Biogeosciences Discuss.,
doi:10.5194/bg-2016-235-AC1, 2016

Biogeosciences
Discussions

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.

Wenjie Xiao et al.

yunpingxu@pku.edu.cn

Received and published: 17 July 2016

Response to reviewer 1's comments: On behalf of my coauthors, I really appreciate the reviewer to acknowledge the merit of our work. As the reviewer said, "The authors present an interesting manuscript, based on an extensive dataset compiled from previous publications. The figures are well chosen and convey the message clearly." In addition, we also thank the reviewer providing a number of useful comments, which are helpful to improve our manuscript. Here, we tried our best to address the reviewer's comments point by point.

Anonymous Referee #1 1) Main comments (short, they are elaborated on below). It is interesting that the IIIa/IIa ratio increase significantly in offshore marine sediments. However, the authors have not attempted to explain this by comparing the compounds this ratio is composed of (IIIa, IIIa', IIa or IIa'). This lessens the value of this study, by narrowing its implication for palaeoenvironmental studies. In the Kara Sea (Arctic Ocean), De Jonge et al. (2016) have clearly shown that brGDGT IIIa' increases in increasingly marine conditions (Yenisei River outflow), while brGDGT IIa' does not. The Iberian Sea (Sinninghe Damste et al., shows a different pattern). If the authors can shed light on which mechanism acts on marine sediments globally, this has implications for which temperature proxies can be used (also see De Jonge et al. (2016)).

Response: In our study, we used 2D LC-MS to separate 5-methy and 6-methyl brGDGTs. The reason we combined them together in the manuscript is that most previous studies using one dimensional LC-MS did not separate these two types of isomers. The first study to report 6-methyl brGDGTs was published in 2013 by De Jonge et al. So far only very limited studies paid attention to this issue. Nevertheless, we agree with the reviewer that the separation of 5-methyl and 6-methyl brGDGTs may provide more accurate proxies for source and environmental information of brGDGTs. In the revised manuscript, we added comment on this points We wrote in the conclusion as "We also note a relatively large scatter of the IIIa/IIa ratio within both terrestrial and marine realms, and different environmental responses of 5-methyl and 6-methyl brGDGTs (e.g., De Jonge et al., 2014, 2016; Xiao et al., 2015). As a result, the separation of these two types of isomers is needed in future studies to develop more accurate brGDGTs' proxies." We expect more data about 5-methyl and 6-methyl brGDGTs available in future, so we can compile them and develop new molecular proxies.

2) I find the reasoning behind the absence of a temperature difference between soil/peat and marine brGDGTs incomplete. I expect a very large difference in temperature between soil and marine bottom water, even at similar latitudes.

Response: This is a good comment. Recent studies suggested that the production of GDGTs in deep water is possible. If so, large temperature gradient between surface and deep water in ocean inevitably affects brGDGTs' compositions. In the revised manuscript, we consider this factor for different brGDGTs' compositions between land and sea. In section 3.2, we rewrote the whole paragraph (line 486-549) as "Why do marine sediments have higher IIIa/IIa values than soils? It has been reported that relative number of methyl groups positively correlates with soil pH and negatively correlates with MAT (Peterse et al., 2012; Weijers et al., 2007b). The IIIa/IIa ratio is actually an abundance ratio of hexamethylated to pentamethylated brGDGT, and thus is also affected by ambient temperature and pH. Unlike iGDGTs which is well known to be mainly produced by Thaumarchaeota (Schouten et al., 2008; Sinninghe Damsté et al., 2002), the marine source of brGDGTs remains elusive. Here, we assume that marine organisms producing brGDGTs response to ambient temperature in the same way as those soil bacteria producing brGDGTs, i.e., a negative correlation between relative number of methyl group of brGDGTs and ambient temperature. In order to evaluate temperature effect on brGDGTs' compositions, we need consider the locale where brGDGTs are produced. If brGDGTs in marine environments are predominantly produced in euphotic zone, a significant difference for the IIIa/IIa ratio would not be observed between soils and marine sediments because both soils and marine sediments are globally distributed, leading to no systematic difference between soil temperature and sea surface temperature. Alternatively, if brGDGTs in marine sediments are partially derived from deep-water dwelling or benthic organisms, cold deep water (generally 1âĂŠ2 oC) would cause higher IIIa/IIa values in marine sediments, as we observed. Besides temperature, pH can also alter compositions of brGDGTs (Weijers et al., 2007). Based on global soil data, the IIIa/IIa ratio shows a strong positive correlation with soil pH (R2=0.51; Fig. 6). In our study, the majority of soils are acidic or neutral (pH<7.3) and only 8% of soil samples mainly from semi-arid and arid regions have pH of >8.0 (e.g., Yang et al., 2014a). In contrast, seawater is constantly alkaline with a mean pH of 8.2. With this systematic difference, bacteria living in soils tend to produce higher proportions of brGDGT IIa, whereas unknown marine organisms tend

