

The authors present a manuscript where they attempt to connect incremental thermal mass loss (TML) to various metrics associated with soil quality indicators (SQI), soil health, and soil microbial activity. Standard protocols for assessing SQI typically require multiple subsamples that are prepared for different measurements at different moisture contents and narrow temperature ranges. Authors suggest that TML may be a feasible technique to acquire data for multiple SQI metrics with a single measurement by correlating TML to select SQI. The TML temperature ranges are compared to measurements of SQI and linear regression is used to create models that are predictive of SQI values based on TML measurements. Although the authors present an interesting case for investigating connections between TML and SQI, their analytical approach does not clearly answer their objective due to obscure correlations that are not clear in interpretation. The predictive equations generated from their modeled data do not seem to provide a more reliable method of interpreting SQI and the authors fail to make a case for why they believe the generated equations have merit for SQI assessment. A different approach to analysis is suggested, and if authors do not find an analysis that is more fitting to the objective, perhaps a different experimental design is also needed.

18 – SQI are not officially standardized into groups or arranged in any official capacity. Authors should mention that the SQI listed here are the ones that they have considered and that the listed parameters do not cover all SQI that could be measured

We agree with the comment, we can extend the statement.

22 – physical, chemical, and biological soil properties can change because of slight or major soil modification. I suggest avoiding categorizing them in this way because it limits which SQI are chosen to represent different soil processes.

Thank you for suggestion.

28 – What do the authors imply here by ‘number of methods’. Do you refer to different methods that measure the same property or different methods to measure different SQI?

It was meant “different methods to measure different SQI”.

45 – the authors state that mass losses using TG do not have a clear meaning unless connected to accessory information. This is partially accurate, but there are many experiments connecting TG measurements to accessory measurements in ways that greatly increase the ability for TG to be predictive of certain soil properties. Thinking specifically of how gravimetric water content is measured and how the C:N ratio to soil organic matter is measured. The authors suggest that fractionated TML may also be useful for assessing SQI but fail to reasonably address that existing methods are conducted at narrow temperature ranges because those narrow ranges are typically

most associated with the property being measured. How does a single measurement of TML over all those ranges collect valuable information

We agree, that in some cases TG can provide a valuable information. We feel, we should better introduce the TG technique and meaning of TML.

85 – this step to reach the same relative humidity across all samples seems unnecessary. Many researchers would instead focus on reaching a constant dry mass before analysis

Yes, we agree.

In the original paper of Siewert (2004; DOI10.2136/sssaj2004.1656), where this approach was used for the first time, is reported the correlation of mass losses with SOC, TN, clay content and carbonates. In later works, we discussed (paper of Siewert and Kucerik) the necessity to expose the soil to constant relative humidity due to comparable conditions prior the analysis. Each soil has its capacity to adsorb some humidity when exposed to relative humidity. The final humidity of each soil is different but it reflects the properties of soil structure and enables the determination of SOC, TN etc. Without the equilibration, the soils would have different starting moisture contents which would affect the determined mass losses (determined as mass loss in a temperature interval divided by total mass including moisture). Consequently, this would affect the determined SOC, TN etc...

88 – what is the rationale for this heating rate? A heating rate of 5°C per minute from 20-950°C minutes is approximately 186 minutes of heating on a 0.2 g sample. Do the authors have a reason for this protocol and why they expected this to produce reasonable results? There is no reference mentioned in this section

Heating rate 5°C/min is based on long-term experience with use of TG in soil analysis and it started by the first paper on this “series”, Siewert 2004. Since this time we use it in our experiments and it allows us to compare all our results.

From the material science point of view, this heating rate is optimal also due to poor thermal conductivity of analysed soils, conditions of oxidation (air flow rate) and higher sample mass.

Importantly, in our works we do not use ground soil, which may cause a problem with reproducibility. Nevertheless, 0.2 is still enough to have good reproducibility of measurements without grinding and soil homogenization. It should be noted that 0.2 g is quite large sample mass, as in TG smaller sample masses are used. In addition, even the thermobalances providers prefer to decrease sample mass and increase the sensitivity, thus the commercially available devices can rarely use this mass.

