_{SOM_slow}) was the only parameter that consistently ran into the
upper boundaries, set to 35 %. In fact, initial calibrations were done where f_{SOM_slow} was constrained to 95 %; even
then, it tended to run into that constraint (**Figure S 8**) and led to much faster turnover rates (k_{SOM_slow}) than were
560 published before. These high values of f_{SOM_slow} were so far above much greater than the published 10 % for the
Mueller (1997) dataset and, 30 % for Bruun (2003) but also any-, and other published model, that this two pool
models. Therefore, the poorly constrained f_{SOM_slow} parameter was considered as caused by a model formulation
problem, which did not depend on whether the DSI was included in the Bayesian calibration or not. Only when
the humification efficiency was restricted in the Bayesian calibration, the turnover of fast and slow SOM aligned
with the earlier published rates. Only when the humification efficiency was restricted in the Bayesian calibration,
565 the turnover of fast and slow SOM aligned with the earlier published rates. If a parameter is problematic, such as
 f_{SOM_slow} , it could mean that there is a lack of data. However, if parameters are constrained, but run into implausible
values, it usually means that the model structure is suboptimal (Poeter et al., 2005) and should be altered.

4.3 Model structure determines SOM turnover times in two-pool models

The rate of SOM decomposition remains of major interest, especially with respect to the potential of SOM as a
570 global carbon sink (Minasny et al., 2017). First Some of the first conceptual approaches proposed SOM pools with
residence times of 1000 years and longer (e.g. in CENTURY, Parton et al., 1987) Parton et al., 1987), but the SOM
models were calibrated to fit data measured in long-term experiments that included vegetation. The pool structure
of early SOM models such as DAISY and CENTURY were rather similar as were the turnover rates of SOM pools

hat formatiert: Schriftart: Kursiv, Englisch (Vereinigte Staaten)

(see summary in **Table 5**). An improved understanding of actual amounts of carbon inputs to the soil, which still remain challenging to measure, led to faster turnover rates in more recent model versions (e.g. by Bruun, 2003). The reason is probably that inputs of carbon and nitrogen to the soil were often initially underestimated as it is very difficult to measure root turnover and rhizosphere exudation inputs without expensive in situ ¹³C or ¹⁴C labeling. The underestimated inputs were then likely counterbalanced in the model calibration by slower turnover rates resulting in acceptable model outputs (SOM dynamics and CO₂ emissions) for the time being. However, as our summary of more recent studies underlines (**Table 5**), the earlier published turnover rates seem to be subject to a systematic underestimation. As the comparison of our Bayesian calibration to other recent Bayesian calibration studies suggest, the relatively fast turnover rates of this study are in alignment with other recent findings (**Table 5**), as all five examples have published turnover rates for the slow SOM pool, which are at least one order of magnitude faster than early assumptions from the 1980s and 90s.

~~This also shows how~~ It is critical ~~it is~~ to understand model uncertainties and to test fundamental assumptions of how SOM is transferred between the pools (Sulman et al., 2018). The comparison between constrained and unconstrained humification efficiency in the Bayesian calibrations suggest that the sequential flow of carbon through the system might be assuming a condensation of stable carbon that does not actually explain the vast majority of ~~slow~~ more stable SOM formation.

From a theoretical perspective, one may wonder how large amounts of less complex SOM should become complex SOM without any involvement of living soil organisms. The way that the formation of complex carbon is represented in DAISY is probably a remainder of earlier humification theories from the 1990s that mostly ignored microbe involvement, while most of the recent studies suggest that the vast majority of SOM is of microbial origin (Cotrufo et al., 2013). A simple adaption for two-pool SOM models such as DAISY that include SMB pools could acknowledge this paradigm shift: The partitioning between slow and fast turnover SOM could be at the death of the microbial biomass (**Figure 7**) without any transfer of SOM from fast to slow pools. ~~(a brief test of this new structure is provided in the supplementary material Figure S 10).~~ This would also be in alignment with the DSI concept, as aliphatic carbon should not spontaneously transform to aromatic carbon on its own. Then DAISY would fit better to the DSI and other proxies linking measurable fractions to SOM pools (the same is true for CENTURY and other models, which apply the same humification principle). The way that pools are linked in the current setup, the actual turnover time of recalcitrant SOM consists of the turnover of the fast pool and the slow pool combined as it moves through these pools sequentially (**Figure 1**).

How strongly the basic assumptions influence SOM simulation is also reflected when differences between one- and two-SOM pool models are compared. The turnover rates of the one-pool models are in between those of slow and fast pools. However, our comparison shows that models with similar structure come to similar conclusions for SOM turnover. For example, the one-pool model in Clifford et al. (2014) was quite similar in turnover rates to that in Luo et al. (2016), but does not match well with two-pool models. Then again the rates for the two-pool models of this study, and the studies by Ahrens et al. (2014) and Hararuk et al. (2017) were very similar in their minima and maxima, for both the slow and fast SOM pools, which shows that only models with a similar number of pools and transformations could be compared.

The 95 % credibility intervals of half-lives in DAISY were in the range from 278 to 1095 years for the slow pool and from 47 to 90 years for the fast pool for the combination of sites presented here in this study. If these values

were reasonable – and as the three recent Bayesian calibrations including this study are quite close in turnover rates (Table 5), this seems to be the case, SOM could be lost at much faster rates under mismanagement and global warming than earlier modeling results suggest. The rates ~~still may~~ also be biased towards an underestimation of turnover, as even with intense efforts it is next to impossible to keep bare fallow plots completely free of vegetation (weeds) and roots from neighboring plots. Recent studies are in alignment with the possibility of relatively fast SOC loss across various scales from field scale (Poyda et al., 2019) to country scale, ~~for~~ For example in Germany, agricultural soils are much more often a carbon source than a sink (Jacobs et al., 2018). This highlights the importance of ~~proper~~adequate SOM management and a deeper understanding of the processes at different scales. Especially in the context of understanding the response of SOM to climate change it is not enough if the SOM balance is simulated appropriately, but also fluxes within the plant-soil system need to be quantified. The reason is that under a warmer climate and ~~dryer soils~~changing soil moisture levels, the plant-derived carbon inputs will change. Furthermore, soil enzymatic analysis at regional and field level (Ali et al., 2015, 2018) suggest that pools of different complexity have different temperature sensitivities (Lefèvre et al., 2014), which is also realized in new models (Hararuk et al., 2017). If ~~the~~ different pools ~~would~~ have different responses to temperature, the formula by Bruun and Jensen (2002) for SOM pool distribution could not be used anymore, as it implicitly assumes a similar temperature sensitivity for all pools. In ~~the~~ light of this, new proxies such as the DSI, soil fractionation or ¹⁴C use (Menichetti et al., 2016), which could also be combined, are crucial for making SOM pools chemically or physically meaningful and to reduce model uncertainty and equifinality. ~~As the DSI also had a good correlation with structurally protected SOM (Demyan et al., 2012) it could also fit very well to models that directly simulate the protection of SOM as a function of microbial activity (Sulman et al., 2014).~~ A better understanding and the use of meaningful proxies such as DRIFTS, pyrolysis with DRIFTS (Nkwain et al., 2018) or thermal deconvolution (Cécillon et al., 2018; Demyan et al., 2013) in combination with Bayesian calibration and a wide range of long-term experiments are needed. The discrepancy between simulating SOM of tropical and temperate soils, which ~~still~~ points towards a lack of understanding of fundamental difference in processes at work on the global scale would be the best test for future proxies and SOM models, which should be facilitated by freely available datasets for model testing and calibration.

5 Conclusion

We tested the use of the DRIFTS stability index as a proxy for initializing the two SOM pools in the DAISY model and used a Bayesian calibration to implement this proxy. A statistical analysis of model errors suggested that the DRIFTS stability index initialization significantly reduced model errors in most cases, especially ~~those~~ with initially poor performance. It therefore seems to be a robust proxy to distinguish between fast and slow cycling SOM in order to initialize two-pool models, and ~~also~~ adds ~~physiochemical~~physicochemical meaning to the pools. As ~~also~~ other studies ~~show~~have also shown, statistically sound approaches such as Bayesian calibration are needed to grasp the high uncertainty of SOM turnover, which is often neglected in ~~modelling~~modeling exercises. Meaningful proxies such as DRIFTS, physical/chemical fractionation or ¹⁴C are likely to be the most robust way to initialize SOM pools; ~~but their measurement method needs to be optimized to overcome known constraints, such as water and mineral interference in the case of DSI.~~ The results of this study suggest that the turnover of SOM could be much faster than assumed by ~~most~~commonly used SOM models. For example, the ~~95% credibility intervals of the~~DAISY slow SOM pool half-life ~~of this~~life estimated in our study ranged from 278 to 1095 years.

