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Interactive comment on "Water availability determines branched glycerol dialkyl glycerol tetraether distributions in soils of the Iberian Peninsula" *by* J. Menges et al.

J. Menges et al.

carme.huguet@uab.es

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Anonymous Referee #1 Received and published: 16 July 2013 General comments In this study, the authors analysed branched GDGTs in 23 soil samples collected across the Iberian Peninsula covering a wide range of precipitation. They showed that the methylation degree of branched GDGTs (MBT') was correlated with precipitation rather than with air temperature. This suggests that soil moisture can have an influence on the distribution of branched GDGTs in dry environments. This paper deals with a subject of topical interest and confirms the fact that temperature and pH are not the only environmental parameters controlling the distribution of branched GDGTs. Nevertheless,

several issues need to be solved before the manuscript can be published.

1) The discussion section needs to be improved and is not sufficient in the present form. It is mainly based on the paper by Peterse et al. (2012) who recently published an extended soil calibration between MBT'/CBT and temperature and showed that the MBT' did not correlate with temperature in arid regions. Nevertheless, several papers already discussed the effect of soil moisture on branched GDGT distribution, for example Loomis et al. (OG, 2011) in soils, Huguet et al. (OG, 2010) in peat and more recently Dirghangi et al. (OG, 2013) who studied the distribution of branched GDGTs in soils from arid and wet environments collected along two environmental transects in the USA. The conclusions of the latter paper are very similar to the present one, i.e. MBT/CBT-derived temperatures depend on precipitation amount. The authors have to strengthen the discussion part by using these other papers. The investigation of the impact of humidity of branched GDGT distribution is not something totally new.

*We have incorporated the suggested references to the discussion and also, when relevant, to the introduction as suggested by rev. 2.

2) Were isoprenoid GDGTs also analysed? It would be worth showing the corresponding data and to look if some of the isoprenoid GDGTs are more abundant than some others in dry soils. Dirghangi et al. (2013) notably observed that crenarchaeol and its regioisomer (i.e. Thaumarchaeota) were very abundant in dry soils.

*The focus of the paper is on the appraisal of the MBT/CBT indices to reconstruct MAT, and thus on the distributions of brGDGTs. In this sense, we prefer not to discuss the data on iGDGTs in our paper and instead focus on the brGDGTs since they are used in the here discussed MBT/CBT index. The iGDGT data were added just for reference but can be removed if the reviewer deems it necessary.

3) The authors found a correlation between the aridity index and the MBT'. Nevertheless, I am not sure the aridity index is very convenient, since mean annual precipitation and mean annual potential evapotranspiration data have to be available. The authors

should comment on this. In any case, the validity of the correlation between the MBT' and the aridity has to be confirmed by analysing branced GDGTs in a large number of soils. The authors should comment on this. In any case, the validity of the correlation between the MBT' and the aridity has to be confirmed by analysing branced GDGTs in a large number of soils.

*We have used one of the standard methods to estimate aridity, which is easily available online [Trabucco, A., and Zomer, R.J.: Global Aridity Index (Global-Aridity) and Global Potential Evapo-Transpiration (Global-PET) Geospatial Database. CGIAR Consortium for Spatial Information. Published online, available from the CGIAR-CSI GeoPortal at: http://www.csi.cgiar.org, 2009]. Furthermore, rather than just using precipitation amount data, the AI integrates mean annual precipitation and evaporation and offers the advantage to be a measure of the general hydrological conditions and as such water availability in soils at the site. For example, even in areas with a lot of rain, water availability for plants and microorganisms in the soil, differs largely depending on whether evaporation is high or low. Our data also show, that the MAT residuals are better explained when the AI index is used instead of MAP (see Fig. 4). 70% vs. 60% of variability is explained by the AI. We believe this points to water availability in soils rather than just rainfall amount as a mechanism for our observations and this can only be inferred by using the AI. There is some additional text on this in the manuscript.

Clearly, the reviewer is correct to note that for a robust statistical analysis, a larger number of soils should be investigated. We see our study as the first step towards appraising the use of brGDGT indices and the effects of hydrology in the distributions of compounds, and constraining their use as proxies. One of our aims actually is to encourage more research in arid soils environments.

Detailed comments Page 9046, lines 5-10. The authors have to specify in this part of the introduction that isoprenoid GDGTs are produced by Archaea and branched GDGTs by still unknown bacteria (even though Acidobacteria could be one potential source for branched GDGTs, as recently suggested by Sinninghe Damsté et al.

(2011)).

