Biogeosciences Discuss., 9, C1864–C1868, 2012
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Biogeosciences Discussions

Interactive comment on "Degradation state of organic matter in surface sediments from the Beaufort Shelf: a lipid approach" *by* J.-F. Rontani et al.

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Received and published: 11 June 2012

Dear Reviewer #1, The text has been revised according to your comments. Please find below our detailed response to your comments and suggestions.

Comment: Questioning whether terrigenous material is refractory in deltaic and shelf environments may be relatively new (see discussion and references on page 3883), but the observation of a faster degradation rate for predominantly terrestrial sterols than predominantly marine sterols is not. Answer: Concerning the faster degradation rates of sitosterol and campesterol than brassicasterol observed, it is now indicated in the text that Yunker et al. (2005) and Canuel and Maertens (1996) previously observed

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similar trends. We added (page 3890, line 21) the following sentence:"It is interesting to note that Yunker et al. (2005) previously also reported a faster removal rate relative to organic carbon of campesterol and sitosterol than of brassicasterol in sediment cores from the Beaufort and Chukchi seas and Canuel and Martens (1996) observed a faster degradation rate for sitosterol than brassicasterol in nearshore sediments from North Carolina".

Comment: Sitosterol and campesterol do have predominantly terrestrial sources in the Mackenzie River and shelf of the Beaufort Sea. This point is made by Goñi et al. (2000), as is mentioned at the beginning of section 2.7, but the main focus of the Goñi et al. paper was the lignin results, and the original 1995 paper by Yunker et al. (1995) and the subsequent paper by Yunker et al. (2005) are more pertinent to the interpretation of this work. Answer: The paper of Goni et al. (2000) gave very useful information (based on isotopic data) about the terrigenous contribution to sitosterol and campesterol in Beaufort Sea sediments. This reference seems thus for us particularly well suited to the attribution of the source of these two sterols in our samples. A sentence was added in order to say that lower contribution of terrigenous material to campesterol than to sitosterol was also outlined by Yunker et al. (1995; 2005). We added (page 3891, line 1) the sentence: "This lowest contribution of terrigenous material to campesterol was also outlined by Yunker et al. (1995; 2005)".

Comments: Hence, the observation of higher degradation rates for campesterol and sitosterol than of brassicasterol does not justify the conclusion that terrestrial material degrades faster on the shelf, because marine sources of sitosterol and likely campesterol (marine inputs for campesterol are mentioned on page 3891) are likely to be a significant source of the degradation products . . . then the conclusions in the Abstract that "that autoxidation, photooxidation and biodegradation processes act much more intensively on higher plant debris than on phytoplanktonic organisms" and "do not support the generally expected refractory character of terrigenous material deposited in deltaic systems" appear to be premature, and certainly need more discussion in light

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of the findings of Yunker et al. (1994; 1995; 2005). Answer: Our data do not support a high contribution of marine material to sitosterol and campesterol in the sediments investigated. Indeed, if these sterols mainly originated from phytoplankton, they should exhibit a similar degradation state than brassicasterol or 24-methylenecholesterol (typical phytoplanktonic sterols, Volkman, 1986; 2003) and this is not the case. Sitosterol and campesterol are very strongly autoxidized (see Figure 3), while brassicasterol or 24-methylenecholesterol (data not shown) are practically unaffected. From a chemical point of view, brassicasterol and 24-methylenecholesterol are potentially more reactive than campesterol and sitosterol towards free radical oxidation processes (presence of two double bonds instead of one, Rontani et al., 2007). Consequently, if these four sterols mainly originated from phytoplankton, a very strong autoxidation of brassicasterol and 24-methylenecholesterol should be also observed. In the sediments investigated, sitosterol and to a least degree campesterol thus appear to mainly originate from terrestrial higher plants, this assumption is in good agreement with the previous isotopic data of Goňi et al. (2000). Our conclusion (i.e. that autoxidation, photooxidation and biodegradation processes act much more intensively on higher plant debris than on phytoplanktonic organisms) seems thus to be valid. Reference: Rontani J-F., Jameson I., Christodoulou S. et Volkman J.K. (2007) Free radical oxidation (autoxidation) of alkenones and other lipids in cells of Emiliania huxleyi. Phytochemistry 68: 913-924.