(95 % credibility intervals). The variability of parameters highlights the importance to include meaningful proxies into SOM models and to conduct research on a larger gradient of soils with bare fallow and planted sites, and over longer time frames.

655 6 Acknowledgements

This ~~work and manuscript were~~research was supported by the German Research Foundation (DFG) under the ~~project~~projects PAK 346 and the following FOR1695 “Agricultural Landscapes under Global Climate Change – Processes and Feedbacks on a Regional Scale” within subproject P3 (CA 598/6-1). We would like to thank Elke Schulz from the Department of Soil Ecology, Helmholtz Centre for Environmental Research in Halle/Saale for the provision of samples from Bad Lauchstädt. We would also like to thank Steffen Mehl, from the UCODE development team, for his help with the weighing of observations and the troubleshooting during the setup of UCODE_2014 on the bWUniCluster. Finally, we thank the editor and all reviewers, especially Lauric Cécillon for the fruitful discussions during the review process. The authors acknowledge support by the state of Baden-Württemberg through bwHPC.

665 7 Data availability

Data of SOC from Ultuna and Bad Lauchstädt ~~has~~have already been published in the last decades and ~~is~~are cited in the text. The data of Kraichgau and Swabian Jura has not been published yet, but is provided in the graphs. All measurements of DRIFTS are unpublished to this point. We are happy to make the full dataset publicly available, once accepted for publication.

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

670

8 References

Abramoff, R., Xu, X., Hartman, M., O'Brien, S., Feng, W., Davidson, E., Finzi, A., Moorhead, D., Schimel, J., Torn, M. and Mayes, M. A.: The Millennial model: in search of measurable pools and transformations for modeling soil carbon in the new century, *Biogeochemistry*, 137(1–2), 51–71, doi:10.1007/s10533-017-0409-7, 2018.

Ahrens, B., Reichstein, M., Borken, W., Muhr, J., Trumbore, S. E. and Wutzler, T.: Bayesian calibration of a soil organic carbon model using $\Delta^{14}\text{C}$ measurements of soil organic carbon and heterotrophic respiration as joint constraints, *Biogeosciences*, 11(8), 2147–2168, doi:10.5194/bg-11-2147-2014, 2014.

Ali, R. S., Ingwersen, J., Demyan, M. S., Funkuin, Y. N., Wizemann, H.-D., Kandeler, E. and Poll, C.: Modelling in situ activities of enzymes as a tool to explain seasonal variation of soil respiration from agro-ecosystems, *Soil Biol. Biochem.*, 81, 291–303, doi:10.1016/j.soilbio.2014.12.001, 2015.

Ali, R. S., Kandeler, E., Marhan, S., Demyan, M. S., Ingwersen, J., Mirzaeitalarposhti, R., Rasche, F., Cadisch, G. and Poll, C.: Controls on microbially regulated soil organic carbon decomposition at the regional scale, *Soil Biol. Biochem.*, 118(December 2017), 59–68, doi:10.1016/j.soilbio.2017.12.007, 2018.

Andrén, O. and Kätterer, T.: ICBM: The introductory carbon balance model for exploration of soil carbon balances, *Ecol. Appl.*, 7(4), 1226–1236, doi:10.1890/1051-0761(1997)007[1226:ITICBM]2.0.CO;2, 1997.

Bailey, V. L., Bond-Lamberty, B., DeAngelis, K., Grandy, A. S., Hawkes, C. V., Heckman, K., Lajtha, K., Phillips, R. P., Sulman, B. N., Todd-Brown, K. E. O. and Wallenstein, M. D.: Soil carbon cycling proxies: Understanding their

- critical role in predicting climate change feedbacks, *Glob. Chang. Biol.*, 24(3), 895–905, doi:10.1111/gcb.13926, 2018.
- 690 Barré, P., Plante, A. F., Cécillon, L., Lutfalla, S., Baudin, F., Bernard, S., Christensen, B. T., Eglin, T., Fernandez, J. M., Houot, S., Kätterer, T., Le Guillou, C., Macdonald, A., van Oort, F. and Chenu, C.: The energetic and chemical signatures of persistent soil organic matter, *Biogeochemistry*, 130(1–2), 1–12, doi:10.1007/s10533-016-0246-0, 2016.
- 695 Bruun, S. and Jensen, L. S.: Initialisation of the soil organic matter pools of the Daisy model, *Ecol. Modell.*, 153(3), 291–295, doi:10.17665/1676-4285.20155108, 2002.
- Bruun, S., Christensen, B. T., Hansen, E. M., Magid, J. and Jensen, L. S.: Calibration and validation of the soil organic matter dynamics of the Daisy model with data from the Askov long-term experiments, *Soil Biol. Biochem.*, 35(1), 67–76, doi:10.1016/S0038-0717(02)00237-7, 2003.
- 700 Campbell, E. E. E. and Paustian, K.: Current developments in soil organic matter modeling and the expansion of model applications: a review, *Environ. Res. Lett.*, 10(12), 123004, doi:10.1088/1748-9326/10/12/123004, 2015.
- Cécillon, L., Baudin, F., Chenu, C., Houot, S., Jolivet, R., Kätterer, T., Lutfalla, S., Macdonald, A., van Oort, F., Plante, A. F., Savignac, F., Soucémariadin, L. N. and Barré, P.: A model based on Rock-Eval thermal analysis to quantify the size of the centennially persistent organic carbon pool in temperate soils, *Biogeosciences*, 15(9), 2835–2849, doi:10.5194/bg-15-2835-2018, 2018.
- 705 Clifford, D., Pagendam, D., Baldock, J., Cressie, N., Farquharson, R., Farrell, M., Macdonald, L. and Murray, L.: Rethinking soil carbon modelling: a stochastic approach to quantify uncertainties, *Environmetrics*, 25(4), 265–278, doi:10.1002/env.2271, 2014.
- 710 Coleman, K. and Jenkinson, D. S.: RothC-26.3 - A Model for the turnover of carbon in soil, in *Evaluation of Soil Organic Matter Models*, pp. 237–246, Springer Berlin Heidelberg, Berlin, Heidelberg, 1996.
- Cotrufo, M. F., Wallenstein, M. D., Boot, C. M., Deneff, K. and Paul, E.: The Microbial Efficiency-Matrix Stabilization (MEMS) framework integrates plant litter decomposition with soil organic matter stabilization: do labile plant inputs form stable soil organic matter?, *Glob. Chang. Biol.*, 19(4), 988–995, doi:10.1111/gcb.12113, 2013.
- 715 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(2), 189–199, doi:10.1111/j.1365-2389.2011.01420.x, 2012.
- Demyan, M. S., Rasche, F., Schütt, M., Smirnova, N., Schulz, E. and Cadisch, G.: Combining a coupled FTIR-EGA system and in situ DRIFTS for studying soil organic matter in arable soils, *Biogeosciences*, 10(5), 2897–2913, doi:10.5194/bg-10-2897-2013, 2013.
- 720 Franko, U. and Merbach, I.: Modelling soil organic matter dynamics on a bare fallow Chernozem soil in Central Germany, *Geoderma*, 303(May), 93–98, doi:10.1016/j.geoderma.2017.05.013, 2017.
- Gelman, A. and Rubin, D. B.: Inference from Iterative Simulation Using Multiple Sequences, *Stat. Sci.*, 7(4), 457–472, doi:10.1214/ss/1177011136, 1992.
- 725 van Genuchten, M. T.: A comparison of numerical solutions of the one-dimensional unsaturated—saturated flow and mass transport equations, *Adv. Water Resour.*, 5(1), 47–55, doi:10.1016/0309-1708(82)90028-8, 1982.
- Giacometti, C., Demyan, M. S., Cavani, L., Marzadori, C., Ciavatta, C. and Kandeler, E.: Chemical and microbiological soil quality indicators and their potential to differentiate fertilization regimes in temperate agroecosystems, *Appl. Soil Ecol.*, 64, 32–48, doi:10.1016/j.apsoil.2012.10.002, 2013.
- 730 Good, W. D. and Smith, N. K.: Enthalpies of combustion of toluene, benzene, cyclohexane, cyclohexene, methylcyclopentane, 1-methylcyclopentene, and n-hexane, *J. Chem. Eng. Data*, 14(1), 102–106, doi:10.1021/je60040a036, 1969.
- Hansen, S., Jensen, L. S., Nielsen, N. E. and Svendsen, H.: *DAISY - Soil Plant Atmosphere System Model*, Copenhagen: The Royal Veterinary and Agricultural University, 1990.
- Hararuk, O., Shaw, C. and Kurz, W. A.: Constraining the organic matter decay parameters in the CBM-CFS3 using

