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Discussions

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Interactive comment on "Evaluation of bacterial glycerol dialkyl glycerol tetraether and ^{2}H$-^{18}$O biomarker proxies along a Central European topsoil transect" *by* Johannes Hepp et al.

Anonymous Referee #1

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Hepp et al. measured branched GDGT concentrations, hydrogen isotopes of leaf waxes, and oxygen isotopes of sugars from surface soils collected throughout Germany and Sweden. They use their measurements to add to existing calibrations of brGDGT proxies for soil pH and temperature, and to test a proposed method to reconstruct relative humidity from paired $\delta2$H values of n-alkanes and $\delta18$O values of sugars. While I agree that improving calibrations of paleoclimate proxies is important for interpreting them, I have some major concerns about the utility of the present manuscript. Unfortunately, I do not think the study is suitable for publication in Biogeosciences as presently written. With some major restructuring and rewriting, I think the authors could still publish something useful from their data set.

Major issues: 1) The brGDGT calibration presented here is of limited use, since the study uses an outdated method to measure brGDGTs and does not distinguish between the 5 methyl and 6 methyl compounds. Hepp et al. thus calibrate indices (CBT and MBT') that have fallen out of favor and been replaced by the more robust CBT' and MBT5Me indices. The new indices and new methods developed by De Jonge et al. (GCA, 2014, doi: 10.1016/j.gca.2014.06.013) and Hopmans et al. (Organic Geochemistry, 2016, doi: 10.1016/j.orggeochem.2015.12.006) are not even mentioned in the text, and the limitations of the brGDGT data presented here are not acknowledged. Without reanalyzing these samples with a method that resolves all isomers, I fear that the present sample set has limited value for the calibration of brGDGT-based proxies.

2) There are some big assumptions in the proposed approach for reconstructing relative humidity using paired δ2H values of n-alkanes and δ18O values of sugars. In particular, the assumption that biosynthetic fractionation for these compounds is constant is contradicted by lots of existing work, which is briefly mentioned by the authors in their discussion. Figure 8 is not a very good advertisement for the utility of the paired δ2H-alkane/δ18O sugar approach, and the lack of correlation suggests that some of the many assumptions that go into this method are not valid. This paired approach has not caught on beyond the Zech group, and the data presented here suggests that it may not be useful as presently conceived. The authors state they have shown the "great potential" for this proxy. I remain unconvinced by the data and analysis shown here.

3) The writing is in places unclear and difficult to follow. I have noted a few of these instances in my technical corrections, but the manuscript would benefit from more careful editing.

Specific comments:

Line 110: This adds up to more than 16, some sites were considered to be more than one of these categories? Would be good to rewrite to clarify

Line 114: Was there a threshold for what was considered "close-by"?

Line 133: Machine learning techniques like random forest aren't so commonly used in Biogeosciences and it would be helpful to provide more details here. How many trees did you use? How was data partitioned into training and testing sets? What metric was used to assess model performance? What was the minimum number of samples in the terminal nodes? What was the maximum number of terminal nodes? What variables ended up being ranked as most important (could be useful to show a plot of ranked variable importance in the supplemental materials)?

Line 136: Why wasn't it possible? Lack of measured data for a robust training data set? Please specify

Lines 128-139: How did the calculated values you obtained for the German sites compare to OIPC? What is your evidence for your approach providing superior estimates of precip isotopes than OIPC? OIPC is obviously not perfect, but as written, we have no evidence to evaluate if your results are any more accurate. There is also no discussion of the implications of using one target for precip isotopes in the southern half of your transect and a different one in the northern half.

Section 2.3.1: No internal standard was added? How do you account for losses of brGDGTs during sample handling?

Lines 165-171: This is not the most current method used for robust brGDGT analysis (see Hopmans et al., Organic Geochemistry, 2016. DOI: 10.1016/j.orggeochem.2015.12.006). Does your method allow for 5' and 6' methyl brGDGTs to be distinguished from one another? If not, severely diminishes the accuracy of results. Based on the results that are shown, it seems like this method does not distinguish the different isomers.

Lines 172-173: how was the pH measured?

Section 2.3.2: Were the n-alkanes quantified prior to measuring their stable isotopes? Also, please briefly describe the operating conditions of the GC-pyr-IRMS (or cite an-

other publication that used an identical method and provides all the relevant details)

Line 199: It is not clear how you had 29 samples from 16 sites. Were some of the sites sampled in duplicate?

Lines 211-221: The more robust indicator of soil pH is CBT' and the more robust indicator of soil temperature is MBT5me (De Jonge et al., GCA, 2014, DOI:10.1016/j.gca.2014.06.013).

Lines 227-229: A number of papers have shown that ebio is not constant and different among plant types and seasonally. See for example Feakins & Sessions 2010 (cited previously), Eley et al., GCA, 2014 (DOI: 10.1016/j.gca.2013.11.045), Cormier et al., New Phytologist, 2018 (DOI: 10.1111/nph.15016).

Lines 383-385: are these concentrated weighted means? That is what is typically used to compare d2H values of n-alkanes where not all homologues are present in all samples

Line 395: I think you mean "unenriched xylem water"?

Lines 431-432: This is not particularly convincing, the reconstructed precipitation isotopes are not correlated with the GIPR/OIPC precipitation isotopes. No evidence is provided to show that this approach is any better than the most up to date methods for obtaining precipitation isotopes from leaf wax n-alkane isotopes alone. For example, how do your results compare to the predictions from the proxy system model developed by Konecky et al. (JGR-Biogeoscience, 2019, DOI: 10.1029/2018JG004708)? Maybe your approach is better, but you need to prove this by providing a direct comparison, rather than just telling us

Lines 448-450: If this was the case, wouldn't you expect all the coniferous sites to be biased in the same direction? Instead, they are evenly distributed above and below the 1:1 line

Line 454: Is this signal damping correction shown anywhere? How would this work

practically in sediments?

Lines 467-468: Actually, there are plenty of n-alkanes in roots and they have very different H isotopic composition than in leaves. See work from Guido Wiesenberg's group and Gamarra and Kahmen. I'm also confused about what you are referring to as "the discussion". There is not a separate discussion section to this manuscript.

Lines 489-494: Not stated here is that there is no correlation between the reconstructed and measured RH values. This suggests that this approach for reconstructing RH is not particularly useful Line 565: The data in the paper is not very convincing that there is great potential for the coupled d2H n-alkane d18O sugar approach

Lines 566-567: I don't see evidence of this in your analysis, nor examples of how you would take vegetation into account when applying this proxy.

Technical corrections and typing errors:

Lines 54-56: The way this sentence is written is confusing. Suggest rewriting as "Climate proxies based on molecular fossils, also known as biomarkers, have great potential...

Line 56: don't need the comma after "particular"

Line 59: "need to be known"?

Line 61: It would be better to start this paragraph with a clear link back to the previous one

Line 74: don't need commas before and after "it is known"

Line 79: Again, some sort of transition would be helpful to begin this paragraph

Line 82: "all along the way" too wordy

Lines 93-94: "as well as concerning possible effects related to" awkward phrasing

Figure 1: would be nice to have a legend on panel B or have the axis colors match the

variable colors. At the moment we are left to guess that blue bars are precip and the red dots are temp, since this is not stated in the figure caption or the legend.

Also would be nice to offset the panel letters with a () or . to break them apart form the title of the panel

Line 180: No "the" needed in front of ETH

Line 225: the n at the beginning of n-alkane should be italicized. Check throughout

Line 234: Generally, figures should be numbered in the same order that they are referenced in the text