Biogeosciences Discuss., 9, C1154–C1162, 2012
www.biogeosciences-discuss.net/9/C1154/2012/

Biogeosciences
Discussions

Interactive comment on "Occurrence and distribution of ladderane oxidation products in different oceanic regimes" *by* D. Rush et al.

D. Rush et al.

darci.rush@nioz.nl

Received and published: 14 May 2012

We'd like to thank Dr. Elvert for his thorough and helpful comments on this manuscript. There were two main points mentioned by the reviewer. We address these here as well as the minor comments below.

1) Storage of Arabian Sea sediment samples:

At several places, the reviewer expresses concern about the storage of the Arabian Sea sediment samples. This is unfortunately partly due to a misinterpretation, and lack of information in the manuscript, on how the samples were stored. To clarify, sediments were sampled on board the ship and after sampling immediately frozen at -20°C. Sediments were kept at this temperature until extraction (see Lengger et al., 2012). Once

samples had been freeze-dried, extracted, and worked-up, the extracts from the Arabian Sea sediments were then stored at 4°C. Bligh-Dyer and Soxhlet extracts from the Cariaco Basin, the Arabian Sea water column, and the Peru Margin were stored at -20°C because these TLEs were to be used for IPL work. Once the saponifications had been performed, however, all fatty acids fractions were stored at 4°C as fatty acids are relatively stable upon storage. This procedure was not specifically mentioned in the manuscript and will be amended. Owing that the β-oxidation of original ladderane lipids to short chain ladderane lipids is likely performed microbially (Rush et al., 2011; Beam and Perry, 1974), there was no concern for the degradation to occur in the fatty acid fractions. Indeed, the Cariaco Basin extracts were treated in exactly the same way as the other extracts, yet no degradation product were observed, indicating that degradation does not occur in extracts stored at 4°C.

2) NL5:

The referee expresses concern about the usefulness of the NL5 index for this paper. Indeed, the other referees also raised questions regarding the NL5 index. We emphasize that the intention of this paper was neither to validate, nor analyse the NL5 proxy (as this has been done in Rattray et al. 2010, and reassessed for the water column briefly in Rush et al. 2012). Here, we wish to use NL5 as an indicator of the origin of original ladderane fatty acids, to highlight the difference between the production of original ladderane fatty acids in the water column and the in situ production in the sediment. We believe that the NL5 temperature in the OMZ water column also reflects a "dead material pool" (the NL5 was derived from IPLs from living as well dead anammox cells sinking through the water column). Anammox bacteria was found to reside at a specific depth (600 m; Pitcher et al., 2011). The CTD measured temperature at this depth (12.0°C) is a good fit with the NL5 derived temperature (13.9°C), where the in situ signal dominants over the sinking material from above. However, the dead sinking pool gives more of a mixed water column signal in the rest of the depths we analysed. This would explain why we have a constant NL5 temperature profile in the water col-

umn, and no trend with depth (not drifting up and down of bacteria, as suggested by the referee).

Specific comments:

Page 2349, Lines 17-21: Why should 14[5] and 14[3] not be produced as such if 16[3] has been detected in an enrichment culture? Other unidentified anammox bacteria may produce them de novo. Give some statements here or later. Additionally, information about the internal variations of SCLs would be of good value because I assume a relative increase of 14[3] and 14[5] with time and elongated oxygen exposure.

- Neither of the C14 ladderane fatty acids have ever been identified in any anammox enrichment cultures investigated so far, nor were they present in the original biomass used for the oxic degradation experiment (Rush et al. 2011). The C16-ladderanes observed in Rattray et al. (2010) also only occurred in minor amounts in 3 enrichment cultures (C16, C22, and C24-ladderanes combined made <2% of all ladderane fatty acids).Thus, short chain ladderane fatty acids are quite uncommon. Furthermore, in the Cariaco basin we do not find any short chain ladderane products. Assuming that in this basin Scalindua is also predominating, as it does in most marine environments (Kuypers et al., 2003; 2005), it suggests that there is no large contribution of de novo short chain ladderane fatty acids. All our observations are more consistent with a progressive degradation rather than de novo synthesis. Nevertheless, we will acknowledge that we cannot refute that an unidentified anammox species is producing them de novo in small amounts.

Page 2355, Lines 7-9: The statement that SCLs are only predominantly the result of oxidation implies another formation pathway. This could be in situ production.

- We do not agree. This statement was meant to indicate that the other part of the short chain ladderanes concentration peak probably comes from the burial of degraded ladderanes settling from the water column rather than being produced during sediment burial. We will now specify this.

Page 2355, Lines 9-13: Why is the in situ signal of ladderanes, including original ones and especially SCLs, that quickly removed from the sediment? All other sediments show a persistence of the SCLs with depth which would mean they are pretty stable against degradation. Who is degrading the signal? Is preservation by adsorption to the sediment matrix, as stated later for Peru Margin sediments, a possible explanation here?