- 735 Canadian National Forest Inventory data and a Bayesian inversion technique, *Ecol. Modell.*, 364, 1–12, doi:10.1016/j.ecolmodel.2017.09.008, 2017.
- Heinlein, F., Biernath, C., Klein, C., Thieme, C. and Priesack, E.: Evaluation of Simulated Transpiration from Maize Plants on Lysimeters, *Vadose Zo. J.*, 16(1), 0, doi:10.2136/vzj2016.05.0042, 2017.
- 740 Herbst, M., Welp, G., Macdonald, A., Jate, M., Hädicke, A., Scherer, H., Gaiser, T., Herrmann, F., Amelung, W. and Vanderborght, J.: Correspondence of measured soil carbon fractions and RothC pools for equilibrium and non-equilibrium states, *Geoderma*, 314(November 2017), 37–46, doi:10.1016/j.geoderma.2017.10.047, 2018.
- Jacobs, A., Flessa, H., Don, A., Heidkamp, A., Prietz, R., Dechow, R., Gensior, A., Poeplau, C., Riggers, C., Schneider, F., Tiemeyer, B., Vos, C., Wittnebel, M., Müller, T., Säurich, A., Fahrion-Nitschke, A., Gebbert, S., Hopfstock, R., Jaconi, A., Kolata, H., Lorbeer, M., Schröder, J., Laggner, A., Weiser, C. and Freibauer, A.: Landwirtschaftlich genutzte Böden in Deutschland – Ergebnisse der Bodenzustandserhebung - Thünen Report 64, Johann Heinrich von Thünen-Institut, Bundesallee 50, 38116 Braunschweig, Germany., 2018.
- 745 Jensen, L. S., Mueller, T., Nielsen, N. E., Hansen, S., Crocker, G. J., Grace, P. R., Klír, J., Körschens, M. and Poulton, P. R.: Simulating trends in soil organic carbon in long-term experiments using the soil-plant-atmosphere model DAISY, *Geoderma*, 81(1), 5–28, doi:http://dx.doi.org/10.1016/S0016-7061(97)88181-5, 1997.
- 750 Joergensen, R. G. and Mueller, T.: The fumigation-extraction method to estimate soil microbial biomass: Calibration of the kEC value, *Soil Biol. Biochem.*, 28(1), 25–31, doi:10.1016/0038-0717(95)00102-6, 1996.
- Kätterer, T., Bolinder, M. A., Andrén, O., Kirchmann, H. and Menichetti, L.: Roots contribute more to refractory soil organic matter than above-ground crop residues, as revealed by a long-term field experiment, *Agric. Ecosyst. Environ.*, 141(1–2), 184–192, doi:10.1016/j.agee.2011.02.029, 2011.
- 755 Kirchmann, H., Haberhauer, G., Kandeler, E., Sessitsch, A. and Gerzabek, M. H.: Effects of level and quality of organic matter input on carbon storage and biological activity in soil: Synthesis of a long-term experiment, *Global Biogeochem. Cycles*, 18(4), n/a-n/a, doi:10.1029/2003GB002204, 2004.
- Klein, C., Biernath, C., Heinlein, F., Thieme, C., Gilgen, A. K., Zeeman, M. and Priesack, E.: Vegetation Growth Models Improve Surface Layer Flux Simulations of a Temperate Grassland, *Vadose Zo. J.*, 16(13), 0, doi:10.2136/vzj2017.03.0052, 2017.
- 760 Klein, C. G.: Modeling fluxes of energy and water between land surface and atmosphere for grass- and cropland system, Fakultät Wissenschaftszentrum Weihenstephan., 2018.
- Kozak, M. and Piepho, H. P.: What's normal anyway? Residual plots are more telling than significance tests when checking ANOVA assumptions, *J. Agron. Crop Sci.*, 204(1), 86–98, doi:10.1111/jac.12220, 2018.
- 765 Laub, M., Blagodatsky, S., Nkwain, Y. F. and Cadisch, G.: Soil sample drying temperature affects specific organic mid-DRIFTS peaks and quality indices, *Geoderma*, 355, 113897, doi:10.1016/j.geoderma.2019.113897, 2019.
- Lefèvre, R., Barré, P., Moyano, F. E., Christensen, B. T., Bardoux, G., Eglin, T., Girardin, C., Houot, S., Kätterer, T., van Oort, F. and Chenu, C.: Higher temperature sensitivity for stable than for labile soil organic carbon - Evidence from incubations of long-term bare fallow soils, *Glob. Chang. Biol.*, 20(2), 633–640, doi:10.1111/gcb.12402, 2014.
- 770 Lu, D., Ye, M. and Hill, M. C.: Analysis of regression confidence intervals and Bayesian credible intervals for uncertainty quantification, *Water Resour. Res.*, 48(9), 1–20, doi:10.1029/2011WR011289, 2012.
- Lu, D., Ye, M., Hill, M. C., Poeter, E. P. and Curtis, G. P.: A computer program for uncertainty analysis integrating regression and Bayesian methods, *Environ. Model. Softw.*, 60(October), 45–56, doi:10.1016/j.envsoft.2014.06.002, 2014.
- 775 Luo, Z., Wang, E., Shao, Q., Conyers, M. K. and Liu, D. L.: Confidence in soil carbon predictions undermined by the uncertainties in observations and model parameterisation, *Environ. Model. Softw.*, 80, 26–32, doi:10.1016/j.envsoft.2016.02.013, 2016.
- 780 Margenot, A. J., Calderón, F. J., Bowles, T. M., Parikh, S. J. and Jackson, L. E.: Soil Organic Matter Functional Group Composition in Relation to Organic Carbon, Nitrogen, and Phosphorus Fractions in Organically Managed Tomato Fields, *Soil Sci. Soc. Am. J.*, 79(3), 772, doi:10.2136/sssaj2015.02.0070, 2015.

