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Interactive comment on "Ubiquitous production of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in global marine environments: a new source indicator for brGDGTs" *by* Wenjie Xiao et al.

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On behalf of my coauthor, I really appreciate the reviewer 2 supplying very detailed comments, which are helpful to improve our manuscript. Overall, the reviewer 2 acknowledge the merit of our paper. As he or she said that "the work by Xiao et al. is a very interesting and valuable contribution to the study of the distribution and origin of branched GDGTs (brGDGT) in mesophilic marine environments and their use as climate proxies" and "This finding, in my opinion, should grant the paper publication in a number of (bio)geochemical journals". The main concern of the reviewer 2

is not 100% sure of in situ brGDGTs in aquatic environments. In our opinion, more and more studies support that brGDGTs are also biosynthesized by aquatic organisms. Presently, the in-situ production of brGDGTs in aquatic environments has been accepted by most organic geochemists. For examples, Peterse et al. (2009a), Zhu et al. (2011), Liu et al. (2014) Weijers et al. (2014) and Zell et al. (2014) all observed different brGDGT compositions between marine sediments from different seas and soils on adjacent lands, so they proposed in situ production of brGDGTs in marine environments. Similar conclusions have been reached for lacustrine settings by Sinninghe Damsté et al. (2009), Tierney & Russell (2009) and Tierney et al. (2012) as well as for rivers by Zhu et al. (2011), De Jonge et al. (2015), French et al. (2015) and Zell et al., (2015). Most those studies were published after 2010, so more and more organic geochemists accepted the view that brGDGTs were produced in aquatic environments. Peterse et al. (2009) compared the brGDGT distribution in Svalbard soils and nearby fjord sediments, and found that concentrations of brGDGTs (0.01–0.20 μg/g dw) in fjord sediments increased towards the open ocean and the distribution was strikingly different from that in soil. Zhu et al. (2011) examined distributions of GDGTs in surface sediments across a Yangtze River-dominated continental margin, and found evidence for production of brGDGTs in the oxic East China Sea shelf water column and the anoxic sediments/waters of the Lower Yangtze River. At the global scale, Fietz et al. (2012) reported a significant correlation between concentrations of brGDGTs and crenarchaeol ($p < 0.01$; R2 = 0.57–0.99), suggesting that a common or mixed source for brGDGTs and iGDGTs are actually commonplace in lacustrine and marine settings. Weijers et al. (2014) found that distributions of African dust-derived brGDGTs were similar to those of soils but different from those of distal marine sediments, providing a possibility to distinguish terrestrial vs. marine brGDGTs based on molecular compositions. More recently, Sinninghe Damsté (2016) reported tetraethers in surface sediments from 43 stations in the Berau River delta (Kalimantan, Indonesia), and this result, combined with data from other shelf systems, are coherent with the hypothesis that brGDGTs are in situ produced in shelf sediments especially at water depth of 50–

300 m. In the remote ocean where no direct impact from land erosion via rivers takes place, eolian transport and in situ production are major contributors for brGDGTs. So in our opinion, based on recent studies and our study, the in-situ production of brGDGTs is a ubiquitous phenomenon in marine environments, as our title states. We try our best to address all comments point by point as follows. In addition, all changes are highlighted in the revised manuscript.

Comment: Lines 34 and 35: to estimate environmental variables in the past Response: we accept this suggestion and rewrote the sentence as "These lipids have been a focus of attention of organic geochemists for more than ten years because they can be used to estimate environmental variables in the past such as temperature, soil pH, organic carbon source and microbial community structure"

Comment: Line 45: the attribution of the brGDGTs is still hypothetical. But in any case it is unclear. why the authors claim that their preferential occurrence in soils/peats means that they are derived from bacteria Response: the source assignment of branched GDGTs to bacteria is based on structural configuration (1,2-di-O-alkyl-sn-glycerol configuration). It is generally accepted by Organic Geochemists.

Comment: Li 48-50: the text should be rewritten, it is unclear what the authors are trying to say Response: in revised manuscript, we rewrote the sentences as: "So far, only one brGDGT with two 13,16-dimethyl octacosanyl moieties was unambiguously detected in two species of Acidobacteria (Sinninghe Damsté et al., 2011), which hardly explains high diversity and ubiquitous occurrence of up to 15 brGDGT isomers in environments (Weijers et al., 2007b; De Jonge et al., 2014). Therefore, other biological sources of brGDGTs, although not yet identified, are likely."