- Organic matter that is protected by sorption to the mineral matrix of the sediment is more resistant to degradation (Hedges and Keil, 1995; Hoefs et al., 2002). The in situ produced ladderane fatty acids were likely unassociated with the sediment matrix, as opposed to the ladderanes which had settled form the water column. Water column ladderanes would be better preserved due to the sorptive preservation of organic matter in marine sediment (Keil et al., 1994), which is why we don't observe the in situ signal below the depth horizon where it is being produced. Which microbes exactly are degrading the original and the short chain ladderanes is unknown.

Page 2355, Lines 17-20: How deep is oxygen penetrating into the sediment? Any information about that would be of benefit. Otherwise this is weak statement. If oxygen is depleted rapidly, I would assume anammox being active in the sediment. It would be at shallower depth than at station 10 where higher oxygen is around. If the authors intend such a process in lines 23-27, I would suggest rewriting in order for better clarification of the reader.

- Anammox bacteria thrive in environments where oxygen concentration is low. At Station 4, the oxygen penetration depth is 4 mm (Lengger et al. 2012), Thus below this depth (i.e. at 2 cm where we observe a peak in original ladderane fatty acids), we expect anammox activity to be occurring in the sediment without the occurrence of β-oxidation to short chain ladderane fatty acids. We will clarify this statement in the manuscript.

Page 2356, Lines 23-25: Does the absence of matrix-bound ladderane lipids not simply

indicate the absence or very low activity of anammox at the time of sediment deposition at the Peru Margin below a certain sediment depth?

- Indeed, the absence of anammox activity at the time of deposition is an alternative explanation for no short chain ladderanes being detected below 42.2 mbsf. However, the time period where ladderane lipids are no longer detected ($\sim$100 kyr; MIS 5) corresponded to a period of increased organic carbon concentrations as the result of increased primary productivity (Wefer et al. 1990; Meister et al., 2005) in the Peru Margin. This would probably have led to bottom water anoxia, where we would expect anammox to thrive. Therefore, we cannot say simply that anammox bacteria were not active at the time of sedimentation.

Page 2357, Lines 11-13: Please rephrase this sentence. There is no real trend of decreasing SCLs with time. Concentrations of SCLs at station 1 are even higher in the sediments than original ladderanes in the water column (Figure 3c) or the top sediments (Figure 6a). That is why the authors cannot provide a correlation for this station in Figure 8d. How can such a ïňĄnding be best explained? In situ production? Sediment remobilization? Likewise results are shown from the Peru Margin (Figure 7). Unfortunately, water column data are not presented.

- It is not possible to compare water column and sediment data as they are normalised to different measurements (gram sediment vs. litre sea water). The sediment represents a flux of material falling from the water column. The simplest explanation for how there are more biodegraded short chain ladderane lipids in the sediment record than there are original ladderane fatty acids in the core tops is that the short chain ladderane fatty acids are formed already in the water column and are settled from there. The remaining original ladderanes that make it to the sediment surface continue to be degraded into short chain ladderanes.

Page 2358, Lines 9-11: Can the authors provide an explanation for the discrepancy relative to the Jaeschke et al. result? It is from a very similar location.

- Jaeschke et al. (2009) detected original ladderane fatty acids in an Arabian Sea core to 140 kyrs. The core used in Jaeschke et al. was recovered on the Murray Ridge (920 m), within the current OMZ, which would increase organic matter preservation. Station 1 in this study was also located within the OMZ and should reflect similar degradation rates. However, degradation calculations indicate that the time for the detection limit for original ladderane fatty acids to be reached is 13 kyr. We are therefore not really able to explain this discrepancy We do note, however, that a substantial decrease (probably due to degradation) in concentrations of ladderanes normalized to TOC in the core of Jaeschke et al. is evident starting from 60 kyr.

Figure 1: It would be of help when the authors show the presumed degradation pathway from one ladderane lipid to the other (simple arrows?). However, I assume that the degradation of 18[5] to 14[5] goes along via 16[5]. Why is this compound not detected? 16[3] and 14[3] from 18[3] are seen simultaneously. Is this because of a different oxic degradation pathway? Double beta-oxidation?

- In the natural environment, the C16-[3]-ladderane is found in much lower abundances than either the C14-[3]-ladderane or C14-[5]-ladderane (Rush et al., 2011). Perhaps the stereochemistry of the 5 cyclobutane rings in the [5]-ladderanes (vs. the 1 cyclohexane and 3 cyclobutanes of the [3]-ladderane) is more conducive to the completion of the β-oxidation to a C14-[5]-ladderane. However, the C16-[5]-ladderane was not detected in the original oxic degradation experiments, which may indicate that the [5]-ladderanes undergo a double β-oxidation, or the C16-[3]-ladderane is in vivo produced. This is the reason for excluding the C16-[3]-ladderane in the detection method.

Figure 2: I recommend to remove this Figure. It is not a global data set that we deal with here. Secondly, the inserts are not needed since both give no more detailed information as does Figure 5.