*Done as suggested.

Page 9046, lines 10-11. I disagree with this sentence, which has to be modified. Several studies clearly showed that branched GDGTs were also produced in situ in aquatic environments. Therefore, in lakes, branched GDGTs can originate from surrounding soils but can also be produced in the water colum and/or sediment.

*This sentence has been removed.

Pages 9046, lines 13-15. This sentence is unclear and should be rephrased. I would simply say that MBT is correlated to air temperature and pH and that CBT mainly depends on soil pH.

*Sentence has been rephrased.

Page 9047, lines 4-7. This sentence has to be clarified. The errors of the calibrations developed by Weijers et al. (2007) and Peterse et al. (2012) are similar: 5.0 âŮę C for the original calibration by Weijers et al., 4.8 âŮę C for the extended calibration by Peterse et al. Nevertheless, the temperature estimates based on the extended calibration seem to be generally more consistent with recorded temperatures.

*Rephrased as suggested. Now the errors of the two calibrations are mentioned and a better explanation is given.

Page 9047, line 15. The authors do not need to refer to the review paper by Schouten et al. (2013), since they already quote a large number of papers.

*The reference has been removed.

Page 9047, lines 16-24. As specified above, several other papers aldreay discussed the fact that other environmental parameters than temperature and pH could have an effect on branched GDGT distribution. This could be briefly mentioned in the introduction.

*References have been added through the article.

Page 9048, lines 7-9. When were the soil samples collected? Please also refer to Fig. 1a at the end of the sentence.

*Date of sampling has been added.

Page 9048, line 14. What is the UNEP? I do not think it is useful to provide the values of the aridity index in two tables.

*United Nations Environment Program, this was then referenced (1997) in the reference list. The acronym is now defined in the text. Since we think this is a crucial parameter (see above) we prefer to leave the values in both tables.

Page 9049, section 2.2. I am wondering why the TOC contents were estimated by the loss on ignition technique and not by using an elemental analyzer.

*LOI is one of the methods commonly used to quantify organic carbon contents in soils. Even though the EA is more accurate, the amount of sample analyzed used in an EA is very small. Thus even with 3 replicates one measures a very small portion of the soil sample and this must be thoroughly ground to ensure homogeneity of the material. The LOI instead is done in much bigger samples and thus a higher portion of the sample can be analyzed. Soil structure is much more complex than sediments and even homogenized samples will still present certain level of heterogeneity. By measuring larger samples we expected to average out some of that microheterogenity and thus compensate for the lower accuracy of the technique.

Page 9049, section 2.3. Why do the authors use the abbreviation “GR” for the internal standard? Is the internal standard the same as the one described in the publication by Huguet et al. (2006)? Please specify how many extractions were carried out. Why did the authors use silica rather than alumina (as in most of the papers for the separation of core lipid GDGTs) for lipid separation?

*The term “GR” for the internal standard is not really an abbreviation but the name

given to the standard by the person who synthesized it: G. Rethore (we have added a reference in the text). It is not the same standard as the one used in Huguet et al. 2006. There was only one extraction carried out per sample, which is the standard procedure when using a microwave extraction. Only one sample was extracted and processed 5 times and the analytical errors were estimated with this. This is explained in the method section. On the use of silica vs alumina, we showed in Escala et al (2009; cited in the text) that either adsorbent are suitable to clean up the extracts and it really depends on the lab which one is preferentially used.

Page 9051, lines 9-11. Were the residuals also calculated for the CBT?

*Yes, see Fig, 2b and CBT(pHest, using CBT)on original manuscript.

Page 9051, lines 14-24. The concentrations of branched GDGTs reported by the authors are very low and are usually higher in soils (several μg/gTOC). Please compare your concentrations to those reported in soils in other papers. In tables 1 and 2, the samples should be listed in the same order in order to improve the readability of the paper.

*Thanks for the comment. The units have been revised and corrected. The order of the samples is now the same in both tables.

Page 9052, lines 1-3. Please specify the average LOI % value at the end of the first sentence. Please refer to Fig. 4a, which indeed suggests that branched GDGT abundance is correlated with MAP.

*This is now modified as:

“These soils are associated with high MAPim values and LOI% values above average (average LOI % is 5.1). In fact the CER soil has the highest LOI (18.3%) in the study area (Tables 1 and 2). Thus our data suggest that brGDGT abundance is controlled by both precipitation (Fig. 4a) and to a lesser extent by TOC abundance, in agreement with previous studies (e.g. Wang et al. 2013)”.