- Menichetti, L., Kätterer, T. and Leifeld, J.: Parametrization consequences of constraining soil organic matter models by total carbon and radiocarbon using long-term field data, *Biogeosciences*, 13(10), 3003–3019, doi:10.5194/bg-13-3003-2016, 2016.
- 785 Minasny, B., Malone, B. P., McBratney, A. B., Angers, D. A., Arrouays, D., Chambers, A., Chaplot, V., Chen, Z.-S., Cheng, K., Das, B. S., Field, D. J., Gimona, A., Hedley, C. B., Hong, S. Y., Mandal, B., Marchant, B. P., Martin, M., McConkey, B. G., Mulder, V. L., O'Rourke, S., Richer-de-Forges, A. C., Odeh, I., Padarian, J., Paustian, K., Pan, G., Poggio, L., Savin, I., Stolbovoy, V., Stockmann, U., Sulaeman, Y., Tsui, C.-C., Vågen, T.-G., van Wesemael, B. and Winowicki, L.: Soil carbon 4 per mille, *Geoderma*, 292, 59–86, doi:10.1016/j.geoderma.2017.01.002, 2017.
- 790 Mirzaeitalarposhti, R., Demyan, M. S., Rasche, F., Cadisch, G. and Müller, T.: Overcoming carbonate interference on labile soil organic matter peaks for midDRIFTS analysis, *Soil Biol. Biochem.*, 99, 150–157, doi:10.1016/j.soilbio.2016.05.010, 2016.
- Monteith, J. L.: Evaporation and surface temperature, *Q. J. R. Meteorol. Soc.*, 12, 513–522, doi:10.1002/qj.49710745102, 1976.
- 795 Mualem, Y.: A new model for predicting the hydraulic conductivity of unsaturated porous media, *Water Resour. Res.*, 12(3), 513–522, doi:10.1029/WR012i003p00513, 1976.
- Mueller, T., Jensen, L. S. S., Magid, J. and Nielsen, N. E. E.: Temporal variation of C and N turnover in soil after oilseed rape straw incorporation in the field: simulations with the soil-plant-atmosphere model DAISY, *Ecol. Modell.*, 99(2), 247–262, doi:http://dx.doi.org/10.1016/S0304-3800(97)01959-5, 1997.
- 800 Mueller, T., Magid, J., Jensen, L. S., Svendsen, H. and Nielsen, N. E.: Soil C and N turnover after incorporation of chopped maize, barley straw and blue grass in the field: Evaluation of the DAISY soil–organic-matter submodel, *Ecol. Modell.*, 111(1), 1–15, doi:10.1016/S0304-3800(98)00094-5, 1998.
- Nguyen, T., Janik, L. and Raupach, M.: Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy in soil studies, *Soil Res.*, 29(1), 49, doi:10.1071/SR9910049, 1991.
- 805 Nkwain, F. N., Demyan, M. S., Rasche, F., Dignac, M.-F., Schulz, E., Kätterer, T., Müller, T. and Cadisch, G.: Coupling pyrolysis with mid-infrared spectroscopy (Py-MIRS) to fingerprint soil organic matter bulk chemistry, *J. Anal. Appl. Pyrolysis*, 133(April 2017), 176–184, doi:10.1016/j.jaap.2018.04.004, 2018.
- 810 Nocita, M., Stevens, A., van Wesemael, B., Aitkenhead, M., Bachmann, M., Barthès, B., Ben Dor, E., Brown, D. J., Clairotte, M., Csorba, A., Dardenne, P., Demattê, J. A. M., Genot, V., Guerrero, C., Knadel, M., Montanarella, L., Noon, C., Ramirez-Lopez, L., Robertson, J., Sakai, H., Soriano-Disla, J. M., Shepherd, K. D., Stenberg, B., Towett, E. K., Vargas, R. and Wetterlind, J.: Soil Spectroscopy: An Alternative to Wet Chemistry for Soil Monitoring, in *Advances in Agronomy*, vol. 132, pp. 139–159., 2015.
- O'Leary, G. J., Liu, D. L., Ma, Y., Li, F. Y., McCaskill, M., Conyers, M., Dalal, R., Reeves, S., Page, K., Dang, Y. P. and Robertson, F.: Modelling soil organic carbon 1. Performance of APSIM crop and pasture modules against long-term experimental data, *Geoderma*, 264(November 2015), 227–237, doi:10.1016/j.geoderma.2015.11.004, 815 2016.
- Parton, W. J., Schimel, D. S., Cole, C. V. and Ojima, D. S.: Analysis of Factors Controlling Soil Organic Matter Levels in Great Plains Grasslands, *Soil Sci. Soc. Am. J.*, 51(5), 1173, doi:10.2136/sssaj1987.03615995005100050015x, 1987.
- 820 Parton, W. J., Scurlock, J. M. O., Ojima, D. S., Gilmanov, T. G., Scholes, R. J., Schimel, D. S., Kirchner, T., Menaut, J.-C., Seastedt, T., Garcia Moya, E., Kamnalrut, A. and Kinyamario, J. I.: Observations and modeling of biomass and soil organic matter dynamics for the grassland biome worldwide, *Global Biogeochem. Cycles*, 7(4), 785–809, doi:10.1029/93GB02042, 1993.
- Piepho, H. P., Büchse, A. and Richter, C.: A Mixed Modelling Approach for Randomized Experiments with Repeated Measures, *J. Agron. Crop Sci.*, 190(4), 230–247, doi:10.1111/j.1439-037X.2004.00097.x, 2004.
- 825 Poeplau, C., Don, A., Dondini, M., Leifeld, J., Nemo, R., Schumacher, J., Senapati, N. and Wiesmeier, M.: Reproducibility of a soil organic carbon fractionation method to derive RothC carbon pools, *Eur. J. Soil Sci.*, 64(6), 735–746, doi:10.1111/ejss.12088, 2013.

- Poeter, E. P., Hill, M. C., Banta, E. R., Mehl, S. and Christensen, S.: UCODE_2005 and six other computer codes for universal sensitivity analysis, inverse modeling, and uncertainty evaluation, U.S. Geological Survey Techniques and Methods 6-A11, 283p. (As updated in Feb 2008), 2005.
- 830 Poeter, E. P., Hill, M. C., Lu, D., Tiedeman, C. R. and Mehl, S.: UCODE_2014, with New Capabilities to Define Parameters Unique to Predictions, Calculate Weights using Simulated Values, Estimate Parameters with SVD, Evaluate Uncertainty with MCMC, and More, Integrated Groundwater Modeling Center Report Number: GWMI 2014-02., 2014.
- 835 Poyda, A., Wizemann, H.-D., Ingwersen, J., Eshonkulov, R., Högy, P., Demyan, M. S., Kremer, P., Wulfmeyer, V. and Streck, T.: Carbon fluxes and budgets of intensive crop rotations in two regional climates of southwest Germany, *Agric. Ecosyst. Environ.*, 276, 31–46, doi:10.1016/j.agee.2019.02.011, 2019.
- ~~Puttaso, A., Vityakon, P., Rasche, F., Saenjan, P., Treloges, V. and Cadisch, G.: Does Organic Residue Quality Influence Carbon Retention in a Tropical Sandy Soil?, *Soil Sci. Soc. Am. J.*, 77(3), 1001, doi:10.2136/sssaj2012.0209, 2013.~~
- 840 S. Hansen, P. Abrahamsen, C. T. Petersen and M. Styczen: Daisy: Model Use, Calibration, and Validation, *Trans. ASABE*, 55(4), 1317–1335, doi:10.13031/2013.42244, 2012.
- Segoli, M., De Gryze, S., Dou, F., Lee, J., Post, W. M., Deneff, K. and Six, J.: AggModel: A soil organic matter model with measurable pools for use in incubation studies, *Ecol. Modell.*, 263, 1–9, doi:10.1016/j.ecolmodel.2013.04.010, 2013.
- 845 Sohi, S. P., Mahieu, N., Arah, J. R. M., Powelson, D. S., Madari, B. and Gaunt, J. L.: A Procedure for Isolating Soil Organic Matter Fractions Suitable for Modeling, *Soil Sci. Soc. Am. J.*, 65(4), 1121, doi:10.2136/sssaj2001.6541121x, 2001.
- Sulman, B. N., Phillips, R. P., Oishi, A. C., Shevliakova, E. and Pacala, S. W.: Microbe-driven turnover offsets mineral-mediated storage of soil carbon under elevated CO₂, *Nat. Clim. Chang.*, 4(12), 1099–1102, doi:10.1038/nclimate2436, 2014.
- 850 Sulman, B. N., Moore, J. A. M., Abramoff, R., Averill, C., Kivlin, S., Georgiou, K., Sridhar, B., Hartman, M. D., Wang, G., Wieder, W. R., Bradford, M. A., Luo, Y., Mayes, M. A., Morrison, E., Riley, W. J., Salazar, A., Schimel, J. P., Tang, J. and Classen, A. T.: Multiple models and experiments underscore large uncertainty in soil carbon dynamics, *Biogeochemistry*, 141(2), 109–123, doi:10.1007/s10533-018-0509-z, 2018.
- 855 Tinti, A., Tugnoli, V., Bonora, S. and Francioso, O.: Recent applications of vibrational mid-infrared (IR) spectroscopy for studying soil components: A review, *J. Cent. Eur. Agric.*, 16(1), 1–22, doi:10.5513/JCEA01/16.1.1535, 2015.
- Vrugt, J. A.: Markov chain Monte Carlo simulation using the DREAM software package: Theory, concepts, and MATLAB implementation, *Environ. Model. Softw.*, 75, 273–316, doi:10.1016/j.envsoft.2015.08.013, 2016.
- 860 Wattenbach, M., Gottschalk, P., Hattermann, F., Rachimow, C., Flechsig, M. and Smith, P.: A framework for assessing uncertainty in ecosystem models, in (eds). Proceedings of the iEMSS Third Biennial Meeting: “Summit on Environmental Modelling and Software”. International Environmental Modelling and Software Society, Burlington, USA, July 2006. CD ROM. Internet: <http://www.iemss.org/iemss2006/sessions/all>, 2006.
- 865 Wizemann, H.-D., Ingwersen, J., Högy, P., Warrach-Sagi, K., Streck, T. and Wulfmeyer, V.: Three year observations of water vapor and energy fluxes over agricultural crops in two regional climates of Southwest Germany, *Meteorol. Zeitschrift*, 24(1), 39–59, doi:10.1127/metz/2014/0618, 2015.
- 870 Yeasmin, S., Singh, B., Johnston, C. T. and Sparks, D. L.: Evaluation of pre-treatment procedures for improved interpretation of mid infrared spectra of soil organic matter, *Geoderma*, 304, 83–92, doi:10.1016/j.geoderma.2016.04.008, 2017.
- Zimmermann, M., Leifeld, J., Schmidt, M. W. I., Smith, P. and Fuhrer, J.: Measured soil organic matter fractions can be related to pools in the RothC model, *Eur. J. Soil Sci.*, 58(3), 658–667, doi:10.1111/j.1365-2389.2006.00855.x, 2007.

