Biogeosciences Discuss., 9, C8893–C8899, 2013
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Interactive comment on "Bacteriohopanepolyols record stratification, nitrogen fixation and other biogeochemical perturbations in Holocene sediments of the Central Baltic Sea" *by* M. Blumenberg et al.

M. Blumenberg et al.

martin.blumenberg@geo.uni-goettingen.de

Received and published: 8 March 2013

This study investigates distributions of bacteriohopanepolyols as well as organic chemical properties and other lipid biomarkers for terrestrial and marine plants in Holecene sediments of the Baltic Sea. Distribution of BHPs seems to well reflect variation of organic composition, hence Baltic Sea's history. As a general question, however, are there any contributions from modern bacterial activities into the BHP pool in the sediments? Some BHPs analyzed in this study are possessed by living bacteria. The drastic increase of BHP concentration after the Littorina transgression can be explained by

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modern bacterial activities because of enriched carbon substrates in the sediment.

Reply: This is indeed an interesting aspect. However, many lines of evidence argue against a considerable contribution of lipids in general from in situ living sedimentary bacteria to the TOC and lipid pool in high-productivity marine settings such as the Central Baltic Sea. Basically there are two major arguments supporting that the vast majority of lipids (including hopanoids) are sourced from the water column.

1.) From biogeochemical profiles and published rate measurements we know that the sulfate-methane transition zone, wherein methane is anaerobically oxidized (through AOM), is generally located in the upper 50 to 100 cm (e.g. Piker et al., 1998; unpublished data of Gregor Rehder (Warnemünde)). Detailed unpublished investigations directed on specific biomarkers for consortia performing AOM and for methanogenic archaea failed to detect signals of these in situ processes in the respective depth intervals (a similar situation was found in the Black Sea, where no strong methane seepage occurs; own unpublished data). In these high productivity areas, in situ microbial activity is mostly obscured by the massive influx of organic matter from pelagic organisms, and it is very likely that the majority of BHPs have a similar i.e. water column source (further supported by similar distributions in recent sediments and the water column (Berndmeyer et al., 2013)).

2.) Unfortunately no data on cell counts of the only plausible anaerobic sources of BHPs in marine sediments, sulfate reducing bacteria (SRB; Blumenberg et al., 2012 and references therein), exist for the Gotland Deep sediments, but data from a comparable setting further indicate a relatively low contribution of SRB to sedimentary BHPs. For a Black Sea sediment core, the theoretical upper limit of SRB BHP production was calculated to be at maximum in the permil range of total BHPs (even if considering the unlikely scenario that all SRB present produced BHPs in the highest reported abundances; Blumenberg et al,. 2009). Like-

wise, in Gotland Deep sediments the SRB-specific anteiso-branched fatty acids were found throughout the core (unpublished data), but they maximized at 15 μg/gTOC, which is 40 times less than the major BHP peak (fatty acids are usually much higher concentrated in cells than BHPs). Quite neglectable lipid contribution from sedimentary versus water column microorganisms is also the major cause why water column proxies (e.g. TEX86) are not severely altered by phylogenetically related sedimentary archaea. Whereas we consider a major contribution from sedimentary bacteria to the overall BHP pool unlikely, the addition of less abundant BHPs, particularly 35-aminobacteriohopanetetrol, e.g. from pioneering SRB at the beginning of the Littorina stage can not be totally excluded. But this is already discussed in the manuscript so that we don't see the need for respective modifications.

Furthermore, a significant contribution of cyanobacterial source into sedimentary organic matter after the Lottorina transgression is a major premise for the discussion in this manuscript. Some more evidences for cyanobacterial contribution need to be shown in the manuscript using previous studies. If these information are included, the discussion will be much more persuasive. I have some other comments. I think it should be publishable after revision.

Reply: Under 5.1 we discussed the importance of cyanobacteria in the recent central Baltic Sea and during the Littorina stage (and give seven references to that topic). We nevertheless modified one sentence in the respective paragraph:

New: "The increasing importance of nitrogen-fixing cyanobacteria after the Littorina Sea transgression is demonstrated by enhanced occurrences of cyanobacterial carotenoid pigments and molybdenum, which is an essential micronutrient to facilitate nitrogen fixation (Poutanen and Nikkila, 2001; Kunzendorf et al., 2001; Borgendahl et al., 2007).

Comments: Introduction: It would be better if you add an explanation about the utility

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of BHPs as paeloenvironmental proxies.