to biosynthesize higher proportions of brGDGT IIIa if they response to ambient pH in a similar way as soil bacteria in term of biosynthesis of brGDGTs. Taking together, we attributed the occurrence of higher IIIa/IIa values in marine sediments to higher pH and lower deep water temperature. Further studies are great needed to disentangle relative importance of these two factors."

3) The introduction of previous studies describing marine in-situ produced brGDGTs is too concise. Furthermore, in the discussion I miss how the conclusions from the authors fit with previously published manuscripts? Can we say anything about the water depths at which brGDGTs are produced?

Response: we discussed in more details about in-situ of brGDGTs in the revised manuscript. Please see our response below (line 97-90). To the best of our knowledge, there is no study addressing production of brGDGTs at different water depth. However, a recent study from Kim et al. (2015) has demonstrated an influence of deep water derived iGDGTs on TEX86. So if brGDGTs are also produced in deep water, it would alter brGDGTs' proxies. We discussed this point in section 3.2 "Why do marine sediments have higher IIIa/IIa values than soils?". From line 535 to 543, we said "Alternatively, if brGDGTs in marine sediments are partially derived from deep-water dwelling or benthic organisms, cold deep water (generally 1âĂŠ2 oC) would cause higher IIIa/IIa values in marine sediments, as we observed in this study. Although to the best of our knowledge, there is no study reporting in situ production of brGDGTs throughout water column in ocean. Recent studies (Kim et al., 2015; Taylor et al., 2013) have suggested that Thaumarchaeota thriving in the deeper, bathypelagic water-column (>1000 m water depth) biosynthesized iGDGTs with different compositions as surface dwelling Thaumarchaeota, and thereby influences signals of TEX86."

Minor comments: 4ïijĽL14. Rephrase this so the "presumed source" of brGDGTs (soil, peat) is introduced first.

Response: we made change in the revised manuscript as: "Presumed source specificity of branched glycerol dialkyl glycerol tetraethers (brGDGTs) from bacteria thriving in soil/peat and isoprenoid GDGTs (iGDGTs) from aquatic organisms led to the development of several biomarker proxies for biogeochemical cycle and paleoenvironment."

5ïijĽL33: Use 'have been' instead of 'have become'.

Response: we made correction according to reviewer's comment.

6ïijĽL43: Rephrase, this is a confusing sentence. The stereoconfiguration of the glycerol moiety indicates that they are produced by bacteria, not the fact that they are abundant in soils.

Response: We rewrote as "In contrast, the 1,2-di-O-alkyl-sn-glycerol configuration of brGDGTs is interpreted as an evidence for a bacterial rather than archaeal origin for brGDGTs (Sinninghe Damsté et al., 2000; Weijers et al., 2006)" in the revised manuscript.

7) L49: Please include that 15 brGDGT compounds are generally encountered in soils. Besides the variation in the number of methyl groups and cyclopentane moieties, the location of the outer branches has been shown to shift as well.

Response: we accept this suggestion, and rewrote sentences as "So far, only two species of Acidobacteria were identified to contain one brGDGT with two 13,16-dimethyl octacosanyl moieties (Sinninghe Damsté et al., 2011), which is contrast to high diversity and ubiquitous occurrence of 15 brGDGT isomers in environments (De Jonge et al., 2014; Weijers et al., 2007b)."

8) L54: Use Thaumarchaeota instead of crenarchaea.

Response: we made change in the revised manuscript.

9) L58: Here, you can also refer to 'Weijers et al. (2014), Constraints on the sources of branched tetraether membrane lipids in distal marine sediments, OG 72'.

Response: We added the reference of "Weijers et al., 2014" in the revised manuscript.

10) L87-90. As this manuscript discusses brGDGTs produced in marine systems, I would expand a bit more on all studies that have provided evidence for the in-situ production of brGDGTs in the marine environment (instead of just listing them up). Now, only the recent Sinninghe Damste (2016) paper is introduced.