In fact, in our work we use two different systems, Mettler Toledo and TA Instruments and each device is specific. Mainly, MT can accommodate large sample mass (up to 1 g), in this case we use an oxygen flow of 200 ml/min. The TAI used a lower samples mass, and to obtain comparable conditions, we use an oxygen flow of 100 ml/min. This was extensively tested in past (unpublished results).

We agree with the reviewer and have added method references.

102 – what is meant by water holding capacity compared to water content? I interpret this to mean the water holding capacity of an intact soil sample based on porosity, texture, and related factors. Was WHC measured on these soils based on their natural state before being disturbed?

Yes, the interpretation of the reviewer is correct, it is derived from WHC measured in samples before being disturbed.

141 – at this point in the manuscript, the term LTML has not been described. I think it should not be abbreviated here.

Yes, it is erroneously described on the line 94 and 95.

144 – how are the TML being correlated to soil parameters here. Is the same TML range for each soil sample being correlated to the soil parameter measurement for each soil sample? It seems like this is what is being done, but please elaborate more clearly for readers.

Yes it is as stated by the reviewer. We have corrected it in the text.

160 – Although people highly versed in the field may know this information, it is important to include citations about the 30-600°C temperature range you are referring to for SOM degradation.

Yes, we agree and have added in a reference.

169 – What is the meaning of the equations when two or more TML ranges are used. How are we to interpret the meaning of each variable attached to this equation?

The TML have thus far no direct biogeochemical or physical meaning (although it has physically meaningful unit), they can be considered as indicators, thermal fractions, or general proxies with no clear meaning. The aim of the work was to find possible links, i.e. correlations, between TML or LTML with soil properties. Thus, we combined either one or more TML to see whether this correlation exists. If exists, then, if it is possible to use it for prediction of soil properties. Importantly, this correlation does not imply causality.

171 – Does your selection of large thermal mass loss areas have a significant quantitative meaning? It seems that you have selected wide ranges but do not explain a meaning for each lower and upper limit. This is also important because LTML values from table 2 are used to determine which linear equations are appropriate for further discussion in table 3 and beyond.

Criteria of selection came from our previous works, in particular from paper DOI: 10.1007/s10973-014-4256-7. For soils from all over the world, regardless the type and origin, the mutual correlations of TML resulted in regions of temperatures, where the TMLs mutually correlated; those areas are limits of LMTLs. In particular, we observed the areas up to 100°C, 100-200, 200-300, 300-450, 450-550°C and others. In other words, these are TG fractions, which are distinguished from others by mutual relationships of their components. These TG fractions correlate with classical soil fractionation techniques (10.1016/j.geoderma.2019.114124), e.g. with fractions obtained by approach

suggested by Zimmermann et al. (10.1111/j.1365-2389.2006.00855.x). Also, their correlation with C, N and clay is close but not straightforward (10.1016/j.geoderma.2017.12.001).

179 – for table 4, are there fewer applicable results for grassland because grassland had a smaller sample size? This outcome should have more explanation.

No, but the reviewer is right, this should be better explained.

190 – you state that the closeness between TML and LTML correlation is close with a few exceptions. Is there interpretation about why some correlations were not close and others were (other than TN, for which you do provide speculation)? Does it have something to do with the LTML ranges selected for correlation? Other factors?

As aforementioned, TMLs (and also LTMLs) have no clear meaning and represent indicators or thermal fractions of soil. Soil organic matter, which is the part of soil degraded within 200 to around 550°C, is a continuum of large amount of molecules separated based on their thermal stability. One molecule or group of molecules, can be due to various stabilization mechanisms degraded in various TMLs. For this reason, the choose of LTML range may not be that important as it seems to be.

The aim of the paper was not to search for reasons of correlations, we provided only several hypothesis in cases we considered most important and logical. The aim was to find if the correlations exist, how can be mathematically described and whether are applicable. What we found that there is a link in some cases, but the applicability is problematic.

193 – Although there is speculation about why TN was among the biggest differences between the two soil types, the authors neglect to mention the relevant temperature ranges for soil N and why correlations with TML outside of those ranges would have meaning in this measurement. Are the authors confident that N is a significant part of mass loss across the entire range specified?