Reply: We modified the paragraph slightly and added one reference.

P4, line 1: Some more evidences for cyanobacterial contribution should be added here as described above.

Reply: We think that modification of a sentence and the cited references (see above) clearly argue for the high importance of nitrogen fixing cyanobacteria in that setting.

Section 3.1: Show accuracy and precision for EA and EA-IRMS analyses.

bf Reply: We added an explaining sentence saying that for quantitative analyses of C and N the error was <2 and 5%, respectively. For δ15N analyses the error of $\pm$0.1 permil is now given.

Section 3.2: As reviewer 1 mentioned, microwave extraction is not a common method for lipid (hopanoid) extraction from sediments. Recovery and effect of microwave extraction on original BHP structure should be examined for quantitative analysis of BHPs.

Reply: Microwave-assisted extraction is a widespread technique in organic geochemical studies and is frequently also used for studies of functionalised lipids such as intact polar lipids (IPLs, e.g. Rossel et al., 2008) and bacteriohopanepolyols (BHPs; e.g., Schmidt et al., 2010; Schmale et al., 2012; Berndmeyer et al., 2013). In previous studies, we also used a different extraction technique (ultrasonic-assisted) for similar samples and did not recognize transformation of BHPs. The most common degradation product among BHPs is the diagenetically stable 32,35-anhydroBHT (Bednarczek et al, 2005), which was absent in the topmost sample in our study. Moreover, it was also not found in the particulate organic matter in the overlying water column, for which also the microwave-extraction technique was used (Berndmeyer et al, 2013).). Concern-

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ing the extraction efficiency; for a surface sample from the Gotland Deep pooling the upper 5 cm, we extracted 460 μg/g TOC BHPs using ultrasonic extraction, which is in the same range as the 590 and 370 μg/g TOC observed for the 0-1 and 7 cm samples reported in Berndmeyer et al. (2013). Considering the use of different samples from different cruises and potentially related sample heterogeneities and the ±20% analytical error, the efficiency of the method is therefore comparable to the routinely used ultrasonic based techniques. Therefore, and because of the opportunity of a high sample throughput with standardized conditions, we selected microwave extraction also for the study of BHPs.

P8, line 12-14: Is it possible that concentration of dinosterol show in absolute value, not in relative value? Correlation between conc. of dinosterol and TOC looks very well in Fig. 4. So, I am interested in how large is the concentration relative to those of BHPs.

Reply: Under the conditions used, the TMS-ether of dinosterol co-elutes with the TMS-ether of n-triacontanol. This complicates the quantification. However, we agree that the overall concentrations are interesting and re-evaluated the total ion chromatograms considering the co-elution. Figure 4 was modified accordingly.

P12, line 24-P13, line 5: This conclusion conflicts with the premise of cyanobacterial origin of organic matter in this field.

Reply: We don't agree with the reviewer's comment. We did not find much BHPs specific to cyanobacteria, despite the fact that we are studying an environment with high contributions of organic matter from cyanobacteria. But this not necessarily means that cyanobacteria are the major BHP contributors to the sediments, as other, e.g. redoxcline-specific bacteria, may be particularly important for BHP inputs. The important cyanobacteria from the Baltic Sea are as yet unstudied for BHPs, but in fact most marine species studied so far lack BHPs, or they produce very unspecific structures. We think that the paragraph describes

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this potential paradigm.

P14, line8-10: I could not understand why possibility of SRB origin for 35-aminobacteriohopanetetrol and –triol can be turned down. Please clarify this issue.

Reply: See explanation above. However, we will add in the revised MS the following statement.

New: "Moreover, a quantitative estimate on sedimentary SRB in a comparable sedimentary setting (the Black Sea), clearly argued against these bacteria as considerable contributor to the BHP pool in this setting (Blumenberg et al., 2009).

P14, line 26: Hopanoid input and low N/P ratio cannot be linked directory due to lack of evidence for low N/P ratio at the Littorina Sea stage although it is an understandable scenario. Rewriting is required for this part.

Reply: We agree with the reviewer that low N/P ratios are a likely scenario for the Littorina stage. But, we don't agree with the criticism that no evidence for low N/P ratios exist. There are several cited publications in which a high importance of nitrogen-fixing cyanobacteria is demonstrated (microorganisms which only flourish if the nitrogen is relatively limited). Moreover, in Bianchi et al. (2000) a direct measure of N/P ratios over that time interval is presented, supporting our statement. We added this reference in the respective paragraph.

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