Response: We added more discussion about potential marine-derived brGDGTs. We wrote as "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. 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, supported a widespread biosynthesis of brGDGTs in shelf sediments especially at water depth of 50–300 m. "

11) L 91-99 could be restructured, they are not easy to understand.

Response: We rewrote this paragraph as "However, so far no robust molecular indicator is available for estimating source of brGDGTs in marine environments. Considering this, we conduct a detailed study about GDGTs in three cores from the Bohai Sea which are subject to the Yellow River influence to different degree. Our purpose is to evaluate the source discerning capability of different brGDGT parameters, from which the most sensitive parameter is selected and applied for globally distributed marine sediments and soils to test whether it is valid at the global scale. Our study supplies an important step for improving accuracy of brGDGT-derived proxies and better understanding the marine carbon cycle and paleoenvironments."

12) L 106: 'the marine carbon cycle'

Response: we made change in revised manuscript.

13) L 112. 'the mean depth is' and 'the Bohai Strait, at the east'.

Response: we made the change according to reviewer's suggestion.

14) L 114: 'the second largest river in the world, concerning sediment load (+reference)'

Response: We rewrote this sentence and added the reference as "Several rivers, including Yellow River, the second largest river in the world in terms of sediment load (Milliman and Meade, 1983), drain into the Bohai Sea with a total annual runoff of 890×108 m3."

15) L 115: 'One gravity core of 64 cm was: : :'

Response: we made correction in the revised manuscript.

16) L 118: respectively can be removed here.

Response: we already removed "respectively".

17) L 125: If this extraction and separation protocol has been described elsewhere, you can simply refer to this original publication. The same goes for the analysis of the GDGTs on the LC system.

Response: This is a good suggestion. In the revised manuscript, we delete the details about extraction and analysis methods. We started this paragraph as "The detailed procedures for lipid extraction and GDGT analyses were described in previous studies (Ding et al., 2015; Xiao et al., 2015)."

18) L 183: This can be rewritten as: De Jonge et al., 2015, 2016.

Response: We made change.

19) L 206: Can the authors not give an indication at which BIT values (both on the local and global scale) the proportion of marine brGDGT becomes problematic? This would be useful from the viewpoint of palaeoclimate reconstructions.

Response: As we stated in the manuscript, "However, the BIT index itself has no ability to distinguish terrestrial vs. aquatic brGDGTs because brGDGTs and crenarchaea used in this index are thought to be specific for soil organic carbon and marine organic carbon, respectively (Hopmans et al., 2004)". Only the combination of BIT and IIIa/IIa can reveal that when BIT is lower than 0.16, a contribution of marine brGDGTs becomes problematic, which was discussed in section 3.3 and figure 7.

20) L 235-237: Is a repetition of the L 237-242.

Response: we deleted this sentences in the revised manuscript.

21) L282. It surprises me that the authors indicate here that Crenarchaeota/Thaumarchaeota are the probable producers of marine brGDGTs. Is there any indication that this would be the case? Alternatively, I would remove this statement.

Response: We agree with reviewer that more solid evidence is needed to draw such conclusion. Trommer et al. (2009) indeed postulated the existence of distinct crenarchaeota community in the Red Sea due to unusally environmental condition. Considering these facts, we did not specify crenarchaeota in the revised manucript. In stead we rewrote the sentecne as "Under such extreme environment, distinct microbial populations may be developed and produced GDGTs different from that in other marine settings (Trommer et al., 2009)".

22) L303. The argument that continental and marine temperatures are significantly different is put aside much too quickly. Indeed, they are both globally distributed, but the temperature of your water bodies will be much more stable throughout the year (which

has an implication of the production temp as soil-derived brGDGTs are thought to be produced mainly in spring-autumn, especially at sites that are partially frozen throughout the year. Furthermore, if marine brGDGTs are produced at the sediment/water interface, this will of course be much colder than the sea surface temperature. Taking this into account, I doubt that the authors will be able to make a strong case on their proposed absence of a temperature difference between soil and marine brGDGTs.

Response: This is a good comment and already mentioned in major comment. We added detailed discussion in our revised manuscript. Please see our response for Comment #2, particularly about production of GDGTs in surface and deep water with large different temperature.

