General comments

This technical note presents a correction method to determine soil organic content and soil inorganic content in single analysis. Using Rock-Eval thermal analysis offers some benefits over dry combustion method with elemental analyzers, where pretreatments or calculation are needed to get the two values of organic and inorganic carbon contents. Rock Eval eliminates the chances of calculation error, and experimental error associated with the elemental analysis method. The main conclusion by the authors is that Rock-Eval analysis can accurately determine SOC and SIC contents thanks to corrections based on a machine learning model. This result is highly promising to facilitate C studies in calcareous soils, however I have some reservations regarding the description, the application and the validation of these corrections. How did you definy the term “validated” ? Please explicit your criteria, the domain of validity and the correction itself? I hope that the authors can amend their manuscript to explicit the corrections, enhance the quality of the methodological work and discuss more their results in order to impede the paper to be taken as an advertisement for Rock-Eval® equipment with the Geoworks software. Please find some specific comments and questions below.

Answer : We thank the reviewer for their careful reading of the draft and constructive comments.

Specific comments

L.8 I did not understand the initial data set? What does it mean?

Answer : The « initial data set » corresponds to the data obtained by analyzing the samples on the RE6 Turbo machine at Sorbonne University. This is the data set that was split into a learning and a validation set. The other data set refers to data obtained using RE6 and RE7 machines at Vinci Technologies. We recognize that this sentence is confusing and will be modified in the revised manuscript.

Please add few lines on SIC, their distribution, the role of SIC in the soil properties, the eventual management of SIC (limestone inputs, Enhanced Rock Weathering…). Why is it important to consider the SIC contents as the SOC contents.

Answer : We can indeed provide more information on the interest of quantifying SIC. We propose to add the following paragraph to the revised draft.

Global stocks of SIC and SOC are of comparable size (~2500 Pg) when the soil is considered down to a depth of 2m (Zamanian et al., 2021). Not all soils contain SIC, but the presence of carbonates is frequent, particularly in arid or semi-arid soils (Zamanian et al., 2016; Pfeiffer et al., 2023). The presence of SIC influences soil pH and therefore nutrient availability (e.g., Mkhonza et al., 2020). This explains the usual agricultural practice of liming to reduce soil acidity. In addition, recent studies have shown that the amount of SIC can vary significantly over short time scales (~10 years) due to soil acidification resulting from certain farming practices (nitrogen fertilization, irrigation, etc.) (Zamanian et al., 2021; de Soto et al., 2024), suggesting that it may be worthwhile to assess the potential role of carbonates as a source or sink of C in a context of global climate change.

You did mention alternative thermal analysis to quantify SOC and SIC content in a single subsample, but you did not discuss your results with Rock-Eval against this alternative thermal method. Why a CHN elemental analyser (and we do not know which one) was selected for comparison and not an analyser with a thermal analysis ramp (such a LECO)? Does using Rock-Eval thermal analysis offer extra benefits over other thermal analysis that exists? Please add some words on the availability of the Rock-Eval equipment and the cost of the analysis. Is it a method easily available in several soil analysis labs?

Answer : The aim of the draft was to compare data from an accredited reference laboratory using standardized methods. In the revised version, we will provide more details on the protocols used by the LAS to quantify SOC and SIC. Briefly, total carbon is determined using a CHN analyzer (Thermofisher Flash 2000) and inorganic carbon is quantified using a Bernard calcimeter. In carbonated samples, organic carbon is determined as the difference between total carbon and inorganic carbon. Our mention of thermal analysis concerned previous studies using thermogravimetry or Rock-Eval®. We are not aware of any works published in the scientific literature using LECO analyzers to quantify SOC and SIC in one batch.

I did not understand in L. 36-37, if Koorneef et al. has proposed some corrections to estimate SOC and SIC and why you did not discuss your results as you did with Hazera et al. corrections with Koorneef corrections. Did you suggest that Koorneef et al. and Hazera et al. did not present validate results in their paper? Please discuss the domain of validity of each study and how you improve the method.

Answer : There is indeed no correction proposed in Korneef et al. One of the conclusions of this manuscript is that it would be useful if a correction can be developed. From our point of view, the correction proposed by Hazera et al. is not validated. For a method to be validated, we consider that it must be independently evaluated and that metrics informing on the adequacy between corrected values and target observations must be presented (RMSE, BIAS).

Additional information on the LAS analysis should be add to be more convincing. We have to trust the authors about the accuracy of the LAS data, no mention on the incertitude or if there is any replicates. The method used to get SOC and SIC content are not mentioned (calculation, direct measures with or without pretreatments for SIC or SOC ?). As it is a methodological work, it should be nice to insert some reference geostandard samples in the data set to check the accuracy of the LAS and Rock-Eval® analysis.