Comment: Li 58-59: the BIT index is used for what? Response: we rewrote the sentence as "Since its advent, the BIT index has been increasingly used to trace soil organic matter in different environments" in revised manuscript.

Comment: Li 58-60: in here the authors should also comment the often overlooked

drawback of the BIT index, namely that is dependent on the input of chrenarcheol, which is linked to marine productivity. Consequently, BIT values are not just dependent on the inputs of soil brGDGTs, but also on the productivity of marine Archaea. For instance, sites with equal inputs of terrestrial brGDGTS but different local productivity would display different BIT values. There are a number of references out there discussing this issue, for instance: *Herfort, L., S. Schouten, J. P. Boon,M. Woltering, M. Baas, J. W. H. Weijers, and J. S. Sinninghe Damsté (2006), Characterization of transport and deposition of terrestrial organic matter in the southern North Sea using the BIT index, Limnol. Oceanogr., 51, 2196–2205, doi:10.4319/lo.2006.51.5.2196. *Fietz, S., Martínez-Garcia, A., Huguet, C., Rueda, G., & Rosell-Melé, A. (2011). Constraints in the application of the Branched and Isoprenoid Tetraether index as a terrestrial input proxy. Journal of Geophysical Research, 116(C10), 1–9. *Smith, R. W., Bianchi, T. S., & Savage, C. (2010). Comparison of lignin phenols and branched/isoprenoid tetraethers (BIT index) as indices of terrestrial organic matter in Doubtful Sound, Fiordland, New Zealand. Organic Geochemistry, 41(3), 281–290. http://doi.org/10.1016/j.orggeochem.2009.10.009 Response: This is a good comment. In the revised manuscript, we added this comment as well as related references. We wrote as "However, the BIT index is not just dependent on the abundance of brGDGTs, which reflects the input of soil organic matter, but also on the abundance of chrenarcheol, which is linked to marine productivity (e.g., Herfort et al., 2006ïijŻSmith et al, 2010; Fietz et al., 2011)."

Comment: Li 76: "The premise of all brGDGT", do you the authors mean: the underlying assumption? Response: Yes, that is what we meant. In order to avoid confusion, we changed "premise" into "underlying assumption" in the revised manuscript.

Comment: Li 79: "supporting in situ production of brGDGTs": the authors cited hypothesized the occurrence of in situ production, so their studies supported the hypothesis of the occurrence of... Response: Actually, there are a number of studies supporting in-situ production of brGDGTs aquatic environments such as lake, river and marginal seas, such as Svalbard, Norway(Peterse et al., 2009a, OG); Yangtze River and estuary (Zhu et al., 2011, OG); Black Sea and Cariaco Basin (Liu et al., 2014, Mar Chem); equatorial West African coast (Weijers et al., 2014, OG); Portuguese margin (Zell et al., 2014; Biogeosciences). So the in-situ production of brGDGTs is generally accepted by organic geochemists.

Comment: Li 89: instead of "supported" use "findings were coherent with the hypothesis that brGDGTs are in situ produced in marine environaments". Response: Although we are pretty sure for the existence of in-situ production of brGDGTs in aquatic environments (see our response above), we rewrote as "this result, combined with data from other shelf systems, are coherent with the hypothesis that brGDGTs are in situ produced in shelf sediments especially at water depth of 50–300 m."

Comment: Li 91: instead of "river" use "fluvial inputs or run off" Response: we accepted this comment and changed "river" into "fluvial inputs"

Comment: Li 93-94: brGDGTs have not been analyzed in that many dust samples to date, but it may be obvious to assume in the meantime that their concentration in dust will be as high, proportionally, to the contents of soil particles in dust. In this section it is relevant to cite as well the just published paper by Yamamoto et al., 2016, GCA, 191,15 October 2016, Pages 239–254.

Comment: Li 95: "became": why just in the past? Response: we change "became" into "are major contributors for brGDGTs".

Comment: Li 112: mean depth Response: we already corrected this spelling mistake.

Comment: Li 115-116: One 64 cm long gravity core Response: we accepted this suggestion and made change in revised manuscript.

Comment: Li 117: namely? Response: we deleted "namely" and rewrote the sentence as "while other two cores, M3 (38.66°N, 119.54°E; 53 cm long) and M7 (39.53°N, 120.46°E; 60 cm long), were collected in July 2013".

Comment: Li 121-122: I would rephrase "cores cover the sedimentation period of less than 100 years" Response: We rewrote the sentence as "showing that the age of the bottom sediments was less than 100 years old".

