Biogeosciences Discussions

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Reply on RC1 (David Naafs)

Frédérique M. S. A. Kirkels et al.

Author comment on "From soil to sea: sources and transport of organic carbon traced by tetraether lipids in the monsoonal Godavari River, India" by Frédérique M. S. A. Kirkels et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2022-116-AC1, 2022

Replies to Dr. Naafs

In this manuscript Kirkels et al. use tetraether lipids together with inorganic data to explore the sources and transport of organic matter in soil, river, and marine sediments in India. In my opinion the two main conclusions are that there is additional evidence for riverine production of brGDGTs (adding to a greater body of literature that finds evidence in support of this) and that brGDGTs in marine sediments cores, even if positioned relatively closes to the coast, are produced in situ in the marine realm and hence can not be used for terrestrial climate reconstructions.

In my opinion this is a solid Biogeosciences paper. Some of the data presented here has been published (Dearing Crampton-Flood et al., 2020), but there is enough novel data to make it worth a publication. The results from this manuscript add to the growing body of literature that highlights the widespread production of brGDGTs in a range of environments and the associated complexity with using these compounds in marine sediments cores for paleoclimate reconstructions. The manuscript is nicely written and the figures are informative. The data support the conclusions.

Reply: We would like to thank Dr. Naafs for his positive assessment of our work and his constructive feedback that will help us to further improve our manuscript.

However, I have three overall comments to improve the manuscript:

- I suggest you shorten the results section. It is very long with a lot of details that sometimes make it hard to follow and some details appear not to be necessary. Condensing the results by focussing on the key results will improve the readability of the manuscript.

Reply: We agree that the results section is very 'complete' and will shorten this section to include only the information that is directly relevant to the interpretation of our data in a revised manuscript.

-Why are the isoGDGTs not discussed? Crenarcheaol is used for BIT, but what about the others? For example cren/cren' ratios can tell us something about the potential source organisms and this differs between mineral soils and aquatic production in some places (Li et al., 2016). The isoGDGTs are measured already (I assume) as part of the brGDGT runs,

so potentially there is a lot of extra information available with minimal effort?

Reply: Thank you for the suggestion. We do indeed have isoGDGT data available. We did not include any of this data in the initial manuscript because we thought that the brGDGT dataset as such was already extensive enough, containing soils, SPM from both wet and dry seasons, riverbed sediments from both wet and dry seasons, as well as fine (<63um) fractions, and a marine sediment core. We were afraid that the manuscript would become too dense and long, and would loose its focus if the isoGDGTs would be added. In addition, the isoGDGT dataset for the Godavari basin is part of a manuscript in preparation by Martinez-Soza et al.

Nevertheless, if the reviewers and editor think that the isoGDGTs are a valuable addition to the current work, we will of course consider this in a revised manuscript. A quick first analysis reveals that the isoGDGT data lead to similar conclusions as the brGDGTs:

- *f(cren') is slightly higher in soils (on average 0.15) than in SPM, riverbed sediments and the marine core (average range 0.05-0.10), indeed implying different producers in soils and aquatic environments as suggested by Dr. Naafs.*
- *GDGT-0/cren is higher in SPM and riverbed sediments collected during the dry season than in the wet season (on average 1.6 vs 0.9), likely due to anoxic conditions in stagnant waters during the dry season and in the upper basin, facilitating methanogens that contribute to GDGT-0.*
- *GDGT-2/GDGT-3 is higher in the marine sediment core (on average 3.8) compared to soils, SPM, and riverbed sediments in the river basin (1.0-1.2), indicating that the isoGDGT signal that is discharged by the river is overprinted by isoGDGTs produced by marine Thaumarchaeota. Similarly, GDGT-0/cren is substantially lower in the marine sediment core (0.2) than in the river basin, and represents 'normal' marine conditions. This is also confirmed by the low BIT index values (around 0.05) reported in Fig. 5c of the original submission.*

-Why is the focus on core GDGTs and not IPLs? For the SPM samples especially, would it not make sense to look at the IPLs to determine in situ production? The signal in the IPLs might be even stronger compared to the core GDGTs?

Reply: We agree that IPLs could have provided a stronger argument for in situ production in the river. However, the logistics in the field did not allow storing our samples frozen after sampling and transport to the lab. Only the SPM filters were stored at 4 °C, but soils and sediments were kept at ambient temperatures during our 1 month field expeditions. Since IPL headgroups are considered to be quickly lost upon cell death, we anticipated that the remaining IPLs (if any) in the samples would not be a reliable representation of the initial IPL abundance, and thus decided to focus on core GDGTs instead.

Related to this, I see (line 221) that some fractions were saponified, but others were not. Although not extracted with a BD protocol, this saponification of the TLE might release IPLs. This affects what fraction of the GDGTs you look at (core for the non-saponified and a mixture of IPL-derived cores and cores for the saponified samples). Couldn't this difference in sample work up in theory explain some of the observed differences between the different sample types? This needs more explanation.