Answer : We agree, we will provide more details in the revised manuscript. The measurement uncertainties of LAS have been determined and will be added in the revised manuscript :

Inc. $SOC = 0.02 * ([SOC]+0.12*[CaCO3]) + 0.49 + 0.12 * (0.016 * [CaCO3] + 0.63)$ *in g/kg*
Inc. $SIC = 0.12 * (0.019*[CaCO3]+0.07)$ *in g/kg*

A reference sample (IFPEN_160000) is measured regularly in Rock-Eval® batch analyses for quality control. The target values are 3.28 ± 0.06 wt% and 3.26 ± 0.07 wt% for TOCre6 and MinC respectively. The machine is recalibrated when TOCre6 and MinC values are outside this narrow range meaning that the acceptable measurement error is ca. 2%.

Are they any replicates on the LAS and Rock Eval analysis? What is the incertitude associated to each of the analysis? This is a methodological work, so readers expect high standard on the description of the methods.

Answer : The incertitudes associated to LAS and RE measurements have been given above. They will be added in the revised version.

L.70 Please can you add some indication of the soil aliquots. You only say ca. 60 mg. I presume it is ground soil (200 µm). Is it OK for any soils, even the soil with very high SIC and very low SOC content? Or the inverse? What are the limit of C detection ? limit of C content of each C pools to be properly measured. Is it possible to have a saturation of the signal for one of the C pool and in a same time to be at the lowest detection limit for the other C pool? As your paper is a technical note, this consideration are worth to be add for the future users of your method.

*Answer : The Flame Ionization Detector (for HC) can be saturated. That is why for pure organic samples, only 10 mg are used. The other detectors get saturated at very high C content that are not reached when working with 60 mg of sample. From our experience, we do not feel comfortable with samples with TOC lower than 1.5 gC/kg. In the range of SOC (*5.37 *to* 44.64 *gC/kg) and SIC (0.5 to 96.8 gC/kg) contents used in our study, we did not have any problem. We agree that we should present very clearly the range for which our correction has been validated. However, we consider that the investigated SIC and SOC ranges are quite large making our correction valid for the vast majority of agricultural topsoils. We can add a few sentences on this in the revised draft.*

L.96-97 How many values of SIC inferior to zero were in the data set? SIC could be calculated inferior to zero for what range of reference SIC values?

Answer : Thanks for your remark. Before correction, SIC can't be inferior to zero. Even in soil without SIC, the MinC parameter would not be zero because a tiny part of OC is erroneously attributed to MinC when using Rock-Eval. This is a well known artifact. This amount of C erroneously attributed to MinC comes from the S3 signals. If we don't have a contribution to the S5 signal to the MinC it means that the soil does not contain SIC. We checked that it was true for the 48 samples that got negative SIC values after corrections. As it was the case, it means that in our sample set, only samples with no carbonates can get (very small) negative SIC values after correction. It is therefore not a problem to correct them to 0.

L.98 « all the RE parameters » and L. 106 "after a correlation analysis…." Please specify the RE6 parameters tested. Furthermore if the reader is not familiar with Rock Eval analysis, he/she cannot understand what you mean without a minimum of explanation on these parameters.

Answer : OK. We will provide some examples of RE parameters (for instance Hydrogen and Oxygen Index) and specify the meaning of the sentence on line 106-107. We tried multivariate models and observed that they were not better than univariate models.

L.105 How have you proceed to choose the calibration and the validation sample sets?

The calibration and validation sample sets are chosen fully randomly by using 160 samples during the training phase, and using the remaining 80 samples for validation. We check that the calibration and the validation data sets follow similar distributions of SIC and SOC. This is shown in the Notebook, note that the calibration and validation sets correspond to the train and test sets.

L.114 are you sure that the conditions given in the application of the correction suggested by Hazera are OK for all of the soil samples of your data set (soils enriched in poorly degraded organic compounds)? Please specify which the land uses are represented in your data set and why the soils are probably enriched in poorly degraded organic compounds.

Answer : We specified (line 45) that we used topsoil samples from agricultural soil. The samples used in Hazera et al. are also coming from agricultural soils and are in a similar

SOC range. For this reason we used the same correction as they did. However, we will investigate what it would have done using the other correction.

Some clarification and homogenisation should be done between the term and the abbreviation using CHN, LAS, Elemental analyser. For example L. 145 “reference CHN value”, but in the figures LAS is mentioned. The same for TOC-RE6 and SOC-RE6. Please try to be clear with all the abbreviation to help the reader to follow.

Answer : We agree, thanks. This will be done in the revised version.

