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Interactive comment on “Distributions of glycerol dialkyl glycerol tetraethers in surface soils of Qinghai–Tibetan Plateau: implications of GDGT-based proxies in cold and dry regions” by S. Ding et al.

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On behalf of my co-authors, we greatly appreciate reviewer 3 to supply many useful comments. Over the past three months, we followed her/his suggestions, rerun our samples with new HPCL-MSn system, re-analyzed the samples and rewrote our manuscript. Here we try our best to address those comments. Generally, there are two major concerns. The first one, also the most important, is the issue about new brGDGTs, called 6-methyl brGDGTs, which was not reported in our original manuscript. The second concern is about the novelty of our work. The 6-methyl

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brGDGTs is very new biomarkers and were identified and reported after 2013. Similar to our original method, many publications also used a single LC column which cannot resolve 5-methyl brGDGTs and 6-methyl brGDGTs. As the result, they misidentified them as one compounds (5-methyl brGDGTs). So far, only very limited researchers such as de Jonge et al. (2013; 2014a, 2014b) and Yang et al. (2015) used advanced chromatography to separate 6-methyl brGDGTs from 5-methyl brGDGTs. In the revised manuscript, we used two tandem LC columns to rerun our soil samples. With this new approach, 5-methyl and 6-methyl brGDGTs were well separated, and the number of identified brGDGTs increased from 9 to 15, including six 6-methyl brGDGT compounds. We organized our new data, re-plot figures and performed statistical analyses. Based on these, we rewrote most parts of our manuscript (which are highlighted). This is a tough work, but we are happy to see much improved accuracy of brGDGTs indices. Furthermore, we found that two new indices based on 5-methyl and 6-methyl GDGTs, called MBT5/6ME and IBT, are useful for reconstruction of MAT and soil pH in the QTP. Please see the revised manuscript for details.

For the second concern, we believe the revised manuscript contains many interesting points. First, our work is the first time to report 6-methyl brGDGTs in the QTP. Several studies about QTP mis-assigned the co-eluted peaks of 5-methyl and 6-methyl to one compound, which like led to large scatter of the brGDGTs-MAT calibration in the QTP. With our new data, both correlation coefficients and RMSE were significantly improved. Second, global calibrations always overestimate MAT in cold regions, and therefore the regional calibration is required. As the third pole, the QTP has cold and dry climate, providing ideal locations to evaluate relationship between brGDGTs' distributions and environmental parameters. Our studies introduced two new indices, MBT5/6ME and IBT, which are useful for the reconstruction of MAT and soil pH, respectively, in the QTP. These quantitative proxies are valuable to understand climate evolutions in QTP. Finally, our data also reveal that the position of methyl groups of brGDGTs play an important role for soil bacteria to adapt ambient pH change. This is also the first time report. Overall, with application of advanced analytical technique, our new data made

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much improvement in accurate reconstruction of temperature and soil pH, which is useful not only for QTP, but also for other cold regions.

Other minor issues. p. 483, l.16. Peterse et al 2012 is about GDGTs, not the methods mentioned here. Replace with references where these caveats are discussed. RESPONSE: this is a good comment. We delete this reference and replaced with new references. We rewrote as “Microfossil assemblages based on pollen, diatom or chironomid are commonly used paleothermometers, but they are also influenced by precipitation, salinity, nutrient or other environmental factors (Keatley et al., 2009; Meriläinen et al., 2000; Seppä & Birks, 2001).

p.483, l. 17. ‘In addition’ sounds strange as the sentence discusses a positive application rather than a caveat. Response: we deleted “in addition’ in the revised manuscript.

p. 483, l.26 : : .lakes, although they: : RESPONSE: We changed this sentence into “A major limitation of UK’37 is that long-chain alkenones are not always present in lakes, although they were reported in some QTP lakes” in the revised manuscript.

p. 484, l. 7. According to their chemical structure: : : RESPONSE: This sentence is related to isoprenoids and branched GDGTs. After separation of 5-methyl and 6-methyl brGDGTs, we thought it is better to focus on these new compounds. So we deleted all contents about isoprenoid GDGTs in the revised manuscript.

p. 484, l. 10-15. A more nuanced BIT distribution can be found in Schouten et al. 2013, OG where endmembers are different than based on older literature. RESPONSE: As mentioned above, we deleted all contents about isoprenoid and BIT index since new 6-methyl brGDGTs was identified with our new method.

p. 485. Can all these calibration equations not simply be summarized in a Table ? Response: we also want to put all equations in one table, but it seems difficult since there are over ten equations in our work. So we still keep them separately.

p. 485. l.8. It is impossible to say if proxies are successful, what you can say is that they

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have been applied. Furthermore, the lake situation is quite different from that of soils, i.e. different calibrations are used because of in situ production (e.g. Tierney 2010, Pearson 2011, etc.). This is different from a ‘regional calibration’, i.e. the MBT/CBT is not used but rather transfer functions of individual GDGT concentrations. This should be made clear in the introduction right here, and not just briefly at p. 486. RESPONSE: We changed “successfully” into “increasingly”. It is true there are more than one calibrations. So we changed “a regional calibration’ into “regional calibrations”.

p. 485, l. 20. Blyth and Schouten was not using soils but stalagmites. Response: We deleted this reference in the revised manuscript.