Comment: The narrow Beaufort Sea shelf close to Alaska is very different than the broad shelf adjacent to the Mackenzie River and the location should refer to the Mackenzie shelf in the Beaufort Sea. Answer: We replaced (page 3381, line 2) the sentence: “The lipid content of surface sediments collected on the Beaufort Shelf was examined” by “The lipid content of surface sediments collected on the Mackenzie shelf in the Beaufort Sea was examined”

Comment: The major and minor sterols differed for some sediments analysed by Yunker et al. (1995) and Belicka et al. (2004) and a brief comparison would be war-

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ranted. Answer: The lowest abundance of cholesterol previously observed by Belicka et al. (2004) in the top layer (0 - 2 cm instead of 0 - 1 cm in the present work) of sediments from the Beaufort Sea was attributed to a quick degradation of zooplanktonic faecal material, which contributes significantly to the sinking particles of this zone and contains high proportion of cholesterol (Rontani et al., this issue), in the second cm of sediments. We added (page 3890, line 16) the sentence: "Similar sterols were previously identified by Belicka et al. (2004) in the top layer (0 - 2 cm) of sediments from the Beaufort Sea. The lowest abundance of cholesterol observed by these authors may be attributed to a quick degradation of zooplanktonic faecal material, which contributes significantly to the sinking particles of this zone and contains high proportion of cholesterol (Rontani et al., this issue), in the second cm of sediments."

Comment: Extensive phytoplankton studies have been done in the Beaufort Sea by Horner and coworkers and it should be possible to confirm the presence or absence of Chlorophytes or Prasinophytes. Horner and Schrader (1982) is cited in this work and other references to Horner et al. are given in Yunker et al. (1995). Answer: In order to underline that Prasinophytes and Chlorophytes were present in summer in this zone and may thus constitute potential sources of campesterol. We replaced the sentence "The reduced degradation observed in the case of campesterol (Fig. 4) may be thus attributed to a significant contribution of weakly altered Chlorophytes or Prasinophytes micro-algae containing high proportions of campesterol (Volkman, 1986) to this sterol." by "The reduced degradation observed in the case of campesterol (Fig. 4) may be thus attributed to a significant contribution of weakly altered Chlorophytes or Prasinophytes micro-algae containing high proportions of campesterol (Volkman, 1986) and present in summer in this zone (Hill et al., 2005), to this sterol".

Comment: Equations (1-3) add length but really do not enhance the discussion. Answer: Concerning the equations 1-8 (page 3895), we think that they are necessary for a good understanding of the text.

- The following references were added in the text and reference list. Belicka, L.L.,

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Macdonald, R.W., Yunker, M.B., and Harvey, H.R.: The role of depositional regime on carbon transport and preservation in Arctic Ocean sediments. Mar. Chem., 86, 65-88, 2004. Canuel, E.A., and Martens, C.S. : Reactivity of recently deposited organic matter: Degradation of lipid compounds near the sediment-water interface. Geochim. Cosmochim. Acta 60, 1793-1806, 1996. Hill, V., Cota, G., and Stockwell, D.: Spring and summer phytoplankton communities in the Chukchi and Eastern Beaufort Seas. Deep-Sea Res., 52, 3369-3385, 2005. Rontani, J.-F., Charriere, B., Forest, A., Heussner, S., Vaultier, F., Petit, M., Delsaut, N., Fortier L., and Sempéré, R.: Intense photooxidative degradation of planktonic and bacterial lipids in sinking particles collected with sediment traps across the Canadian Beaufort Shelf (Arctic Ocean). Biogeosciences (Submitted). Yunker, M.B., Macdonald, R.W., Veltkamp, D.J., and Cretney, W.J.: Terrestrial and marine biomarkers in a seasonally ice-covered Arctic estuary: Integration of multivariate and biomarker approaches. Mar. Chem., 49, 1-50, 1995. Yunker, M.B., Belicka, L.L., Harvey, H.R., and Macdonald, R.W.: Tracing the inputs and fate of marine and terrigenous organic matter in Arctic Ocean sediments: A multivariate analysis of lipid biomarkers. Deep-Sea Res., 52, 3478-3508, 2005.

Interactive comment on Biogeosciences Discuss., 9, 3881, 2012.