Page 9052, lines 9-12. The authors should also discuss the fact that branched GDGTs were detected in all the samples analysed until now, whatever the origin (soils, peat, lakes, coastal environments. These compounds are ubiquitous and it is therefore unlikely that the branched source microorganisms are the same in all the ecosystems. In any case, Sinninghe Damsté et al. (2011) only detected minor traces of one GDGT (Ia) in two Acidobacteria species, which suggest that these microorganisms are very likely only one potential source for branched GDGTs among others.

*This issue is discussed in the text. We added a sentence stating that brGDGTs have been found in a range of environments regardless of the origin or redox state (see Schouten et al. 2013).

Page 9052, lines 18-20. Please refer to other papers who suggested the heterotrophic lifestyle of branched GDGT source microorganisms, e.g. Oppermann et al., 2010; Huguet et al., 2012; Ayari et al., 2013.

*References have been added as suggested.

Page 9052, line 25. Branched GDGT Ic is also present in minor amounts.

*This reads now: The brGDGT's IIIb and c, IIc as well as brGDGT Ic are only present in minor amounts.

Page 9053, lines 12-14. Which additional soil parameters not taken into account in this study could affect the CBT? Please specify.

*This had been modified to: "It is possible that additional parameters not taken into account in this study may affect the CBT estimate, such as changes in vegetation or in brGDGTs producing species."

Page 9053, lines 17-18. When were the air temperatures measured in the field? The day when the samples were collected?

*All meteorological parameters were taken from the digital atlas: Ninyerola M., Pons

X., and Roure J. M.: Atlas climático digital de la Península Ibérica. Metodología y aplicaciones en bioclimatología y geobotánica. Universitat Autònoma de Barcelona, Bellaterra, 2005. This is indicated in the text.

Page 9053, lines 19-21. The MBT' vary from 0.08 (and not 0.09) to 0.59.

*This has been changed.

Did the authors try to reconstruct the temperatures using the original calibration by Weijers et al. (2007)? What would be the difference with the temperatures estimated using the extended calibration by Peterse et al. (2012)? Do the temperatures reconstructed using the original calibration fit better with the instrumental data?

*Using the Weijers et al (2007) index and calibration, we obtained estimates with larger residuals than by using the calibration by Peterse et al., in 2012 and thus we decided it was unnecessary to add the results to the present paper. Temperatures reconstructed using the original calibration do not fit better with the instrumental data. ,

Page 9054, lines 3-6. This sentence has to rephrased: "MBT' and MATim show a weak but negative correlation in contrast to the positive correlation between MBT and MAT observed by Weijers et al. and Peterse et al.". The authors state that the correlation between the MBT' and MATim for their sample set is significant, but did they perform any statistical test? If yes, please provide the p-value. If no, the correlation cannot be considered as significant.

*P value is now provided. This has been changed to: "Interestingly, MBT' and MATim show a weak but significant negative correlation within the Spanish sample set (R2=0.21; P=0.02) in contrast to the positive correlation between MBT and MAT observed by Weijers et al. (2007) and Peterse et al. (2012) (Fig. 2e)."

Page 9054, lines 7-10. I disagree with this sentence. The problem is not that the temperature range over the authors' dataset is just above the MBT/CBT uncertainty (5 âŮęC), but that there is no clear correlation between the MBT' and MATim. Indeed, the

R2 is only 0.21, which is not sufficient to see any clear correlation.

*This sentence has been removed.

Page 9054, lines 20-22. The present paper indicates that the environmental parameters controlling the distribution of branched GDGTs have to be investigated in other parts of the world and that the key parameters are not necessarily only temperature and pH.

*This paragraph has been modified to include the reviewer's suggestion: These findings constrain the use of the MBT'/CBT for paleotemperature reconstructions in the Iberian Peninsula and that the environmental parameters controlling the distribution of brGDGTs have to be investigated in other areas. The present paper also indicates that the key parameters controlling the MBT are not necessarily only temperature and pH.

Page 9054, lines 23-28. This paragraph is unclear and should be rewritten. According to section 2.3., the residuals were calculated by subtracting the estimated MAT (MATest) from the instrumentally measured MAT (MATim). Since MATim is systematically higher than MATest, then the residuals should be positive for all samples. Nevertheless, they are negative for roughly half of the samples (Fig. 3d). This point should be clarified. According to the present version of Fig. 3d, MATest values are underestimated below 10âŮęC and overestimated for the temperatures above. This should also be clarified.