p. 487, l. 7. In the Suppl. Table the range in MAT is much wider than simply 0.1 C. Importantly, how many weather stations are on the QTP and how were the temperature corrections for adiabatic lapse rates done ? RESPONSE: Good comments. We added these information in the revised manuscript. From line 145 to 153, we added sentences as “There are about 70 meteorological stations in the QTP, mainly distributed in the eastern part and northern border of the QTP. Thus, direct observation data on temperature and precipitation at our sampling sites are generally lacking. In this study, we use the WorldClim dataset (Hijmans et al., 2005) to interpolate annual, seasonal and monthly mean precipitation and temperature (Table S1). The local climate is dry and cold. The MAT of our sampling sites ranges from -5.5 to 7.6 °C with a vertical lapse rate of 0.487 °C/100 m to 0.699 °C/100 m (Cheng et al., 2012). The vertical lapse rate of air temperature decreases from north to south of the QTP. The mean annual precipitation (MAP) at different altitudes varies from ca. 85 mm to ca. 495 mm.”.

p. 489. l. 10. I see there has been no correction for the difference in ionization efficiency of the internal standard (a C46 GTGT) compared to GDGTs. This can be quite variable and substantial (see Huguet et al., 2006). Hence, you do not have real absolute concentrations but estimated based on the (likely incorrect) assumption that the internal standard has the same response factor as GDGTs. Please note this caveat. RESPONSE: this is true that ionization efficiency is different between internal standard

C46 GDGTs and brGDGTs. So far, no authentic standard is available and C46 GDGTs has been regarded as the best internal standard for GDGT analysis. Also, the quantification of GDGTs without response factor correction is very popular among organic geochemists. Considering that all brGDGTs proxies are based on relative abundance rather than absolute concentrations, we only used peak areas to calculate the brGDGT ratios. In the revised manuscript, we added the sentence as “Since we assume same response factors among different brGDGTs and C46 GDGTs, our study can be only regarded as semi-quantification.” (Section 2.3)

p. 490, l. 15. Please refer to the recent compilation of Schouten et al 2013 which showed that the average BIT value is 0.90 ± 0.14 . p. 490, l. 20. I do not know of any recent studies who use the BIT in lakes to trace soil OM because of the now well-known large in situ production in lakes. Hence this ‘warning’ is unnecessary. p. 490, l. 2. Cite also Kim et al. 2010 L&O who found lower BIT values at $\text{pH} > 7$ in French soils. Your Fig. 3a looks exactly like their Fig. 6. RESPONSE: As mentioned above, since six 6-methyl brGDGTs were identified from previously co-eluted 5-methyl brGDGTs, the traditional BIT definition is not applicable. So we deleted all contents related to BIT in the revised manuscript.

p. 492. I wonder in how far the RDA results are affected by the limited number of soils and also the specific range in pH, temperature and MAP of QTP. Compared to the different global data sets the range in temperature is relatively small (< 10 C). In particular, the global calibrations shows at $\text{MAT} < 15$ C a pronounced heterogeneity. Can it therefore not be expected that MAP plays a more important role than MAT ? RESPONSE: this is a good suggestion. In the revised manuscript, we performed RDA and pRDA based on new data (including 5-methyl and 6-methyl brGDGTs). Our results showed soil pH is the most important contributor to relative abundance of brGDGTs, followed by MAT, while MAP is the least important one. This result is consistent with the recent study of de Jonge et al. (2014), but contrast with our previous result for the same samples, highlighting the importance of separating 5-methyl and 6-methyl brGDGTs to

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evaluate brGDGT indices. We rewrote as “Our RDA result shows that MAT and pH have a significant independent effect on the brGDGT distribution in the QTP soils, however, no significant correlation was observed between MAP and brGDGTs ($p > 0.05$; Table 1). Soil pH explaining up to 60.1% of the total variables is the largest contributor to the variance, followed by MAT (up to 16.4%) and MAP (up to 10.8%). ” in section 3.2

p. 493. l. 3. Please perform a statistical test to see if the slopes are significantly different between the different calibrations. RESPONSE: After re-calibration based on 5-methyl and 6-methyl brGDGTs, the equation 13 and 15 showed same slope (1.49). In the revised manuscript, we discussed CBT'-pH (De Jonge et al., 2014) and new defined CBT"-pH (this study) in details. Please see section 3.3.2 (line 319-344).

p. 494, l. 15. I think the smaller RSME of your QTP calibration compared to the global calibration is artificial. This is because the temperature range of your data set is much smaller than that of the global calibration (ca. 10 C versus 30 C). So, an error of 2.4 C on a range of 10 C is worse than that of 5 C RSME on a scale of 30 C. This should be discussed more fairly. RESPONSE: this is correct. The lower RMSE of regional calibration is due to its narrow temperature range. We already realized this point and discussed it in section 3.2 from line 292 to 304 in the revised manuscript.

p. 495. l. 26. Perhaps a better way to test this is to see statistically if the correlations for QTP are significantly different from the global correlation or the Yang et al. calibration. Note also that interlaboratory differences between labs may play a big role in the added scatter with the Yang et al 2014 data set mostly coming from a single lab. p. 496, l. 8-17. This part is not clear to me. First I wonder if the slightly better correlation is really statistically significant or just because the temperature range seems larger for this season. I also do not understand on what data the conclusion is based that “more variation in brGDGT compositions occurs in winter”. And I also do not see the connection with soil respiration as stated in the next sentence. This should be clarified. RESPONSE: Very good comments. As mentioned above, after separation of 5-methyl and 6-methyl brGDGTs with improved chromatography, CBT is no longer an important

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factor on MAT. So we deleted the equation 12 and 13 and related discussion from our original manuscript. Instead, we discussed several new indices such as MBT5ME, IBT and CBT". Please see section 3.3 for details.

Table 1. Considering the uncertainty in the quantification of branched GDGTs (see previous comment), the numbers should not be reported with a decimal point. RESPONSE: we made correction in the revised manuscript. As mentioned above, we no longer discussed absolute concentrations of brGDGTs.

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