L.135 The sign “sum” is missing. Please correct the Equation.

Answer : OK, thanks.

L.151 I did not understand if you realised three different models, with three different corrections (non carbonated, carbonated, all soils). I did not see the discussion on the different corrections. One of my problem with your work is that these corrections were not explicit. They will be included in the Geoworks software OK but we do not see how it is calculated. The machine learning procedure is clear but the statistical corrections were somehow cloudy because not explicit in the text. I am not sure that your work could be reproducible.

Answer : Some machine learning models cannot be easily presented in an analytical form. However, our work is fully reproducible as all the data and the codes are available.

Why figure 2, 4 and 5 have different scales? (100 g kg-1 and 50 gkg-1 for SIC and SOC respectively in Fig.2 and 70 and 35 in Figure 4). Please be consistent.

Answer : This will be corrected in the revised version.

The predicted corrections of the ML model were not explicit. Is it possible to do so? Why not?

We thank the reviewer for this question, we shall modify the revised version to make these notions clearer. While it is theoretically possible to represent a Support Vector Regression (SVR) in its analytical form, doing so would require a function whose size depends on the size of the learning set. In our case, this would mean an analytical function containing 160 expressions for each of the points in the learning set.

As a workaround for this issue, the accompanying Notebook contains the Partial Dependence Plots (PDPs) for the SVR model, as well as the other four models we tested. The PDPs show the predicted target as a function of a feature of interest, in our case the SIC and the SOC. It also allows us to visualize the difference between the four proposed ML models.

L.160 “test data” what do you mean? Data in Hazera et al. were compared with reference data, but the data were not statistically adjusted as you did, the corrections proposed were defined from literature (e.g. Disnar et al. 2003).

Answer : The sentence is not appropriate and will be corrected in the revised version. In fact, the correction proposed in Hazera et al. was not learned on one dataset and evaluated on another. To this respect, it is logical that it is not optimal.

Please give a domain of validity of the method. Why do you say is it the first method to be validated? The corrective approach of Hazera did not work as well as yours on your data set, but it seems OK for their own data set. Please discuss and give clue to explain what could explain this discrepancy. Is it a question of SOC and SIC range, of type of soil, or of land use or land cover, type of SOC, type of SIC?

Answer : There is a conceptual difference between the approach proposed in Hazera et al. and our approach. We produced a correction method with a proper evaluation on an independent dataset and evaluated the transferability of our validated correction method. This was not done in Hazera et al. Our study shows that the correction of Hazera et al. improves the initial data, however it is not optimal. At first sight, one might even consider that the Hazera correction is OK for our dataset. However, we consider that it is more relevant to implement the best correction method and our SVM correction is clearly better.

Please discuss more your results, e.g. the incertitude associated to the values to the reference data and to the RockEval data. What are the limits and the perspectives of your work. Could these corrections be applied also on soil fractions? On any king of soil with different organic matter and different calcareous minerals? Are 160 French carbonated soils enough? Does it need further calibration, probably yes on the soil fractions as it is tested in Koorneef et al. What are the possible perspective of this work? You also could further understand why some samples are better predicted than others.

Answer : We can add a few lines of discussion. The uncertainties associated with our method are presented in the figures. We can discuss them. There is no reason to consider that our correction cannot be applied to fractions as long as SIC and SOC contents are in the range of our calibration set.

Regarding the size of the data set, we have tested the precision of the proposed correction when the data set size ranges from 16 samples to 160 samples. We conclude that having at least 100 samples is ideal, while already 50 soil samples provide reliable SVM corrections. The benefit of 160 soil samples is then the fact of representing as many different soil types as we had available. We have added new figures in the supplementary materials of the accompanying Notebook to address these questions.

To conclude, I think this work is worth to be published after major revisions. It gives promising result and improvement to measure SOC and SIC in single aliquot for a large range of soils. I regret that the corrections were not explicit (a statistical adjustment but the coefficient were not given and discussed against the coefficients existing in the literature for SOC or SOC and SIC content). It works on 260 French soil samples. The Rock Eval must be corrected by statistics… is it not possible to fix the cycle of analysis to avoid these corrections? I also regret that the discussion on the proposed method is poor and no perspectives of the work are proposed. It looks like that because the statistical adjustment is OK for 260 French soil samples, the problem of measuring SIC and SOC content in soil with Rock Eval is no more a problem for any kind of soil materials. Please discuss more the result to avoid the feeling that the paper is an advertiser for RockEval and Geoworks. This very interesting work is really promising despite my many comments, it deserves further discussion.

Answer : Thank you for your feedback that will allow us to improve our draft. We will try to improve the discussion but our draft is a « technical note » and should be considered as such.