*We thank the reviewer for pointing this error. While the data were correct we plotted the wrong column in Fig. 3d. This has now been corrected and the paragraph modified to: "Furthermore, our results clearly indicate that MATest residuals are not randomly distributed but rather that using MBT' underestimates values if above 10°C (Fig. 3d). This deviation was observed previously in the global data set but it is more pronounced in the Iberian soils (Fig. 3d). In addition the global dataset shows a negative residual distribution below 10°C (Fig. 3d)."

Page 9055, lines 1-2. There are other studies suggesting that changes in hydrologic moisture regime may have an impact of branched GDGT distribution, as suggested above. This should be taken into account into a revised manuscript.

*This now reads:

"Recent studies have attributed the lack of correlation between MATim and MBT/CBT to factors such as vegetation change, soil type and changes in hydrologic/moisture regime (e.g. Dirghangi et al. 2013; Loomis et al. 2013; Weijers et al., 2011)."

Page 9055, lines 4-6. According to Fig. 2f, the slope of the correlation between MAPim and MBT' for the data from this study should be positive. Nevertheless, according to the equation presented in Fig. 2f, the slope is negative (-0.0003 x MAPim). This point needs to be clarified.

*The equation in the graph has been corrected.

Page 9056, lines 21-23. The link between the two parts of this sentence is not very clear. In any case, the correlation between branched GDGT abundance and MAPim (R2 = 0.68; Fig. 4a) is only slightly higher than the one between branched GDGT abindance and MAPim (R2 = 0.60; Fig. 4c). This should be specified in the text.

*This has been changed to: The correlation with MAPim is slightly higher for brGDGT abundances (R2=0.68) than for the MATest residuals (R2=0.59) (Fig. 4 and b), thus suggesting that brGDGT abundance is not the key factor explaining the MBT'-MATest scatter in our dataset.

Page 9057, lines 3-6. Please provide the data showing that AI can explain 50 % of the variance in MBT' index.

*The data have been added: ..and 50 % of the variance in the MBT' index (MBT'= 0.38AI + 002, n=22, R2=0.53).

Page 9057, lines 6-8. The authors conclude that soil moisture availability, rather than precipitation, is the main factor controlling the MBT' index. This is logical, since branched GDGT source microorganisms live in soils.

*The sentence has been extended for clarification to: "This suggests that it is the soil's capacity to retain water, or its soil moisture rather than just precipitation that drives MBT' besides the known factors temperature and pH."

Page 9057, lines 12-20. The authors should specify that other soils have to be analysed in order to confirm the relationship between the AI index and the MBT'. Other studies should also confirm the AI value under which MBT/CBT-derived temperatures can be biased by the low soil moisture content. These two points should be mentioned in the conclusions. The authors state that hydrological conditions should be evaluated through paleohydrological proxies before using the MBT/CBT for paleotemperature reconstruction. Which paleohydrological proxies? Please give more details.

*Two sentences have been added to that section: The validity of the correlation between the MBT' and the AI has to be confirmed by analyzing brGDGTs in a larger number of soils.

While the exact hydrological threshold below which water availability exerts a stronger control on the MBT/CBT index than temperature will have to be determined in future studies, We also changed the last sentence to: (such as δD, Sachse et al. 2012).

Moreover the following sentence has been added to the end of the conclusions: The validity of the correlation between MBT' and AI as well as the AI threshold below which MBT might be biased needs to be compared in other soil types and study areas.

Page 9058, line 1. Even though the MBT' index was shown to be directly coupled with MAP, the authors should specify that this index is (indirectly) correlated with soil moisture. This is this parameter which is going to directly impact the distribution of branched GDGT-producing bacteria in soils.

*The sentence referred to both the MAP and AI. The AI is in fact what Reviewer 1

asks for: a obviously better suited parameter which seems to more directly impact the distribution of brGDGT-producing bacteria in soils. We have added a sentence to clarify this, once more, in the conclusion.

For clarity we have added the following sentence to the conclusion: The AI is a ratio of MAP and mean annual potential evaporation and increases for more humid conditions. Although the AI was not better correlated to the MBT' index (MBT'= 0.38AI + 002, n=22, R2=0.53, P<0.0001) than the MAP (R2=0.55, P<0,0001), the AI could explain more accurately the differences between the MATim and calculated MAT based on the MBT'/CBT index (MATest). The AI might thus be a better suited parameter, which more directly impacts the distribution of brGDGT-producing bacteria in soils than the total amount of rainfall.

Interactive comment on Biogeosciences Discuss., 10, 9043, 2013.