23) L304. If the authors want to discuss this trend between soil pH and III/II, they have to provide a plot. Does this trend also apply for more extreme pH values? Can it be strengthened by determining which compound causes this trend (IIa, IIa', IIIa, IIIa')?

Response: Good suggestion. We added a figure to show a trend between soil pH and IIIa/IIa (Fig. 6). We agree the separation of 5-methyl and 6-methyl brGDGTs by 2D HPLC-MS may strengthen our hypothesis. However, most available data on brGDGTs did not distinguish these two types of isomers. So we still combine 5-methyl and 6-methyl brGDGTs in current study. But we, along with several groups, are currently using advanced HPLC-MS method to quantify 5-methyl and 6-methyl brGDGTs for more samples. We plan to review 5-methyl and 6-methyl brGDGTs in future when sufficient data are available, but at current stage, this is beyond the scope of this manuscript.

24) L308: The pH of marine water is indeed fairly stable, but it can be very different in pore waters in the sediments. This should be mentioned.

Response: The production of brGDGTs in pore water of sediments cannot be excluded, although they are likely not as important as water column. In the revised manuscript, we added the discussion 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."

25) L367: 'and a compilation of'

Response: we added "a" before compilation.

26) L364-367: I do not agree that the authors have enough evidence and data on this to make this conclusion.

Response: we agree more studies are needed to unambiguously determine source of brGDGTs in marine environments. So in the end of the revised manuscript, we added sentences as "We also note a relatively large scatter of the IIIa/IIa ratio within both terrestrial and marine realms, and different environmental responses of 5-methyl and 6-methyl brGDGTs (e.g., De Jonge et al., 2014, 2016; Xiao et al., 2015). As a result, the separation of these two types of isomers is needed in future studies to develop more accurate brGDGTs' proxies."

27) References: please check the manuscripts guidelines. Journal names are to be abbreviated.

Response: we update the references with abbreviation journal name.

28) General: In the manuscript text, the authors should pay attention to the order of references. Older references should come first.

Response: we reorganized our references according to the requirement of Biogeosciences.

Interactive comment on Biogeosciences Discuss., doi:10.5194/bg-2016-235, 2016.

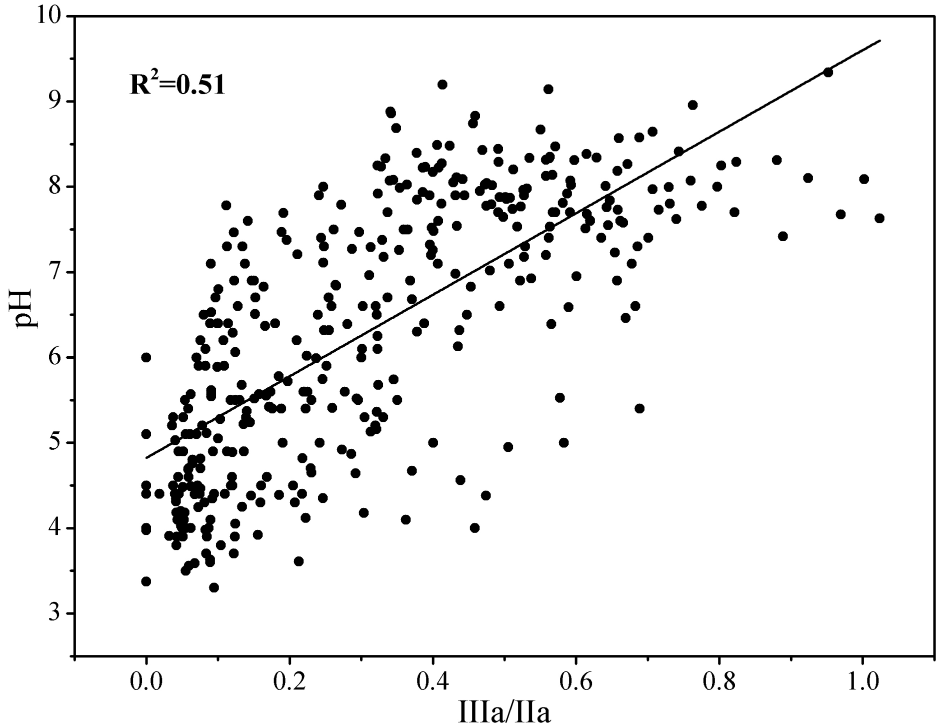

Fig. 1. Fig. 6 a plot showing a positive correlation between IIIa/IIa and pH