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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.

Anonymous Referee #1

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Title: Bacteriohopanepolyols record stratification, nitrogen fixation and other biogeochemical perturbations in Holocene sediments of the Central Baltic Sea

This manuscript by Blumenberg et al., describes observations of the variation in bulk organic properties (%organic carbon, C/N, and ^{13}C of organic carbon), n-C₂₉ alkane abundance, and bacteriohopanepolyol (BHP) abundance and structural diversity in Baltic Sea sediments spanning the Holocene. Distinct changes in the organic composition of these sediments occurs around 7 kyr during the transition from lake to brackish basin and the onset of upper water column stratification. These changes are inter-

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puted as being consistent with an emerging contribution to organic carbon export from nitrogen fixing cyanobacteria and microorganisms associated with the chemocline. A particularly striking result is the emergence of an isomer of BHT – a putative marker for water column suboxia that was previously shown to be associated with suboxic/anoxic marine environments – coinciding with the transition to a brackish basin and the onset of stratification. The observations in this study are novel and are of interest to the biogeochemical and organic geochemical communities. However, I am concerned by the absence of error estimates in the reported data, especially for BHPs. It is not possible to discern the significance of absolute variations in abundance without knowing the uncertainty associated with these measurements. If the authors can address this, then I recommend this paper be published.

Comments:

Microwave extraction was used. Is it known whether some compounds are degraded under these conditions?

Which BHP standards were used for quantification? Was an internal or external standard used? Some more description of the means of quantification would be helpful.

Page 7, lines 14-15: I have some concerns about inferring dates from a comparison of peak OM concentrations to existing cores that have been dated. How closely spaced are these locations? How can it be certain that peaks in OM are widespread and synchronous features of this basin? If the authors insist on using these dates, it would be useful for the reader to assess the robustness of this method by providing a supplementary figure showing the OM profiles from all cores considered and some graphical indication of how the variations in OM were compared/matched between cores.

Page 8, lines 1-15: How do other terrestrial plant markers (e.g. long chain fatty acids) compare with n-C29 concentration profiles? What is the predominance of odd over even chains? This would provide some additional support to interpret this as a decrease in terrestrial plant input (and not a decrease in fossil hydrocarbon source?)

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Page 8, lines 9-14: n-C29 is a fairly refractory compound compared with other components of bulk OM (sugars, amino acids, polar lipids etc). Why would variations in conditions that affect bulk OM preservation would affect alkanes the same?

Page 11, line 25: Adenosylhopane is not proven to be specific to bacteria living in soils, and is, in fact, thought to be an intermediate in the synthesis of BHP side chains (see Bradley, A. S., A. Pearson, J. P. Sáenz, and C. J. Marx. 2010. Adenosylhopane: The first intermediate in hopanoid side chain biosynthesis. *Organic Geochemistry* 41:1075-1081). So, in theory, all bacteria with BHPs should contain some adenosylhopane. It would be more accurate to say that adenosylhopane is generally enriched in soils, and has not been detected in marine bacteria or marine suspended particulate matter.

Page 11, lines 25-27: “Exclude” is too strong of a word for this argument. The low abundance of adenosylhopane certainly suggests that terrestrial BHP input is relatively small compared with marine sources, but it does not exclude the possibility of an adenosylhopane-depleted source of terrigenous material. Compound specific stable isotopic measurements would provide a much more concrete measure of the relative contribution of marine and terrestrial sources to the sedimentary BHP inventory.

Page 12, line 6: The cited paper provides no information on the susceptibility of BHPs to microbial degradation. To my knowledge, the enzymatic pathways for BHP degradation have not been well characterized.

Page 12, line 11: or could be input from an allocthonous source enriched in anhydro-BHT.

Page 12, line 20: I don't understand this argument. Needs some clarification. Do the authors mean the variations in abundances are less pronounced for anhydro-BHT? Are these variations statistically significant given the errors involved in extraction and analysis?

Section 5.2.3 (page 13): Some estimate of error needs to be provided to interpret the

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variations in BHP abundance within this period.

Page 14, line 20: how is intensity of stratification quantified?

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