9 Tables

Table 1 Locations, descriptions, and initial soil organic carbon (SOC) stocks of *Study Sites used study sites*

Study Site	UTM Degrees Lat	UTM Degrees Long	Soil type	Depth of measurements (cm)	Clay (%)	Silt (%)	Initial SOC (%)	Bulk density (Mg/m ³)	Initial SOC stocks in the measured depth (Mg/ha)	Years of bulk soil availability	Types of available measurements
Ultuna	59.821879	17.656348	Eutric Cambisol	0 - 20	37	41	1.50	1.44	43.22	1956, 79, 95, 2005	SOC, DRIFTS
Bad Lauchstädt	51.391605	11.877028	Haplic Chernozem	0 - 20	21	68	1.82	1.24	45.08	1985, 2001, 04, 08	SOC, DRIFTS
Kraichgau 1	48.928517	8.702794	Stagnic Luvisol	0 - 30	18	97	0.90	1.37	37.10	2009 - 16	SOC, DRIFTS, SMB-C
Kraichgau 2	48.927748	8.708884	Stagnic Luvisol	0 - 30	18	80	1.04	1.33	41.61	2009 - 16	SOC, DRIFTS, SMB-C
Kraichgau 3	48.927197	8.715891	Stagnic Luvisol	0 - 30	17	81	0.89	1.44	38.50	2009 - 16	SOC, DRIFTS, SMB-C
Swabian Jura 1	48.527510	9.769429	Calcic Luvisol	0 - 30	38	56	1.78	1.32	70.33	2009 - 16	SOC, DRIFTS, SMB-C
Swabian Jura 2	48.529857	9.773253	Anthrosol	0 - 30	29	68	1.95	1.38	80.85	2009 - 13	SOC, DRIFTS, SMB-C
Swabian Jura 3	48.547035	9.773176	Rendzic Leptosol	0 - 30	45	51	1.91	1.07	61.27	2009 - 13	SOC, DRIFTS, SMB-C

SOC = soil organic carbon, DRIFTS = Diffuse reflectance mid infrared Fourier transform spectroscopy, SMB-C = soil microbial biomass carbon

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

Formatierte Tabelle

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

Table 2 Values of the two initial parameter sets for the DAISY SOM model that were used in this study. A graphical display of the model structure related to these pools and with the most important parameters for this study is found in Figure 1.

Parameter	Default DAISY	Bruun (2003)	Unit
kSOM slow	2.70 * 10 ⁻⁶ #	4.30 * 10 ⁻⁵ x	d ⁻¹
kSOM fast	1.40 * 10 ⁻⁴ #	1.40 * 10 ⁻⁴ #	d ⁻¹
kSMB slow	1.85 * 10 ⁻⁴ *	1.85 * 10 ⁻⁴ *	d ⁻¹
kSMB fast	1.00 * 10 ⁻² *	1.00 * 10 ⁻² *	d ⁻¹
kAOM slow	0.012 *	0.012 *	d ⁻¹
kAOM fast	0.05 *	0.05 *	d ⁻¹
maint SMB slow	1.80 * 10 ⁻³ *	1.80 * 10 ⁻³ *	d ⁻¹
maint SMB fast	1.00 * 10 ⁻² *	1.00 * 10 ⁻² *	d ⁻¹
CUE SMB	0.60 #	0.60 #	kg kg ⁻¹
CUE SOM slow	0.40 *	0.40 *	kg kg ⁻¹
CUE SOM fast	0.50 *	0.50 *	kg kg ⁻¹
CUE AOM slow	0.13 *	0.13 *	kg kg ⁻¹
CUE AOM fast	0.69 *	0.69 *	kg kg ⁻¹
<i>f</i> _{SOM slow} (humification efficiency)	0.10 #	0.30 x	kg kg ⁻¹
part SMB > SOM_fast	0.40 #	0.40 #	kg kg ⁻¹
fraction of SOM_slow at steady state Bruun (2002) equation	0.8483	0.49	kg kg ⁻¹

k = turnover rate, maint = maintenance respiration, CUE = carbon use efficiency, AOM = added organic matter (not considered in this study), part = partitioning; Source: # original Jensen (1997), * modified by Müller (1997), x modified by Bruun (2003)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

Formatierte Tabelle

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

Table 3 Soil properties at the start and end of the bare fallow experiment at each site

Site	Start (year)	End (year)	Depth of modelled layer (cm)	Bulk density of modelled layer (tMg/m ³)	SOC at start (tMg/ha)	SOC at end (tMg/ha)	SMB-C at start (tMg/ha)	SMB-C at end (tMg/ha)	DRIFTS SOM in slow % at start (105°C)	DRIFTS SOM in slow % at end (105°C)	%SOMSOC loss of initial	Number of years	%SOMSOC loss per year of initial
Ultuna	1956	2005	0 - 20	1.44	43.22	26.51	XNA	XNA	54	91	39%	50	0.8%
Bad Lauchstädt	1983	2008	0 - 20	1.24	45.08	41.91	XNA	XNA	70	80	7%	26	0.3%
Kraichgau 1	2009	2015	0 - 30	1.37	37.10	32.59	0.847	0.408	80	98	12%	7	1.7%
Kraichgau 2	2009	2015	0 - 30	1.33	41.61	38.66	0.853	0.314	73	93	7%	7	1.0%
Kraichgau 3	2009	2015	0 - 30	1.44	38.50	35.06	0.672	0.261	76	99	9%	7	1.3%
Swabian Jura 1	2009	2015	0 - 30	1.32	70.33	63.29	1.566	0.654	64	83	10%	7	1.4%
Swabian Jura 2	2009	2013	0 - 30	1.38	80.85	79.61	1.805	0.970	66	83	2%	5	0.3%
Swabian Jura 3	2009	2013	0 - 30	1.07	61.27	70.29	1.350	0.990	61	76	-15%	5	-2.9%

XNA = no data available for this site

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Schriftart: Nicht Fett, Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

Table 4. Least square means of the (~~backtransformed~~ transformed) absolute error of DAISY bare-fallow simulations for SOC and SMB-C for Ultuna, Bad Lauchstädt and Kraichgau + Swabian Jura combined. The values are the estimate for the end of the simulation period (number of years in brackets). Different capital letters indicate significant differences ($p < 0.05$) within columns (not tested between sites). For Bad Lauchstädt, the initialization effect was ~~nonsignificant~~ non-significant, so only the least square means for the effect of the parameter set is displayed.

