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Interactive comment on "Highly branched isoprenoids for Southern Ocean semi-quantitative sea ice reconstructions: a pilot study from the Western Antarctic Peninsula" *by* Maria-Elena Vorrath et al.

Maria-Elena Vorrath et al.

maria-elena.vorrath@awi.de

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We like to thank the reviewer for the very helpful comments. We revised our manuscript taking all concerns into account and uploaded the revised version (see supplement PDF).

Main concerns

1. As stated by the authors, the western Antarctic Peninsula has experienced drastic environmental changes over the past decades with a strong warming and a strong re-

duction of sea ice cover. It is also known to present a very complex oceanography due to the interaction between a westerly flow entering Bransfield Strait from the South and an easterly flow entering by the North. The Drake Passage, where half of the surface samples were retrieved from, is also swept by the strong ACC that transports settling particles to the East and winnows surface sediments. As an example, the influence of the AAP-sourced iron to Southern Ocean surface waters is evident until 0âŮę(de Jong et al.,2012) and even diatoms are transported away from their production zone (Crosta et al., 1997). One may question the behavior of organic compounds in these settings. I reckon that authors may have a limited access to sediment material, but the WAP and Drake Passage are not the best regions to calibrate such a tool due to fast changing conditions and strong lateral transport.

- We are aware of the difficult and complex hydrographic situation in the study area and already mentioned the potential winnowing of fine grained sediment in the Drake Passage (i.e. the Hero Fracture Zone) in the manuscript. However, we'd like to emphasize that we do not claim to provide a calibration of IPSO25 or the herein proposed PIPSO25 index. Here we document the distribution of HBIs and sterols and introduce the PIPSO25 index as an alternative approach to the commonly applied ratio of IPSO25 against the HBI triene. In fact, lateral transport is an important aspect concerning the deposition and accumulation of organic matter and we now comment on this in the manuscript (see comments below).

2. Fast changing conditions are the hypothesis put forward by the authors to explain the unexpected correlation of PIPSO to winter sea ice, while the IP25 (and probably its IPSO counterpart) is known to be produced in spring (Brown et al., 2011). Here lies the main problem to me. Can we state that the PIPSO preserved in surface sediment relate to past spring sea ice cover and that the correlation to modern winter sea ice cover is because of the close resemblance of past spring sea ice cover to modern winter sea ice cover (page 12, lines 10-19)?

- We formulated this hypothesis due to the better resemblance of PIPSO25 values to

the winter sea ice distribution and the 14C ages of surface sediments from the study area.

3. Another explanation is that the relationships between PIPSO and spring sea ice and PIPSO and winter sea ice are exactly the same, as shown by figure 5, but that the correlation is spring sea ice due to a much lower gradient (0-20%) compared to winter sea ice (0-60%) and a greater spread. Additionally, it is worth noting that the relationships between PIPSO and spring/winter sea ice concentration (Fig 5C-D) is evaluated with a simple linear regression while the biplots show an inverse Z with low PIPSO values at low WSIC, a vertical increase (atâĹij30% for WSIC) and high "quenched" PIPSO values at high sea ice concentration. The spread around the regression line appears very large.

- We revised the correlation between the data sets and now consider that changes in sea ice cover and diatom species are non-linear phenomena. So we observe a sigmoid-shaped relationship for the winter sea ice and PIPSO25 values, especially because sea ice estimations between 20% and 80% have a much steeper gradient.

4. Methodological information is lacking. How were stored the freeze-dried samples? In a freezer as recommended? What about potential sulfurization of the HBIs observed in some Southern Ocean sediments? What is the detection limit of the GCMS for organic compounds? I think that there is not a single paper on HBIs that discuss analytical reproducibility to account for analytical errors during extraction and measurement on the GCMS. The concentration value itself is calculated via the integration of the MS peak at the organic compound retention time, which is performed via a software. However, from my own knowledge, each sample needs to be visually check for a robust integration, i.e. how the baseline is drawn. Different slopes, double peaks, tailing, etc...may induce an error and I always wondered how large can be the error if the baseline is moved a bit. As the PIPSO is a ratio of MS-sourced values, there even might be a propagation of the errors. Can they be quantified? I am also surprised that there is no coherent concentrations between studies and laboratories whereby publi-

cations co-signed by Belt present values below 1μg/g sediment of IPSO (Belt et al., 2016) while publications co-signed by Massé present values between few to tens of μg/g sediment for the same regions (references in Belt et al., 2016). As it cannot be related to the nature of the sediment itself (same areas), it might be related to laboratory protocols and analytical differences mentioned above. Although this is beyond the scope of the present paper to deal with general questions, I believe that additional information related to the evaluation of the laboratory protocol used and analytical errors is needed.