Comment: Li 125: samples were ground with a mortar and pestle Response: Based on this suggestion and comment from reviewer 1, we rewrote as "The detailed procedures for lipid extraction and GDGT analyses were described in previous studies (Ding et al., 2015; Xiao et al., 2015). Briefly, the homogenous freeze-dried samples were ultrasonically extracted with dichloromethane (DCM)/methanol (3:1 v:v)."

Comment: Li 137: Define "EtOAc" Response: We deleted EtOAc in the revised manuscript, and rewrote the part of analytical procedure in revised manuscript.

Comment: Li 138; I would rephrase "Samples were injected: : :", where? Response: We rewrote the part of Lipid Extraction and Analyses according to the reviewers' comments. Please see the revised manuscript for details (Section 2.2).

Comment: Li 139: As this is relatively novel, I would indicate from which reference(s) the HPLC method is derived. Response: In the beginning of the paragraph, we added the references as "The detailed procedures for lipid extraction and GDGT analyses were described in previous studies (Ding et al., 2015; Xiao et al., 2015)".

Comment: Li 175: "The dataset in this study are composed of GDGTs from.." absolute/relative concentrations?, fluxes? Response: We changed into "The dataset in this study are composed of relative abundance of GDGTs and derived parameters from 1354 globally distributed soils and 589 marine sediments (Fig. 2 and supplementary data)" in the revised manuscript.

Comment: Li 177: I would rephrase "and have water depth" Response: we changed into "and the water depth ranges from 1.0 to 5521 m".

Comment: Li 197: I would rewrite "Both iGDGTs including crenarchaea and brGDGTs". Chrenarchaea or chrenarcheaol? Response: We rewrote as "A series of iGDGTs including crenarchaeol and brGDGTs including 5-methyl and 6-methyl isomers were detected in Bohai Sea sediments." In the revised manuscript.

Comment: Li 206: "expectable"? Response: we changed into "Such difference is not surprising".

Comment: Li 207-210: iGDGTs are found in soils too. Response: It is true iGDGTs are present in soils at low abundance. So we rewrote the sentence as "However, the BIT index itself has no ability to distinguish terrestrial vs. aquatic brGDGTs because brGDGTs and crenarchaeol used in this index are thought to be specific for soil organic carbon and marine organic carbon, respectively (Hopmans et al., 2004), although crenarchaeol is also present in soils at low abundance (Weijers et al., 2006)."

Comment: Li 208: the statement does not make much sense as the BIT was not "designed" for this purpose as it has already been discussed Response: We agree on that BIT is designed for estimation of terrestrial organic matter in aquatic environments in Hopmans et al. (2004). However, more and more recent studies suggest that branched GDGTs are also in situ products in aquatic environments, such as lake, river and seas. Although the BIT index is still useful for two end-members (aquatic and soil organic matter), but it lack the capability to discern the source of branched GDGTs from terrestrial or in situ aquatic origin in seas. In contrast, the character of brGDGTs' composition (excluding crenarchaeol) can be used to estimate the source of brGDGTs, such as IIIa/IIa ratio proposed in our study. Nevertheless, we rewrote the sentence here as "However, the BIT index itself has no ability to determine the source of brGDGTs (terrestrial vs. aquatic) because brGDGTs and crenarchaeol used in this index are thought to be specific for soil organic carbon and marine organic carbon, respectively (Hopmans et al., 2004), although crenarchaeol is also present in soils at low abundance (Weijers et al., 2006)."

Comment: Li 212-214: I would rephrase this section "all parameters except MI can distinguish Chinese soils from Bohai Sea sediments" Response: we accept this suggestion and rewrote this section. In the revised manuscript, we rewrote as "We performed ANOVA for a variety of brGDGTs' parameters. All results except from MI show a significant difference between Chinese soils and Bohai Sea sediments. The IIIa/IIa ratio is the most sensitive parameter which can completely separate the samples into four groups, Chinese soils (0.39$\pm$0.25; Mean$\pm$SD; same hereafter), M1 sediments (0.63$\pm$0.06), M3 sediments (1.16$\pm$0.12) and M7 sediments (0.93$\pm$0.07)."

