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Interactive comment on "A model based on Rock-Eval thermal analysis to quantify the size of the centennially persistent organic carbon pool in temperate soils" *by* Lauric Cécillon et al.

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We thank Reviewer 2 for his/her constructive and useful comments on our manuscript.

Major point 1: Validation of the multivariate regression model to predict the size of the centennially persistent SOC (CPsoc) pool in "new" soils

(1) Comment from Referee 2

Machine learning is used to find the best regression model predicting the proportion of CPsoc. A high R^2 (0.91) in the calibration dataset is impressive and shows that the thermal stability (RE6) can be linked to biogeochemical stability, which has been

shown before. Now, the interesting thing is the validation: the authors report the same R^2 for the validation set and show that they scatter as nicely along the 1:1 line as the calibration dataset does: Of course, this is the case because the dataset was randomly split, although the samples were not independent but originated from only 4 experiments. So the question is, will the results we similarly good, if for example 3 sites are used to train the model and 1 site is used for validation? This would give a much more honest picture on the validity of the approach. I guess that the prediction would not be as good: According to the Barre et al 2016 paper, at least the three presented thermal stability parameters HI, OI and T50CO2_ox which played an intermediate to important role also in the present study, varied considerably across sites. Also Figure 3A indicates that the 'thermal signature' of the samples is really site dependent. So for me the question is: Can this product really hold what the authors are promising, e.g. in the last sentence of the abstract: 'This model can thus be used to predict. . .'? This has to be clarified and if not the case be discussed with much more caveats. Uncertainties are already huge and they would probably inflate if new samples shall be predicted.

(2) Response to Referee 2's comment

We randomly split our sample set into a calibration and a validation set, therefore including soil samples from the four study sites in both the calibration and the validation set. We thus agree with Reviewer 2 that the validation of the multivariate regression model is not based on truly independent soil samples, even though samples from the validation set were not used in the calibration set. As discussed in the manuscript, the good fit obtained for the current validation set (Figure 4 in the manuscript) indicates that the multivariate regression model can be used to predict the size of the CPsoc pool with a known uncertainty in soils with pedoclimates similar to those found in the four study sites (Versailles, Grignon, Rothamsted and Ultuna; Supplementary material S1).

However, Reviewer 2 asks an important question: "will the results be similarly good, if for example 3 sites are used to train the model and 1 site is used for validation?"

Since each site used in this study has a specific pedoclimate (even the two sites with a similar climate, Versailles and Grignon, have different soil mineralogy, with carbonate soils in Grignon and soils developed in loess in Versailles), we have to slightly rephrase Reviewer 2's question regarding the specificity of our data set. In fact, Reviewer 2 asks if the multivariate regression model is able to predict the size of the CPsoc pool in soils with a different pedoclimate (i.e. a pedoclimate not included in the calibration set). Or more generally, can the model predict the CPsoc proportion outside of the studied sites?

We agree with Reviewer 2 that testing the multivariate regression model sensitivity to pedoclimate (i.e. by validating it on a site with a new pedoclimate) would provide useful information to the readers regarding its applicability on soils from different pedoclimates.

We argue that a necessary prerequisite for applying the multivariate regression model on "new" soil samples from a different pedoclimate is the thermal similarity between the "new" soil samples and samples of the calibration set (i.e. similar range of values for the 30 Rock-Eval parameters that were used as predictors in the multivariate regression model).

All soils from Grignon (carbonate site), and some samples from Versailles and Rothamsted show some important specificities regarding their thermal characteristics, while all soils from Ultuna had thermal characteristics similar to some samples from Versailles and Rothamsted (see the PCA plot in Figure 3 in the manuscript).

(3) Proposed changes in manuscript

We therefore propose to add a second validation scheme to test the sensitivity of the multivariate regression model to a different pedoclimate. Ultuna can be used as a truly independent validation site with similar thermal characteristics but a different pedoclimate than the calibration set.

The results of the predictions for Ultuna samples, using samples from Versailles, Grignon and Rothamsted for calibration of the multivariate regression model are shown in Figure 1 (see below). As expected, the R^2 strongly decreases, yet the error of prediction of the model does not increase strongly (RMSEP = 0.09 vs. 0.07 in the previous validation scheme).

Overall, these new results illustrate the sensitivity of the multivariate regression model to a very different pedoclimate (different climate and soil mineralogy), yet they clearly show the potential of the model based on Rock-Eval analysis for predicting the proportion of CPsoc in "new" soil samples. We thus propose to include and discuss them thoroughly in a revised version of the manuscript.

Specific comments:

(1) Comment from Referee 2

P5, line 8: Why such a huge intercept in the regression (0.4)?

(2) Response to Referee 2's comment

The relatively high value of the intercept may be linked to the fact that when estimating the total organic carbon content, a small amount of organic carbon is not taken into account by the commercial software of Rock-Eval 6 (organic carbon being volatilized as CO or CO2 at high temperatures, that may be inorganic carbon in carbonated soils). Underestimation of SOC concentration by RE6 has already been reported (e.g. Saenger et al., 2013). As soils from Grignon contain carbonates, we chose the same metric of SOC_RE6 for all samples, even if they are slightly biased towards lower values.