An interesting question. The manuscript needs better explain the specifics of TG measurement and meaning TMLs/LTMLs. An important assumption is the close link between C and N; they are linked in biogeochemical cycles and in various forms of N. Yes, we are confident that N is a part of mass loss across the entire range. In fact, mass loss in TG cannot be understood in terms of spectroscopy, where functional groups have some superposition; instead, it is a continuous mass loss caused by degradation or transformation (char formation) reactions. But was a very valuable comment.

200 - It is well known that microbial biomass C and N are correlated with SOM, but your interpretation does not explain why TML in different temperature ranges are useful for this interpretation. For example, many researchers measure SOM by combustion between 300-400°C. Why are measurements outside of this range also valuable? Please elaborate.

This is a valuable suggestion, we will elaborate it.

205 – Belaboring the point here, but this is important for discussion. Microbial respiration in soil and microbial activity above 100°C is unlikely to have much meaning in practical situations. A measurement above 200°C is unlikely to be predictive of any microbial activity unless the prediction is that there is little to no microbial activity. The vast majority of microbes and microbial exudates are not part of the active C fraction at this point and greater. What do these correlations mean?

We agree, this point should be better explained and connected with the discussion about the correlation between TML and respiration.

211-221 – Similar criticisms toward interpretation of N compounds. The authors present speculation with little connection to the objective based on TML and its use to interpret and assess results for different SQI

We agree, better connection to the objective based on TML should be presented.

234 – I would like to see more exploration about how these factors like MB, TN, SOC, etc. overlap in terms of TML within a certain range. Considering most of the temperatures in the incremental TML are outside of microbial activity range of soil, I am curious to know if the correlations are confounded by other factors that are not currently discussed in the manuscript. The authors should discuss this in order to make their argument for using this method more convincing.

That is an interesting suggestion, this may improve the paper.

239 – I think your data do not currently support the idea that rhizosphere inputs for grassland are what negatively affected the validation. As stated on line 247, the sample set is limited and unbalanced. Authors are far too speculative in this regard.

The influence of rhizosphere was the hypothesis of the reasons of observed inconsistencies. We are aware that this hypothesis is not supported by the experiments, it is more a logical deduction. We wanted, among others, to stress out the problems when using thermogravimetry for prediction of microbial data that the sampling under various vegetation cover is in this case an important issue. Yes, the number of samples is limited by the project, but it is still indicative to draw a hypothesis. Perhaps, we should reconsider how to present our hypothesis as a one of many others.

262 – Microbial activity can still be correlated with stable C fractions. This data has been observed. I am not confident that authors have shown that the thermal intervals measured in this way are associated with microbial activity. It would be interesting to see how the measured microbial and SOM parameters correlated to each other rather than the TML.

Indeed, they correlate, we did not show the data, as it would disturb the red line of the paper – finding correlations and their verification. But the reviewer is right, it may

help to improve the understanding the meaning of correlations, we may include it in a supplement.

268 – TML may be a useful proxy for some soil analyses, but the way that authors have analyzed data in this manuscript does not show this. Interpretations in this manuscript drifted away from the proposed objective of showing how TML is connected to various SQI. Authors present very little data and interpretations that answer this question in a coherent way.

As aforementioned, the aim was not to interpret the found correlations, as for that we would need additional analyses. Nevertheless, based on both reviewers suggestions, in some cases, the interpretation can be improved.

267 – authors make claims in this concluding paragraph that are not supported by their data and interpretations. TML does not appear to be a useful proxy for the soil analyses mentioned because authors did not present a strong case for a reliable or more convenient predictive model. The validation step failed in most cases for grassland soil and interpretations of the model for arable soil are not well supported in the manuscript. Authors may benefit from adjusting the overall objective and analysis methods so that the value of TML data is more apparent to readers, specifically for matters of SOM and its various fractions. The TML connection to microbial activity is likely confounded by chemical fractions of SOM that authors did not do a satisfactory job of parsing through in their results and interpretations.

We agree, there are issues in the manuscript that can be improved based on the suggestions of reviewers.

Technical error

59 – the word ‘vary’ may be a typo with the intended word as ‘various’.

We have correct this misspelling.

252 – I think the intention is to write ‘intermediate pools (...’ rather than ‘intermediate (pools...’ Parenthesis after the word ‘pools’.

The reviewer is right, this has been corrected.

Figures 1 and 2 should include the full text of abbreviated terms in the description (e.g. SOC = soil organic carbon).

We have added in the description of these abbreviations.