Comment: Li 234-235: "enhanced IIIa/IIa values in the Bohai Sea sediments is caused by in 234 situ production of brGDGTs." The statement should be rephrased to differentiate between actual findings (i.e. IIIa/IIa values), and their proposed interpretation(s) (i.e. in situ production). Response: It

Comment: Li 237-239: "The site M1 is adjacent to the Yellow River mouth and receives the largest amount of terrestrial organic matter, causing lower IIIa/IIa values". Again, the authors should rephrase the statement to indicate which is their interpretation of the IIA/IIa values, as they do not prove what causes the lower IIIa/IIa values. The same applies to text in lines 262, 272-273, 315, 371-374. Li 240: "comprises of the least amount of terrestrial organic matter", please justify this statement. Li 242: "strongly", why?, is this a subjective claim or is backed up by some stats.? Response: Good comment. We rewrote the sentences as "In our study, the site M1 is adjacent to the Yellow River mouth and receives the largest amount of terrestrial organic matter, causing lower IIIa/IIa values (0.63$\pm$0.06). In contrast, the site M3 located in central Bohai Sea comprises of the least amount of terrestrial organic matter, resulting in higher IIIa/IIa values (1.16$\pm$0.12). The intermediate IIIa/IIa values at the site M7 (0.93$\pm$0.07) is attributed to moderate land erosion nearby northern Bohai Sea (Fig. 2). These GDGTs' results, consistent with other terrestrial biomarkers such as C29 and C31 n-alkanes and C29 sterol (data not showed here), suggest that the higher IIIa/IIa values in the Bohai Sea sediments compared to Chinese soils (0.39$\pm$0.25) is most likely caused by in situ production of brGDGTs."

Comment: Li 246-247: The authors should indicate that they try to validate the ratio as a proxy for something, not to validate the ratio itself, or are they also trying to assess if the IIa and IIIa are ubiquituous? Response: We added the sentence to state this point. In the beginning of this paragraph, we wrote as “Similar to Bohai Sea in this study, the compounds brGDGT IIa and IIIa are also ubiquitously present in these environments.”

Comment: Li 258: compiling or compilation? Response: We changed “compiling” into “Compilation”.

Comment: Li 259: brGDGTs concentrations?, fluxes? Data? Response: It is the concentration of brGDGTs. We made change in revised manuscript.

Comment: Li 274-275: I would rephrase this section. Where is the statistical analysis? Response: we wrote as “We further extend the dataset on global scale (Fig. 5), showing that the IIIa/IIa ratio is still significantly higher in marine sediments than soils ($p<0.01$).” Similar to Bohai Sea, we also perform statistical analysis but detailed results are not shown here.

Comment: Li 278: “unusually low” in which context are they low? Response: Red Sea sediments showed unusually low IIIa/IIa values compared to other marine sediments. So we changed the sentence as “An exception was observed for Red Sea sediments which have unusually low IIIa/IIa values (0.39 ± 0.21) compared to other marine sediments (>0.87).”

Comment: Li 279: “Bab el Mandeb” strait Response: We corrected it.

Comment: Li 279: “litter” or low? Response: we corrected this spelling error.

Comment: Li 280: salinity, no units? Response: We added “PSU” after salinity.

Comment: Li 281-283: The Red Sea is an extreme environment?, the authors do not explain why the ratios from environments as different as those in Fig. 5 (e.g. Arctic, Mediterranean, Chilean margin, South China Sea, river waters and soils) fit within the scheme proposed to interpret the IIIa/IIa ratios, whereas the Red Sea does not. The interpretation proposed is not very convincing, particularly as they seem to argue

through the text that the producers of brGDGTs in soils and marine settings are not the same type of organisms. Response: we explained the reasons why Read Sea is different in brGDGTs' compositions from other marine systems. In the manuscript, we wrote as “the Red Sea has a restricted connection to the Indian Ocean via the Bab el Mandeb Strait. This, combined with high insolation, low precipitation and strong winds result in surface water salinity up to 41 PSU in the south and 36 PSU in the north of the Red Sea (Sofianos et al., 2002). Under such extreme environment, distinct microbial populations may be developed and produced GDGTs different from that in other marine settings (see Trommer et al., 2009 for details).

Comment: Li 284-286: level or values? Response: we changed level into values in the revised manuscript.

Comment: Li 290: “Why do soils have lower IIIa/IIa” and the Red Sea? Response: As we mentioned above, Red Sea is an exception. So we add “generally” in the sentence. Considering the comments from reviewer 1 and 2, we rewrote as “Why do marine sediments generally have higher IIIa/IIa values than soils?”