- We revised the methods section and now refer to the analytical protocols of Belt et al. (2014 – an interlaboratory comparison study) and Stein et al. (2012) and added missing information on the reproducibility of our analyses. Integration of GC-MS peaks is done manually for all compounds (not automatically by the software). We also examined the GC-MS chromatograms of the hydrocarbon fractions of all samples for the C25 HBI sulfide, which may be formed through the intramolecular incorporation of sulfur into a C25:2 HBI alkene (see methods chapter). We cannot comment on the analytical protocol of Massé et al. However, IPSO25 concentrations reported in Belt et al. (2016) vary between 1 and >100 ng/g. IPSO25 concentrations determined for our samples are in the same range (0.6 - 182 ng/g).

5. No information is given on the export and preservation (or potential different degradation) of the organic compounds analyzed here nor on the impact of lateral transport on their distribution. As HBIs and others organic compounds are produced by different organisms and may be exported at different rates, they may suffer from different degradation rates and variable winnowing, thus altering the PIPSO calculation and the calibration. In conclusion, although the present study is extremely important I believe it fails on its main goal and that it is not possible here to provide a semi-quantitative calibration for sea ice.

- We added information about the potential degradation, lateral transport/vertical export and preservation of organic compounds in sections 4.1 and 4.2. (+ improving the

oceanographic setting section). We note that winnowing would affect the biomarker content of the respective surface sediments equally (i.e. winnowing does not lead to a selective removal of specific biomarker compounds – the rate of removal would be the same for all compounds). As already stated in section 4.5, our data set is too small for a full calibration of the PIPSO25 index. As emphasized in the introduction, this study is the first one that provides an overview on the distribution of IPSO25, HBI trienes and sterols in Antarctic marine surface sediments. The combined use of IPSO25 and HBI trienes as well as sterols for a semi-quantitative estimate of the sea ice cover seems promising but a proper calibration requires a larger data set and this is strengthened in the text.

Minor concerns

1. Page 2 lines 5: I do not see how relevant are the listed references, especially Anderson et al. 2009. For impact of sea ice meltwater on intermediate and bottom water formation I would check Shin et al., 2003, Rintoul 2007; for heat and gas see Morisson et al. 2015, Holland 2014.

- We revised the text accordingly.

2. Page 2 lines 6: Total Antarctic sea ice increase.

- We changed this.

3. Page 2 lines 14-16: Diatom and biogenic silica dissolution mainly occur in the photic zone, not in the sediment (Ragueneau et al., 2000).

- We revised this.

4. Page 4. Oceanographic settings are a bit weak. I would recommend to better detail the current. For example, the TBW seems shallower than the TWW, Sangra et al., 2011). What about deeper currents (CDW) than can also winnow particles. What about SST and sea ice cover? Maybe few words on productivity?

- We added information.

5. Page 7, line 1. I would not say that Eucampia antarctica is an open ocean diatom, especially when dealing with its variety recta. Previous works showed that it is mainly affiliated to cold waters and to melting ice (Leventer et al., 2002). So which variety is used here?

- We agree and rephrased this sentence. Because, following Esper and Gersonde (2014), this species is not relevant for the transfer function we deleted this information to avoid confusion.

6. Page 7, lines 5-8. As far as I know, SMMR is available between 1978 and 1987. Since then, sea ice images are based on SSMI, though several sensors were used over the years, or AMSRE since2002.

- We corrected that.

7. Page 8, lines 12-14. Can the presence of PIPSO in central and eastern Bransfield Strait be due to lateral transport?

- We now include the aspect of lateral transport of IPSO25 in the text.

8. Page 8, lines 20-24. What organisms produce the brassicasterols? How B are exported? It is worth noting that winnowing, due to strong ACC in Drake Passage, can strongly bias surface sediment concentration (focusing, winnowing, etc...). For these samples, what can be the impact of lateral transport?

