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Biogeosciences
Discussions

Interactive comment on "The Holocene sedimentary record of cyanobacterial glycolipids in the Baltic Sea: Evaluation of their application as tracers of past nitrogen fixation" *by* Martina Sollai et al.

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We thank the referee for taking the time to comment on our manuscript. Below we respond to the comments by first repeating the question and then answering it.

What are the HG patterns of soil cyanobacteria, and is the input of soil-derived TOC a possible source and also possibly a reason for differences in AL and LS sediments? I seem to remember that lignin biomarker abundance increased at the AL/LS transition.

The referee is correct that N2-fixing cyanobacteria occur in soil and some of them

belong to the heterocystous cyanobacteria (e.g. Nostoc and Calothrix species) and may produce HGs. Erosion of soil could thus potentially lead to an influx of HGs in Baltic Sea sediments. However, since the HG lipids contain an attached sugar moiety, we feel it is unlikely that HGs produced in soil will make it to the sediments of the Baltic Sea since they would be exposed extensively to oxygen during transport and only relatively stable components such as lignin, wax lipids, and branched GDGTs will likely survive this transport to the middle of the Baltic Sea where our core was taken. It is also unknown whether HG-producing cyanobacteria occur in soils surrounding the Baltic Sea and if they are sufficiently abundant to account for the relatively high levels of HGs in the Baltic Sea sediments. We will discuss this briefly in the revised version of our manuscript.

What are the levels of r.u. compared to other depositional settings? Is the Baltic Sea particularly rich in HGs?

It is, at the moment, rather difficult to answer this question. The mass spectrometric response for HGs is quite variable over time, which makes it difficult, if not impossible, to compare different data sets since samples have not been run during the same batch. We have run the set of Baltic Sea sediment samples in one batch and so we are confident that we can compare the HG concentrations relative to each other (i.e. the trend in Fig. 3a) but we feel we are not in a position to compare concentrations between different set of samples. To this end, we would need an HG standard that allows to monitor the mass spectrometric response over time. Such a standard has recently become available in our lab (Bale et al., Organic Geochemistry, 2017) and so this question may be answered in the future but falls outside the scope of the current study.

A second (and interesting) objective was to investigate a fundamental biogeochemical feedback: Because the brackish Baltic Sea (LS and younger stages) experienced several alternations between oxic and anoxic conditions, it is a well-chosen environment to investigate whether or not development of anoxia and the Redfield homeostat (nitrogen fixation balancing a surplus of P originating from sediment or from denitrifica-

tion) are linked, and if cyanobacterial biomass has an influence on the development of anoxia (or if anoxia had an influence of HG production). This is a difficult question and I wonder if it can be answered at all if you normalize your r.u. to %TOC. Are the unnormalised r.u. linearly correlated with %TOC? Figure 3a in comparison to 3e suggests this. That would mean that TOC preserved is the overriding control on HG abundances (but not composition) – by normalizing to TOC, any variation in HG abundance will then be masked. If TOC is high in anoxic and low in oxic phases, the effects of production and preservation can in my opinion not be segregated.

The issue raised is a general one; i.e. do you normalize biomarker concentrations on g dry weight sediment or on TOC? To our opinion, if we are interested in reconstructing water column processes by examining biomarker profiles, like we are here, we should always compensate for the dilution of organic matter (and thus the biomarkers) by the inorganic matter of the sediment. To illustrate this: if we dilute a TOC-rich sediment with a tenfold amount of inorganic matter, the biomarker concentration normalized on g dry weight sediment will drop by a factor of 10, whereas that normalized on TOC will remain the same. Normalization on TOC will also compensate, to a certain extent, for different degrees of oxygen exposure (see also comments by referee #1), although biomarkers are generally more susceptible (i.e. higher degradation rates) than TOC, resulting in a decrease in concentration even when normalized on TOC. However, normalisation on g dry weight sediment will not solve this, so TOC-normalized biomarkers are to be preferred. This means that the TOC-normalized HG-concentration record provides the best possible insight in the presence of N2-fixing cyanobacteria in the Baltic Sea. However, as extensively discussed in our manuscript, there are some issues (such as the rapid decline in the surface section) that prevent us making definitive conclusions with respect to the biogeochemical issues raised by the referee.

Does the downcore decrease in PC1 in the MUC mean that the HG are more labile than bulk TOC? In particular, the relative abundances in Figure 4 suggest to me that C28 keto-diol and C26 keto-ol must be more rapidly degraded that the other moieties.

Have you analysed the principal components for the MUC and GC separately, and are the score patterns similar to those for the entire sample pool?

As discussed in the manuscript, we interpret the downcore decrease in the TOC-normalized HG-concentration in the MUC as either degradation, indicating that they are more labile than bulk TOC, or a decrease in the yearly occurrence of cyanobacterial blooms. However, the potential higher lability of the HGs has nothing to do with the declining scores on PC1 in the MUC since the principal components analysis was performed on the HG distributions. This decline can indeed be attributed to a decrease in the fractional abundance of the C28 keto-diol and C26 keto-ol as shown in Fig. 3. This could be due to preferential degradation of these HGs as suggested by the referee but we interpret this as a subtle change in the composition of the HGs produced in the water column. Indeed, we feel that it is unlikely that there will be a major difference in the degradation rate between the various HGs since their structures are quite similar. We will mention this in the revised version of our manuscript. We did perform principal component analysis on the distributions of the HGs separately but this does not reveal substantial changes. We do feel it is more logical to perform it on the complete set since all sediments comprise the Holocene sedimentary record of the Baltic and separating them in two is just artificially depending on the sampling techniques.

Why do some labs continue to use acidified samples for d15N analyses in the face of ample evidence that this affects the values? But that is not crucial to this paper.

The referee is correct that there is evidence for alteration of the δ15N values when samples are acidified. This problem is especially evident in ecological studies, where δ15N of biomass (which contains a lot of labile organic nitrogen) is present. In sedimentary organic matter most of the really labile nitrogen has been removed already but there are indeed studies that show effects of acidification, so this is a fair comment. We are aware of this problem and we checked the experimental procedure (which was performed by a technician in our lab) and it turns out that we did not perform the δ15N analysis on the decarbonated sediment samples but on a separate sample. So, the

description of our experimental procedure is not accurate and we will adjust it in the revised version of our manuscript. We thank the referee for spotting this since it has raised some concern (see comment of Dan Conley).

We will also address the minor issues raised by referee #2.

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