Comment: Li 302-303: Please explain further what is meant by and why is not related to the IIIa/IIa ratio: “because both soils and marine sediments are globally distributed and their temperatures (MAT vs. sea surface temperature) have no systematic difference”. Response: We accepted reviewer 1 and 2's suggestions, and rewrote the whole paragraph. Pleases see line 352 to 389 for details.

Comment: Li 305: “positive correlation with soil pH ($R2=0.43$)”, really?, with such a R2 value? Response: we already double check this point. In the revised manuscript, we added figure 6 that shows even higher R2 value between the IIIa/IIa ratio and soil pH ($R2=0.51$; Fig. 6) when global soil dataset are included.

Comment: Li 305-312: I would use more caution in this section as most of the evidence used to back the authors' interpretation is hypothetical Response: we added this content in the revised manuscript as: “It should be pointed out that unlike fairly stable pH of overlying sea water, the pH of pore waters in marine sediments can vary significantly, which may influence compositions of brGDGTs. Nevertheless, at current stage, the occurrence of higher IIIa/IIa values in marine sediments is most likely attributed to relatively higher pH and lower deep water temperature. Further studies are needed to disentangle relative importance of these two factors."

Comment: Li 322-324: the regression in Fig. 6 is the product of wishful thinking. One can fit any curve to a group of unrelated data point and get "satisfactory" R2 value. I think that it is evident from Figure 6 that BIT and the III/II ratios are unrelated. There are two cluster of data. Why samples with BIT values below 0.3 (which are supposed to be only typical of sites with low terrigenous inputs) have such an spread of III/II values?, Similarly, how come that values of III/II below 0.8, which are proposed to be only found in soils (li 285) has such an spread of BIT values from 0 to 1. It does not make sense to me if both indicators are indicators of marine vs. terrigenous organic carbon. Should not they fit into a simple straightforward linear regression if IIIa/IIa and BIT are both indexes for assessing soil organic carbon (inputs) in marine settings, as claimed by the authors? . Response: we tried the different correlation between IIIa/IIa and BIT. The exponential correlation has much higher R2 value than linear correlation. This is the reason we showed exponential curve in figure 6 (figure 7 in revised manuscript). But more important, our key point is not correlation between IIIa/IIa and BIT. We want to show different clusters of marine and terrestrial samples based on these two indicators. We chose <0.3 and >0.67 as threshold values because they can include 90% of samples. We highlight this point in the manuscript.

Comment: Li 366-368: it is not necessary to say in the conclusions section that the authors have reached some conclusions. It is redundant. Response: we delete this redundant sentences in revised manuscript.

Comment: Li 369: Please define what is meant by "generally lower", as it stands it is a subjective statement which is followed by values that are purported to reflect objective thresholds (which are not in fact). Response: we changed

Comment: Li 369-370: The authors have not demonstrated the occurrence of terrestrial inputs in all samples studied (e.g. Fig. 6). They cannot claim that high values of III/II occur in sediments "devoid of significant terrestrial inputs". What is meant by significant anyhow?. Response: Good comment. We rewrote as "Our investigation for brGDGTs in three Bohai Sea cores and globally distributed soils and marine sediments shows that the brGDGTs IIIa/IIa ratio is lower than 0.59 in 90% of soils, but higher than 0.92 in 90% of marine sediments devoid of significant terrestrial inputs"

Comment: Fig. 1: m/z of chrenarchaeol? Response: We confirmed as crenarchaeol

Comment: Fig. 4 combines 4 graphs extracted from published papers that are unrelated to each other, and I think that they should go in different figures for coherence sake in the supplementary information section. Explain the abbreviations in the x-axis in fig. 4b in the legend. Response: we combined the comments from reviewers 1 and 2 as well as Dr. Ding He. In order to express more clearly, we still leave the figure 4 in the manuscript.

Comment: Fig.5. The use of symbols of different size prevents the visualization of all the data in the map, as the big dots cover smaller dots, and also are easier to visualize that smaller dots, giving the impression that "there are more of them". Please use another way of visualizing all the data that provides equal weight to data with different range of values. Response: we asked the suggestions from several senior scientists and biogeochemists. They think it is useful to use different size of symbol to reflect high or low values of IIIa/IIa. So we did not make any change in the revised manuscript.

Comment: Table 1: where are the samples from?. Please explain further what is mean by: "Different letters (a, b, c, d) represent significant difference at the level of $p<0.05$." Response: We added more explanation in the title of Table 1.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/bg-2016-235/bg-2016-235-AC3-

supplement.pdf

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