Response to comments from Francien Peterse

Dear Paul Zander and co-authors,

I came across your manuscript based on your Tweet (or whatever that is called these days) and was intrigued by some of the replies that suggested a coupling between the occurrence of the IIIa'' isomer and redox changes. I just read through your work and have a few questions and comments for you to ponder on (this is not an official review, just an exchange of ideas I hope):

I thank you for voluntarily taking the time to provide useful feedback. Responses to comments are in red.

Your Fig. 2 suggests that you also detected IIIa'' in soils, whereas Weber et al 2015 found that it was exclusively produced in lakes. In fact, they used the absence of IIIa'' in soils and the presence of IIIa'' in the lake sediment as their main argument for its aquatic source, later backed up by isotope analysis. Can you comment on the presence of IIIa'' in the soils studied here?

Thank you for bringing this to our attention. The level of IIIa'' in soils does not meet a robust limit of detection criteria. Our automated chromatogram evaluation picked peaks in 5 of 13 soil samples based on the retention time of the IIIa'' compound, and we applied a screening based on exceeding 3x the level of machine noise. However, due to co-elution of the IIIa and IIIa' peaks, this level can be exceeded without a robust peak. We now apply a screening based on the limit of detection as defined by Currie (1999; eq 14) based on the analysis of 17 method blanks. None of the soil samples exceed this limit, whereas all but two of our lake sediment samples do exceed this criteria. Therefore, our data strongly supports the conclusion of Weber et al. Applying this limit of detection does not alter the results or conclusions of our research.

In their follow up study (Weber et al 2018) is mentioned that IIIa'' does not occur in all lakes. Based on the isotopic composition of IIIa''-derived alkanes you could derive preferred production in eutrophic/anoxic lakes (see their Fig 4C-E), but just anoxia is not doing the trick. I can tell you firsthand that IIIa'' is not detected in Lake Chala, although this lake has anoxic bottom waters (resulting in a continuously laminated sediment record; van Bree et al., 2020, Baxter et al 2023). Maybe the fact that Chala is oligotrophic explains its absence, but I would be careful with using IIIa'' as marker for 'just' anoxic conditions.

This is a good point, and seems to require more research to fully understand the constraints on IIIa''. Our data is consistent with the interpretation of a connection with trophic levels as we see higher IIIa'' during times of higher productivity (indicated by org C/chloropigment data). It seems that the presence of IIIa'' is a useful indication that anoxic conditions were present, but your Challa data clearly show that the absence of IIIa'' is not necessarily an indication of the absence of anoxic conditions. We will clarify this interpretation in the text.

Based on all the lake work that has recently appeared in the literature I have started to have serious doubts about the importance of soil-derived GDGTs in lake sediments, especially for lakes that are not connected to any river system. I feel that the vast majority, if not all brGDGTs in lake sediments are produced in situ, and that their production in the water column is strongly impacted by redox conditions, as you already mention in your manuscript, and has also clearly been shown by e.g., Weber et al., 2018, van Bree et al., 2020, Wu et al 2021, and Baxter et al., 2023. Most importantly, these studies have also shown that the producers of the different brGDGT isomers may occupy different niches in the water column. This can make brGDGT production very sensitive to changes in e.g., lake depth (be it climate driven, or by lake basin development or infilling of the lake over time) or mixing regime and affect the reliability of the currently available transfer functions. I know this mostly from working on Lake Chala, where we did very extensive lake monitoring to find this out (see Baxter et al., 2023), and I can imagine that this is not possible for every lake, but we should try to use all available information from these studies in our interpretation of novel lake records. Enfin, the point I wanted to make was that changes in IIIa/IIa may not necessarily reflect soil vs aquatic brGDGT sources, but instead the expansion and shrinking of the niches of their producers within the lake, related to redox. The different zones in the water column occupied by the producers of IIa and IIIa is actually clearly visible in your Fig. 4e.

Following this line or reasoning and letting go of IIIa/IIa as indicator for soil input, this also allows you to interpret the high BIT index values during the Holocene differently, especially since the high BIT index values are not supported by more clastic material (Fig. 7I), but rather with increased productivity, sediment anoxia, and methanogens (Fig. 7GHD). This would fit with a shallower oxycline in the lake, which increases the zone for brGDGT production (in the anoxic zone of the water column; see Weber et al., 2018, van Bree et al., 2020, Wu et al., 2021), and decreases the zone of crenarchaeol production, which, under ideal conditions peaks in the suboxic zone, as is also the case in the modern lake, shown in your Fig. 4C. As Thaumarchaeota exhibit photoinhibition, they cannot thrive in the very upper water layer, and are thus outcompeted during periods with less mixing, more stratification, etc, increasing the BIT index (see Baxter et al., 2021 and 2023 for detailed explanation and illustrating schematics). That this scenario may hold true is also reflected by the absolute abundances of the GDGTs, which show an increase in brGDGTs and isoGDGTs that are produced in the anoxic part of the lake, whereas crenarchaeol remains relatively stable/low during the transition into the Holocene.

I haven't looked in much detail at the part of the record spanning MIS3, so I am not sure what exactly is going on there, and I can only encourage you to keep the water column structure, mixing regime, and lake basin development in the back of your mind when interpreting the data! Looking forward to hearing your thoughts about all of this.

I generally agree with your points about IIIa/IIa and BIT reflecting changes in the environmental niche (mainly redox) of the producers within the lake. We emphasized these indices in the paper as indicators of soil input because they have been the most often cited in the literature, and I think they can be useful in that regard in some settings. But I agree with you that these indices cannot be interpreted as being driven by soil input alone.

All the best,

Francien Peterse

PS. Quick last note for the introduction: the presence of brGDGT Ia in culture was already shown by Sinninghe Damsté et al in 2011. Also, I miss a reference to Weijers et al., 2007 as the paper in which the temperature dependency of brGDGTs was first demonstrated and the MBT was defined.

References:

Baxter et al 2021 QSR

Baxter et al 2023 Nature (check methods section on calibrations and extended data Fig. 2)

van Bree et al 2020 BGS

Sinninghe Damsté et al., 2011 AEM

Weber et al 2015 GCA

Weber et al 2018 PNAS

Weijers et al., 2007 GCA

Wu et al 2021 Chemical Geology

Thank you for the productive exchange and useful reference suggestions, these will also be incorporated in a revised version of the manuscript.

On behalf of all authors,

Paul Zander

References

Currie, L. A.: Nomenclature in Evaluation of Analytical Methods including Detection and Quantification Capabilities, Analytica Chimica Acta, 391, 105–126, https://doi.org/10.1016/S0003-2670(99)00104-X, 1999.