Parameter set	Initialization	Ultuna (50yr)	Bad Lauchstädt (23yr)	Kraichgau + Swabian Jura (7 yr)	Kraichgau + Swabian Jura (7 yr)
		Least square means of errors (SOC tMg/ha)	Backtransformed transformed least square means of errors (SOC tMg/ha)	Backtransformed transformed least square means of errors (SOC tMg/ha)	Least square means of errors (SMB-C tMg/ha)
Mueller (1997)	ratio of steady state assumption	13.91 ^A		4.50 ^A	0.354 ^A
	peak ratio of DRIFTS at 32°C	10.86 ^B	2.22 ^A	4.50 ^A	0.317 ^{AB}
	peak ratio of DRIFTS at 65°C	10.06 ^C		4.42 ^A	0.274 ^{ABC}
	peak ratio of DRIFTS at 105°C	8.52 ^D		4.28 ^A	0.205 ^{CD}
	ratio of steady state assumption	5.84 ^H		3.12 ^B	0.231 ^{BCD}
Bruun (2003)	peak ratio of DRIFTS at 32°C	7.06 ^E	6.01 ^B	3.31 ^B	0.179 ^{CDE}
	peak ratio of DRIFTS at 65°C	6.75 ^F		3.30 ^B	0.160 ^{DE}
	peak ratio of DRIFTS at 105°C	6.15 ^G		3.25 ^B	0.131 ^E

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

Formatierte Tabelle

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

Table 5 Optimized turnover rates and humification efficiency of this study using the combined site analysis with original weighting and DSI compared to other Bayesian calibrations and standard values of commonly used models. If the temperature function was given or site temperature specified, the turnover rates were normalized with an exponential equation to 10°C which is standard in DAISY.

model/Model	DAISY	ICBM	CBM-CFS3	APSIM	own creation	CENTURY	DAISY	DAISY
reference/Reference	This study	Ahrens	Hararuk	Luo	Clifford	Parton	Mueller	Bruun
year/Year	2019	2014	2017	2016	2014	1993	1997	2003
turnover/Turnover rates of the fast pool (recalculated to d ⁻¹ at 10°C)								
minimum	1.07 * 10 ⁻⁴	4.57 * 10 ⁻⁴	6.30 * 10 ⁻⁴	NA	NA - no			
optimum	2.29 * 10 ⁻⁴	4.57 * 10 ⁻³	1.97 * 10 ⁻⁴	NA	temperature	9.32 * 10 ⁻⁵	1.40 * 10 ⁻⁴	1.40 * 10 ⁻⁴
maximum	3.27 * 10 ⁻⁴	2.28 * 10 ⁻²	1.05 * 10 ⁻³	NA	found			
turnover/Turnover rates of the slow pool (recalculated to d ⁻¹ at 10°C)								
minimum	2.99 * 10 ⁻⁶	4.57 * 10 ⁻⁷	9.86 * 10 ⁻⁶	1.00 * 10 ⁻⁴	1.10 * 10 ⁻⁴			
optimum	3.25 * 10 ⁻⁵	2.28 * 10 ⁻⁵	1.10 * 10 ⁻⁵	3.00 * 10 ⁻⁴	1.67 * 10 ⁻⁴	2.10 * 10 ⁻⁶	2.70 * 10 ⁻⁶	4.30 * 10 ⁻⁶
maximum	6.14 * 10 ⁻⁵	4.57 * 10 ⁻⁵	1.32 * 10 ⁻⁵	6.00 * 10 ⁻⁴	2.19 * 10 ⁻⁴			
portion/Portion of fast to slow pool (humification efficiency)								
minimum	0.05	0.05						
optimum	0.34	0.2				0.3	0.1	
maximum	0.35	0.35						

References: (Ahrens et al., 2014; Bruun et al., 2003; Clifford et al., 2014; Hararuk et al., 2017; Luo et al., 2016; Mueller et al., 1997; Parton et al., 1993)

- hat formatiert: Englisch (Vereinigte Staaten)
- Formatierte Tabelle
- hat formatiert: Englisch (Vereinigte Staaten)
- hat formatiert: Englisch (Vereinigte Staaten)
- hat formatiert: Englisch (Vereinigte Staaten)
- hat formatiert: Englisch (Vereinigte Staaten)
- hat formatiert: Englisch (Vereinigte Staaten)
- hat formatiert: Englisch (Vereinigte Staaten)
- hat formatiert: Englisch (Vereinigte Staaten)
- hat formatiert: Englisch (Vereinigte Staaten)
- hat formatiert: Englisch (Vereinigte Staaten)

10 Figures

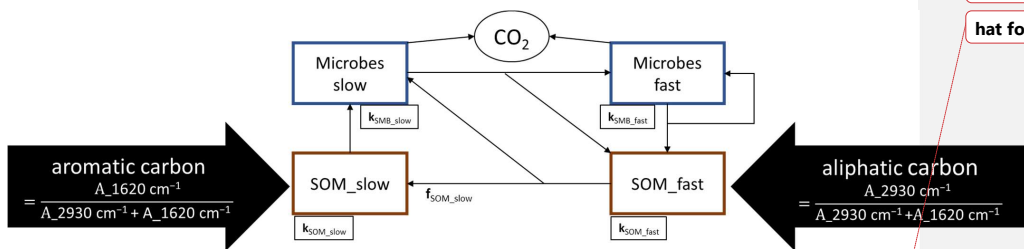


Figure 1 Original structure of the internal cycling of SOM in the DAISY model, as it was used in this study. $A_{XXXX} \text{ cm}^{-1}$ is the area of each peak obtained by DRIFTS. k_{SOM} and k_{SMB} are turnover rates of the pools and f_{SOM_slow} is the humification efficiency. Other model parameters are can be found in Table 2.

hat formatiert: Englisch (Vereinigte Staaten)

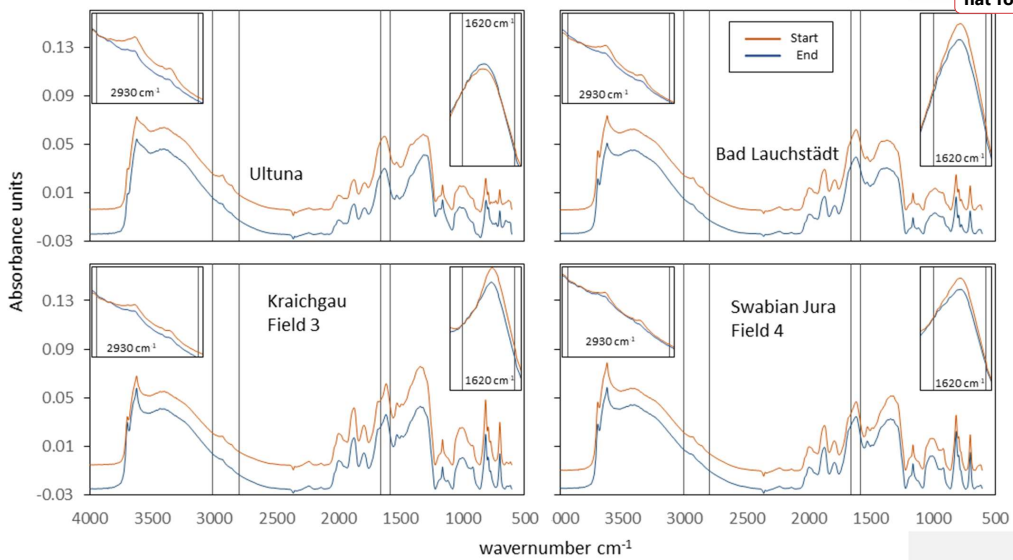
hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Englisch (Vereinigte Staaten)