(1) Comment from Referee 2

P6, line 23: Fixed standard deviation for SOC concentration data? Why, and what is it exactly derived from?

(2) Response to Referee 2's comment

We used a fixed value for the standard deviation for SOC concentration data obtained from elemental analyzer (SOC_EA; 0.75 gC.kg-1 soil). As stated in the manuscript, this value is a conservative estimate of the standard deviation of SOC_EA data estimated by Barré et al. (2010) for the same soils. In the latter paper, the authors stated that "standard deviation [was] estimated from 15 replicate determinations of C in soil samples taken from the same plot in Grignon in 1959 (Barré et al., 2010). The measured standard deviation was 0.3 gC.kg-1. As the C contents at the different LTBF sites were determined on composite samples from the same plot at each site, it was considered that the a priori error on measurements should be less than 0.5 gC.kg-1 for every site". They finally applied a standard deviation of 0.5 gC.kg-1 for every site except Versailles, where the final standard deviation for SOC concentration data was 0.75 gC.kg-1 (Barré et al., 2010).

(1) Comment from Referee 2

P12, line 28: I thought it was 30 RE6 parameters, here it says it was 25?

(2) Response to Referee 2's comment

We have indeed used a total of 30 RE6 parameters in the multivariate regression model, but only 25 of them are RE6 temperature parameters (i.e. unit: °C). In this section of the manuscript (P12, line 28), we only discuss the outcomes of the 25 temperature parameters. We discuss the outcomes of the remaining 5 RE6 parameters (TLHC-index, I-index, R-index, HI and OIRE6) later in the manuscript (P13, lines 12-25).

(1) Comment from Referee 2

Discussion 1: Is very technical and focused on the specific RE6 method and related papers. Authors miss the chance to broaden the perspective and discuss this approach to estimate CPsoc in comparison to other approaches or to establish a clear link to

kinetic models.

(2) Response to Referee 2's comment

Only one out of three sections of the discussion (section 4.2) is devoted to the discussion of the specific RE6 method and related papers. We agree that this section 4.2 is rather technical but we think that critically discussing some technical limitations of our approach is necessary. Section 4.1 of the discussion already broadens the scope of our study and discusses different methodologies that have been used to produce estimates of the CPsoc concentration under various pedoclimatic conditions (i.e. in other long term agronomic experiments or using other analytical techniques and/or models such as radiocarbon (14C) data and steady-state SOC turnover model).

We agree with Reviewer 2 that discussing our approach to estimate CPsoc in comparison to other approaches may be useful to the reader.

(3) Proposed changes in manuscript

We propose to add some references to alternative techniques used for initializing the size of SOC kinetic pools in models of SOC dynamics (e.g. Falloon et al., 1998; Zimmermann et al., 2007) in section 4.3 of the discussion.

(1) Comment from Referee 2

Discussion 2: Is very positive about the overall results (and sample set), and although uncertainty was a clearly stated focus of the study it is not really taken up here: Yes, the sample set is truly unique, but this is also the problem: How uncertain will the CPsoc estimation in soils be, which do not have bare fallow treatments?

(2) Response to Referee 2's comment and (3) Proposed changes in manuscript

Following our response to the major point raised by Reviewer 2 (see above), we propose to revise the manuscript to discuss in section 4.3 the new results regarding the multivariate regression model sensitivity to pedoclimate (i.e. prediction on "new" soils from a different pedoclimate).

References:

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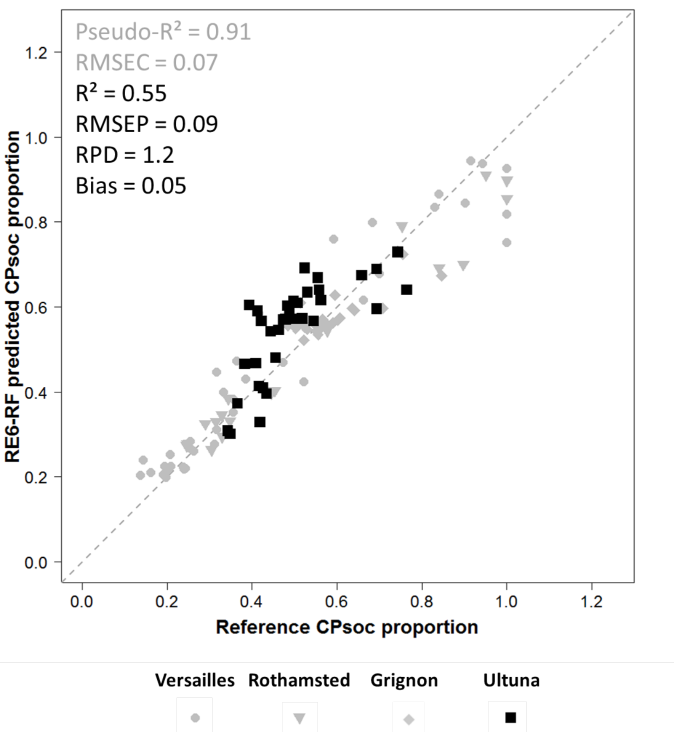

Fig. 1. Performance of the random forests regression model based on Rock-Eval 6 thermal analysis (RE6-RF) for predicting the CPsoc proportion in soil samples from a new pedoclimate