- We now comment on the diverse source organisms for both sterols in the text. We already mentioned that winnowing likely affected the core sites along the Hero Fracture Zone, which lead to the removal of fine-grained sediments (incl. organic compounds). We cannot exclude that winnowing also affected other areas in the Drake Passage. The abundance of fine-grained sediments containing relatively high concentrations of HBI trienes and sterols in the Eastern Drake Passage, however, points to less severe winnowing at these sites. Lateral advection (i.e. additional input) of organic matter

may contribute to the biomarker inventory. The absence of IPSO25 at sites in the permanently open ocean zone of the Drake Passage, however, strengthens that the deposition of this lipid is mainly controlled by climate/environmental aspects rather than lateral transport by the ACC.

9. Page 9, lines 3-6. d13C was not measured on Triene, Brassicasterol and Dinosterols? Not enough carbon or not necessary? I think that B and D d13C would have be interesting to check whether these compounds were synthesized by sea-ice welling or phytoplankton organisms. Especially as B and D have high concentrations in Bransfield Strait, similar to IPSO, and we do not know whether this is an autochthone production, and during which season, or an allochthone production transported by the westerly currents.

- We tried to determine the d13C signature of HBI trienes in samples with a sufficiently high concentration of the lipids but co-elution of other compounds hampered the proper peak identification. d13C values obtained for the respective retention time interval were in the range of -30 ‰ (suggesting a phytoplankton source) but the uncertainty in the exact peak allocation prevented us from reporting these values. Due to technical constraints we did not determine d13C of brassicasterol and dinosterol. Regarding the high concentration of the sterols in the Bransfield Strait we now provide further information on their source organisms in the text.

10. Page 10, line 14. I am not sure that sea ice persists until summer in WAP and BS. At least, low winter sea ice concentrations argue against that. Figure2 also argue against this. As mentioned above this can be solved by improving the oceanographic settings.

- We agree with the reviewer and re-phrased the text.

11. Page 10, lines 16-19. This sentence is not totally true. High values of PIPSO are observed atâĹij60âŮęW in the westernmost BS, where there is no winter sea ice. It should be discussed.

- We note a 25 % sea ice cover for this site, which explains the (admittedly low) abundance of IPSO25 in this sample. In the text, we now include a comment on the transport of IPSO25 via the TWW.

12. Page 11, line 5. Please note that sea ice edge is generally at the 15% threshold. Here 5% means no sea ice.

- We revised this part.

13. Page 11, lines24-26. A WSIC of 23% is very low, indicating a very marginal zone. So maybe sensible not to find IPSO but high concentrations of HBI trienes (Figure 3).

- We revised this part.

14. Page 13, lines5-8. The interpretation of the biplots is to simplistics. The “good” positive correlations are based on linear regressions that link two patches of samples. There is no gradient. We can imagine intermediate samples out of the linear model. Additionally, there are no t-test for the significance of the correlation.

- We revised our interpretation of the correlation of the data sets (see major concern no. 2) and chose a sigmoid-shaped regression based on a cubic function for sea ice data covering the transition zone between consolidated and unconsolidated sea ice.

- The t-test on satellite data and diatom based sea ice estimates showed that the correlation is highly significant ($p<0.01$). Since PIPSO25 values do not reflect the percentage of sea ice cover, a t-test with sea ice concentrations was not performed.

15. Page 17, references. Check spelling of references. The two first ones mention Science (80-.).

- We corrected this.

Comments on figures Figure 2. Add sea ice limits on box B? Caption mentions that the mean WSI and SSI extents were calculated between 1980 and 2010, while it is written1980 to 2015 in the methods section.

- Adding sea ice limits in box B overcrowds the figure. We revised figure 1 and now indicate the maximum sea ice extent to avoid confusion with the data reported in the main manuscript.

Figure 3. There are several ways to present HBIS, ng/g of sediment, normalized to total HBIs, normalized to TOC as in the present study. Are results similar is other options are chosen?

- Normalizing HBI contents to TOC is common to avoid bias by different sedimentation rates. Plotting HBIs as ng/g sediment and normalized to TOC led to very similar distribution patterns. We further note that normalization to TOC does not affect the PIPSO25 values.

Figure 4. I wonder whether that wouldn't be more visual to have colored dots for organic compounds superimposed on WSI concentration fields. Or at least, I would recommend not to interrupt the dash lines for sea ice isocontours.

- We plotted the data as suggested (WSI in the background, PIPSO25 superimposed) but the visual effect was not satisfying. For clarity, we now provide additional maps showing satellite sea ice concentrations of spring and winter (Fig. 4 e and f).

Figure 5. Revise caption whereby plots A-B present spring sea ice concentrations while C-D present winter sea ice concentrations.

- We revised the caption.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2018-518/bg-2018-518-AC1-supplement.pdf

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