hat formatiert: Schriftart: Kursiv

hat formatiert: Schriftart: Kursiv

hat formatiert: Schriftart: Kursiv



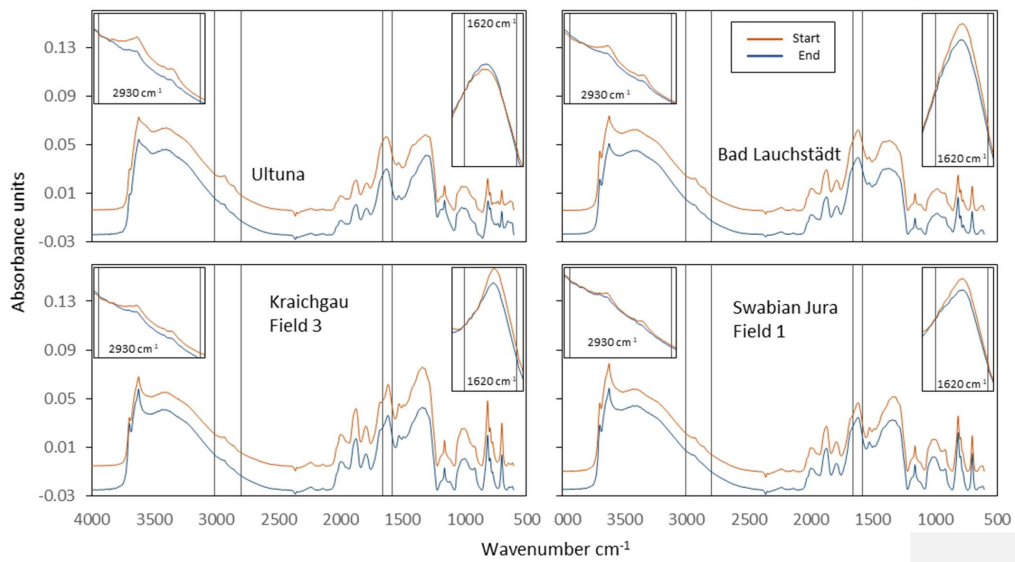
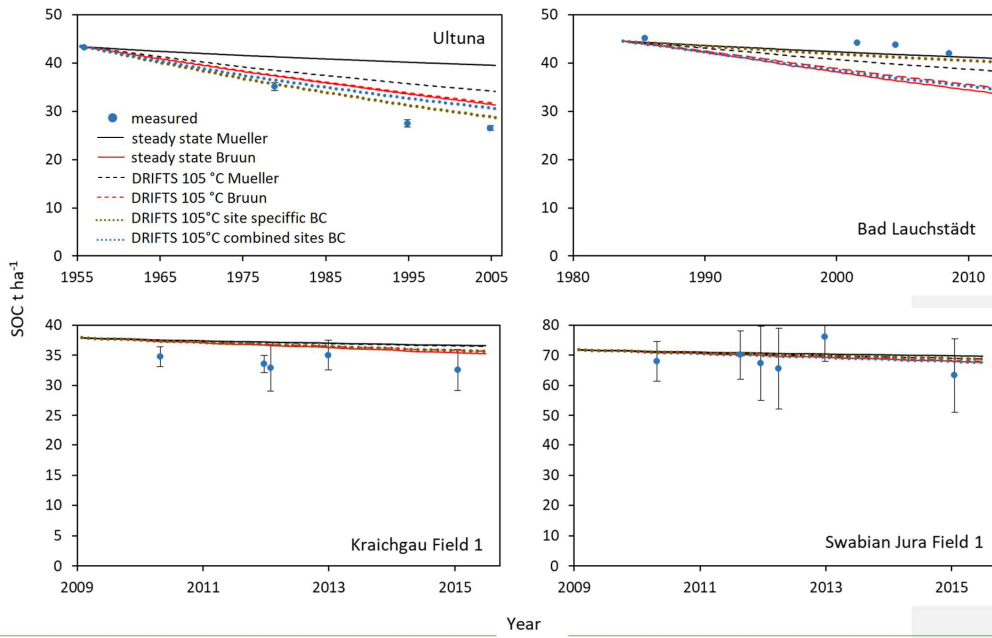


Figure 2 DRIFTS baseline corrected and vector normalized ~~exampleexamples of~~ spectra of bulk soil samples (dried at 105°C) of the first and last year of the bare fallow plots at four sites. Fallow periods were 50 years (Ultuna), 24 years (Bad Lauchstädt) and 7 years (Kraichgau and Swabian Jura). Small pictures on the top left and right, are zoomed in versions of the 2930cm⁻¹ peak and the 1620cm⁻¹ peak, respectively. For better visibility, the full spectra pictures have a y-axis offset, while zoomed in versions share a common baseline. More details on the sites in Table 3.

hat formatiert: Englisch (Vereinigte Staaten)



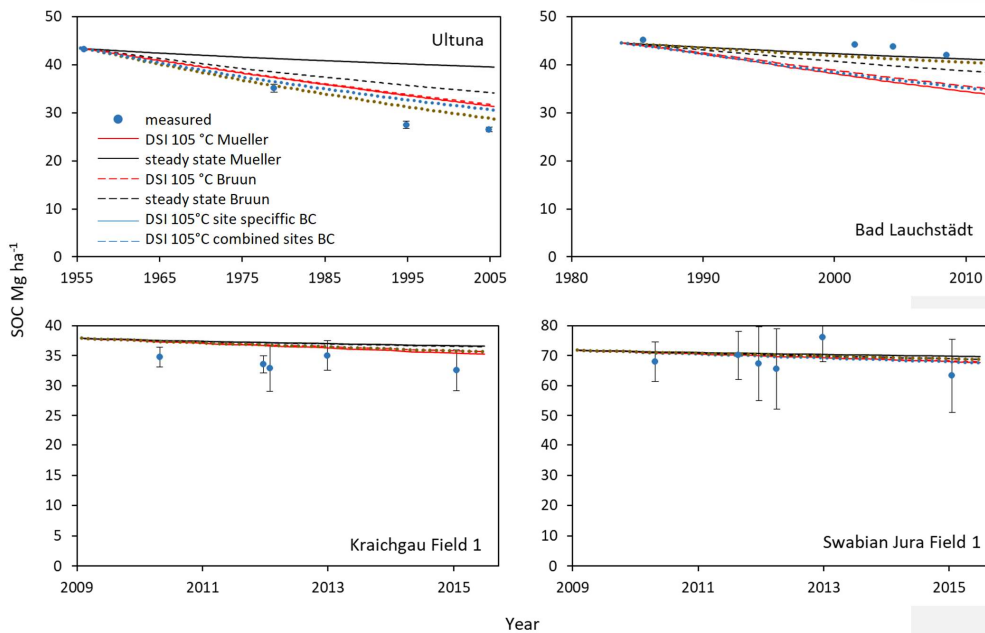
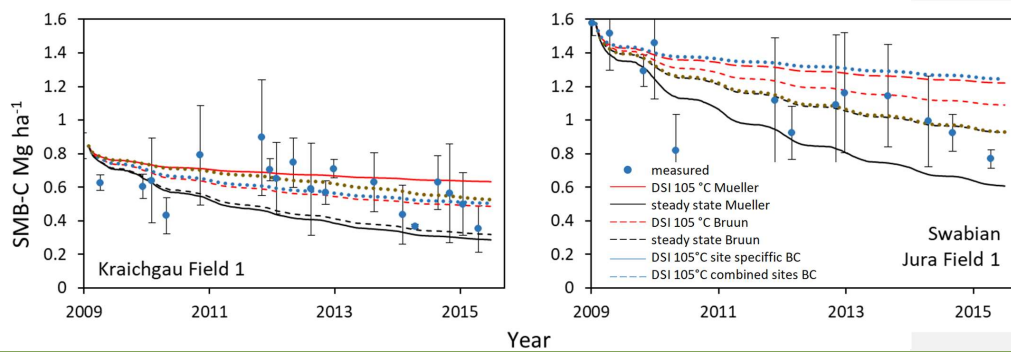


Figure 3 Example of SOC simulations from Ultuna (top left), Bad Lauchstädt (top right), Kraichgau field 1 (bottom left) and Swabian Jura Field 1 (bottom right). Initializations were done (i) assuming steady state using the formula of Bruun and Jensen (2002) (equation 1) with both turnover rates of Mueller et al. (1997) and Bruun et al. (2003) and (ii) by the DRIFTS stability index (DSI) at 105°C drying temperature using both turnover rates for simulations (simulations using the other drying temperatures for DSI in the supplementary). The site specific and the combination of all sites Bayesian calibrations (BC) are also displayed. Example of SOC simulations from Ultuna (top left), Bad Lauchstädt (top right), Kraichgau field 1 (bottom left) and Swabian Jura Field 1 (bottom right). Initializations were done (i) assuming steady state using the formula of Bruun and Jensen, (2002) (equation 1) with both turnover rates of Mueller et al., (1997) and Bruun et al., (2003) and (ii) by the ratio of the 2930 cm^{-1} to the 1620 cm^{-1} peak of DRIFTS spectra Bars indicate the standard deviation of measured values of all plots (n = 3) per field.

hat formatiert: Englisch (Vereinigte Staaten)



at 105°C drying temperature using both turnover rates for simulations (simulations using the other drying temperatures for DRIFTS in the supplementary). The site specific and the combination of all sites Bayesian calibrations (BC) are also displayed. Bars indicate standard deviation of all plots per field.