-We agree that Figure 2 does not need to have the global map, but we do believe that keeping the detailed maps of sampling locations is necessary. This figure will,

therefore, be modified to include only the more detailed map.

References used

Beam H. W. and Perry J. J. (1974) Microbial Degradation and Assimilation of Alkyl-Substituted Cycloparaffins. J. Bacteriol. 118, 394-399.

Hoefs, M. J. L., Rijpstra, W. I. C., and Damste, J. S. S.: The influence of oxic degradation on the sedimentary biomarker record I: Evidence from Madeira Abyssal Plain turbidites, Geochim. Cosmochim. Acta, 66, 2719-2735, 2002.

Hedges, J. I., Keil, R. G.: Sedimentary organic matter preservation: an assessment and speculative synthesis, Mar. Chem., 49, 81-115, 1995.

Jaeschke, A., Ziegler, M., Hopmans, E. C., Reichart, G.-J., Lourens, L. j., Schouten, S., and Sinninghe Damsté, J. S.: Molecular fossil evidence for anaerobic ammonium oxidation in the Arabian Sea over the last glacial cycle, Paleoceanography, 24, PA2202-1-PA2202-11, 2009.

Keil, R. G., Montlucon, D. B., Prahl, F. G., and Hedges, J. I.: Sorptive Preservation of Labile Organic-Matter in Marine-Sediments, Nature, 370, 549-552, 1994.

Kuypers, M. M. M., Sliekers, A. O., Lavik, G., Schmid, M., Jørgensen, B. B., Kuenen, J. G., Sinninghe Damsté, J. S., Strous, M., and Jetten, M. S. M.: Anaerobic ammonium oxidation by anammox bacteria in the Black Sea, Nature, 422, 608-611, 2003.

Kuypers, M. M. M., Lavik, G., Woebken, D., Schmid, M., Fuchs, B. M., Amann, R., Jørgensen, B. B., and Jetten, M. S. M.: Massive nitrogen loss from the Benguela upwelling system through anaerobic ammonium oxidation, P. Natl. Acad. Sci. USA, 102, 6478-6483, 2005.

Lengger, S. K., Hopmans, E. C., Reichart, G.-J., Nierop, K. G. J., Sinninghe Damsté, J. S., and Schouten, S.: Intact and core glycerol dibiphytanyl glycerol tetraether lipids in and below the Arabian Sea oxygen minimum zone: selective preservation and degra-

dation in sediments and consequences for the TEX86, Geochim. Cosmochim. Acta, in press, 2012.

Meister, P., Prokopenko, M., Skilbeck, C.G., Watson, M., and McKenzie, J.A.: Data report: compilation of total organic and inorganic carbon data from Peru margin and eastern equatorial Pacific drill sites (ODP Legs 112, 138, and 201). In Jørgensen, B.B., D'Hondt, S.L., and Miller, D.J. (Eds.), Proc. ODP, Sci. Results, 201: College Station, TX (Ocean Drilling Program), 1–20. doi:10.2973/odp.proc.sr.201.105.2005, 2005.

Middelburg, J. J.: A simple rate model for organic-matter decomposition in marine-sediments, Geochim. Cosmochim. Acta, 53, 1577-1581, 1989.

Pitcher, A., Villanueva, L., Hopmans, E. C., Schouten, S., and Sinninghe Damsté, J. S.: Niche segregation of ammonia-oxidizing archaea and anammox bacteria in the Arabian Sea oxygen minimum zone, ISME Journal, 5, 1896-1904, 2011.

Rattray, J. E., van de Vossenberg, J., Jaeschke, A., Hopmans, E. C., Wakeham, S. G., Lavik, G., Kuypers, M. M. M., Strous, M., Jetten, M. S. M., Schouten, S., and Sinninghe Damsté, J. S.: Impact of temperature on ladderane lipid distribution in anammox bacteria, Appl. Environ. Microbiol., 76, 1596-1603, 2010.

Rush, D., Jaeschke, A., Hopmans, E. C., Geenevasen, J. A. J., Schouten, S., and Sinninghe Damsté, J. S.: Short chain ladderanes: Oxic biodegradation products of anammox lipids, Geochim. Cosmochim. Acta, 75, 1662-1671, 2011.

Rush, D., Wakeham, S. G., Hopmans, E. C., Schouten, S., and Sinninghe Damsté, J. S.: Biomarker evidence for anammox in the oxygen minimum zone of the Eastern Tropical North Pacific, Org. Geochem., in press, 2012.

Wefer, G., Heinze, P., and Suess, E.: Stratigraphy and sedimentation rates in shelf basins of the Peru upwelling region from oxygen isotope composition, organic carbon content and grain size distribution: Holes 112-680B and 112686B, In: E. Suess, R. von Huene et al. Proc. ODP, Sci. Results, 112 355-367, 1990.

Interactive comment on Biogeosciences Discuss., 9, 2343, 2012.