Reply: We understand the concern of the reviewer, but we believe that the differences in GDGT concentrations will be marginal. Firstly, samples have been stored non-frozen during fieldwork and transport, facilitating the degradation of IPLs on the road. And secondly, the extraction with the ASE uses high temperature and pressure, which will also degrade IPLs into core lipids during the process. We, therefore, believe that saponification of the obtained TLE will not further release substantial amounts of IPL brGDGTs.

In addition, the %IPL-derived brGDGTs in soils is generally much lower than the pool of 'fossil' brGDGTs that are present in the soil as core lipids (e.g. Peterse et al., 2010; Huguet et al., 2010; Zell et al., 2013), which thus represent the majority of the brGDGT signal. This is also true in river SPM (e.g., Zell et al., 2013; De Jonge et al., 2014). Given that IPL-derived brGDGTs and core lipid brGDGTs generally have a similar distribution in soils and river SPM, the work up procedure followed here is not considered to introduce large differences in brGDGT distributions nor concentrations the dataset.

We will briefly clarify our assumptions in a revised version.

Other minor comments and typos:

Lines 64-66: both papers cited here are using mineral soils, not peat.

Reply: We will add a reference to Naafs et al., 2017 to also cover peats.

Line 75: also cite culture results from (Halamka et al., 2021)

Reply: We will add this reference.

Line 97: is this due the overall higher pH in rivers compared to soils?

Reply: this is indeed the mechanism that has been proposed by De Jonge et al., 2014. We will clarify this in the revised version.

Results: I suggest you shorten the results section. It is very long with a lot of details that sometimes make it hard to follow. Condensing the results through focussing on the key results will improve the readability of the manuscript.

Reply: As mentioned earlier, we agree with the reviewer here and will revise the results section to improve the readability.

Figure 5 (and associated text); In samples with such a low BIT values, can we ever use MBT'5me? Not sure it makes sense to show this data in this graph.

Reply: The application of MBT'5me in marine settings should always be done with caution and after a thorough assessment of the source(s) of brGDGTs, like we suggest in discussion section 5.5 and the conclusion. Note that a low BIT index does not necessarily indicate little terrestrial input; after all, the BIT index is a ratio and terrestrial input can be masked by enhanced marine production. For example, BIT index values were low in Pliocene North Sea sediments, whereas d13C of the organic matter indicated a primarily terrestrial origin of this material and brGDGTs could be used to infer paleotemperatures for the nearby land (Dearing Crampton-Flood et al., 2018).

In our manuscript, we decided to include MBT'5me in this part of the discussion for the completeness and to enable the comparison with MBT'5me values for the Godavari basin. Importantly, after an assessment of the sources of the brGDGTs -as we suggest to always do before using it as paleothermometer- we do not interpret the MBT'5me record as paleotemperatures. Regardless, we can reconsider including MBT'5me in the revised version if the editor advises us to do so.

Line 485: Figure 5?

Reply: the brGDGT distributions are also given in Fig. 4a, but we will add Fig. 5 here too.

Line 510: how does this fit the with brGMGT data (Kirkels et al., 2022)?

Reply: Kirkels et al., 2022 report that brGMGTs are not widespread in the Godavari basin, in contrast to the marine sediment core, where brGMGTs are continuously present. The occurrence of brGMGTs in the basin appears to be determined by low oxygen/high nutrient conditions (e.g. agricultural soils, inundates soils, stagnant waters) rather than soil type and can, therefore, also not be used to trace basin-specific contributions.

Line 525: you mean low BIT?

Reply: We are not sure what the confusion is here, as this line already says low BIT.

Line 539: PCA

Reply: We assume that the reviewer refers to the second half of this line where we write "This PC further…'. PC refers to PC2 in the previous sentence, not to the PCA. We will clarify this.

Line 573: Cite (Halamka et al., 2021)

Reply: we will add this citation where relevant.

Line 598-604: Explore broader isoGDGT distribution to provide more insights into the archaeal source, for example cren/cren' ratios, etc.

Reply: see our reply to the earlier comment of this reviewer.

Line 741: FIG??

Reply: Thank you for spotting this! In the end we decided to not add yet another figure to support this statement, but instead just describe it in the text. We will remove this reference.

David Naafs

References:

Dearing Crampton-Flood et al., 2018, Earth and Planetary Science Letters 490, 193-205

De Jonge et al., 2014, Geochimica et Comoschimica Acta 125, 475-491.

Huguet et al., 2010, Organic Geochemistry 41, 559-572

Kirkels et al., 2022, Organic Geochemistry 167, 104405

Naafs et al., 2017, Geochimica et Cosmochimica Acta 208, 285-301

Peterse et al., 2010, Organic Geochemistry 41, 1171-1175

Zell et al., 2013, Limnology & Oceanography 58, 343-353