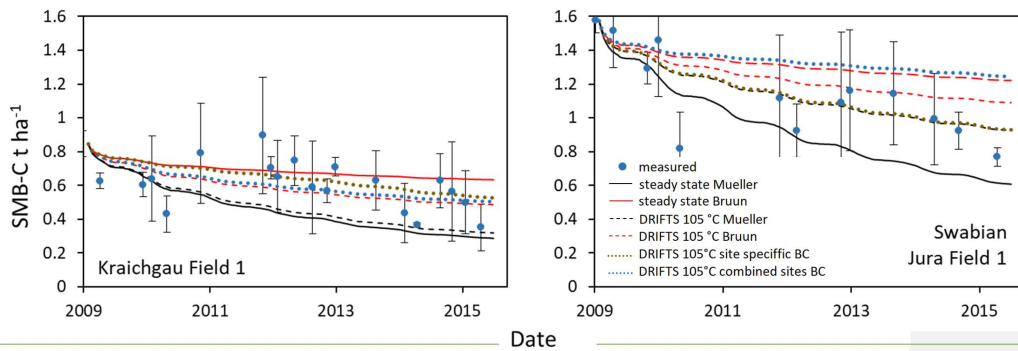
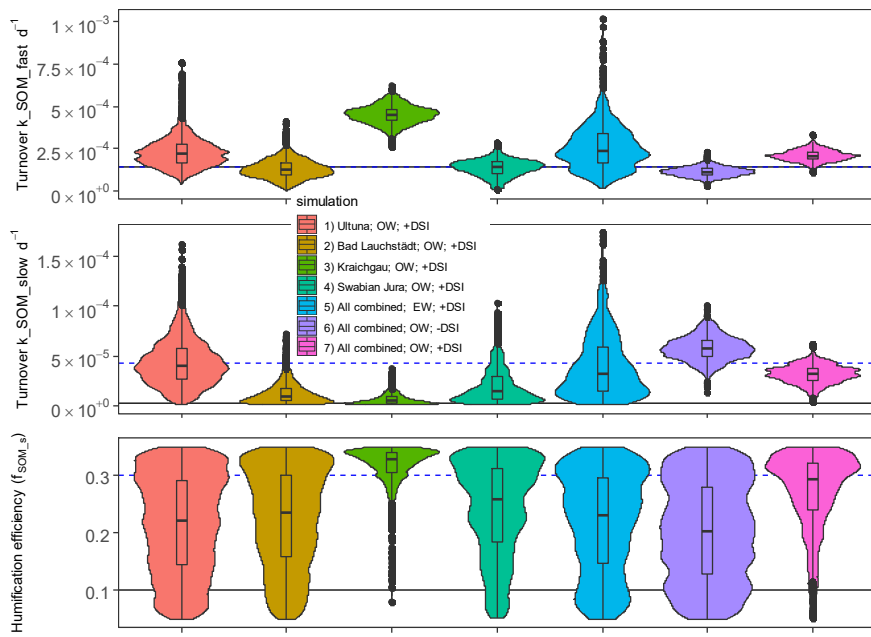


Figure 4 Example SMB-C simulations for Kraichgau field 1 (left) and Swabian Jura Field 1 (right). Initializations were done (i) assuming steady state using the formula of Bruun and Jensen (2002) with turnover rates of Mueller et al. (1997) and Bruun et al. (2003) and (ii) by the DRIFTS stability index (DSI) at 105°C drying temperature using both turnover rates for simulations (simulations using the other drying temperatures for DRIFTS in the supplementary). The site specific and the combination of all sites Bayesian calibrations (BC) are also displayed. Example SMB-C simulations from Kraichgau field 1 (left) and Swabian Jura Field 1 (right). Initializations were done (i) assuming steady state using the formula of Bruun and Jensen, (2002) with turnover rates of Mueller et al., (1997) and Bruun et al., (2003) and (ii) by the ratio of the 2930 cm⁻¹ to the 1620 cm⁻¹ peak of DRIFTS spectra at 105°C drying temperature using both turnover rates for simulations (simulations using the other drying temperatures for DRIFTS in the supplementary). Bars indicate the standard deviation of measured values of all plots (n =3) per field.

hat formatiert: Englisch (Vereinigte Staaten)



The site specific and the combination of all sites Bayesian calibrations (BC) are also displayed. Bars indicate standard deviation of all plots per field.

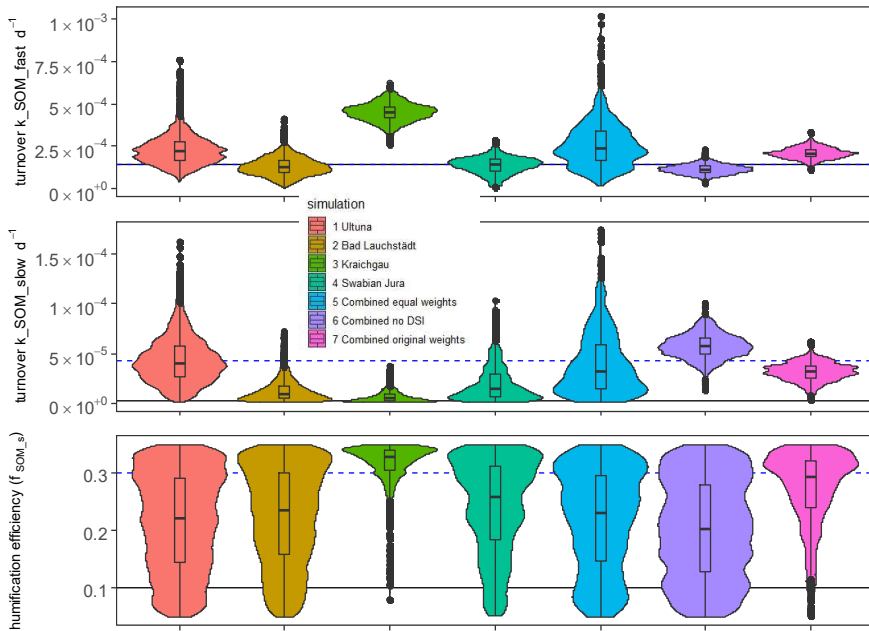


Figure 5 Violin plots of the parameter distributions, obtained by the Bayesian calibration using only the individual sites (1-4) and all sites combined (5-7) with different weighing schemes. (OW = original weight, EW = equal weight calibration; +/- DSI indicates, whether the DSI data was used for calibration). The black line corresponds to the parameters of Mueller (1997), the blue dashed line to the parameters of Bruun (2003). Note: The turnover $k_{SOM\ fast}$ parameter (top figure) is the same in both Mueller (1997) and Bruun (2003)

hat formatiert: Englisch (Vereinigte Staaten)

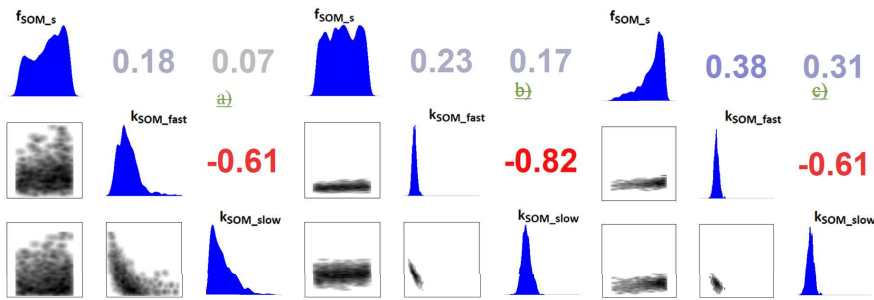


Figure 6 Correlation matrices of posterior distributions from the Bayesian calibrations of a) Allequal weight calibration for all sites combined with equal weights using the DSI (5), b) Alloriginal weight calibration for all sites combined with original weights without using DSI (6), and c) Alloriginal weight calibration for all sites combined with original weights using the DSI (7). The plots of the rest of the individual site simulations (1-4) can be found in the supplemental material.

hat formatiert: Englisch (Vereinigte Staaten)

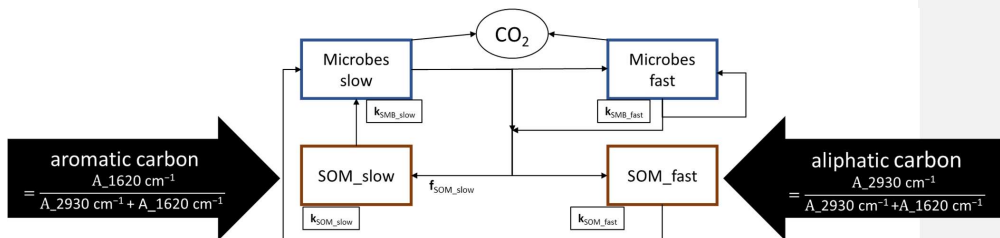


Figure 7 Suggested improvements to the internal cycling structure of SOM in the DAISY model. The division into fast and slow cycling SOM, corresponding to aliphatic and aromatic carbon happens at the death of microbes. Aliphatic carbon no longer becomes complex carbon without the involvement of microbes.

hat formatiert: Englisch (Vereinigte Staaten)