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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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This study examines the effect of several degradation processes on three representative sterols and three major monounsaturated fatty acids in surface sediments from the Mackenzie shelf and margin of the Beaufort Sea. The degradation of organic matter in sediments is a key aspect of the marine carbon cycle and an understanding of the molecular basis of fatty acid and sterol metabolism in sediments can provide important insight into the degradation processes. The authors have a detailed understanding of the molecular basis of the degradation and the derivatisation procedures and GC-MS analyses all appear to be thorough and well done. Nevertheless the authors appear to

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have overlooked several pertinent studies of sterols and fatty acids from the Mackenzie River and Shelf that have implications for the conclusions of this study.

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. Yunker et al. (2005) have 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. Yunker et al. (2005) also provide relative degradation rates for the three unsaturated fatty acids discussed in this work (16:1omega5, 18:1omega9 and 18:1omega7) and Canuel and Martens (1996) present rates for 18:1omega7.

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. The PCA-based labile/marine content from the 2005 study also would be more pertinent to this study than the marine content from Goñi et al. (2000) because the 2005 study includes both fatty acids and sterols in the PCA model and the calculation of labile/marine content.

Sitosterol emerges as one of the best indicators of terrigenous input in the Beaufort Sea in papers by Yunker et al. (1995; 2005). This conclusion is rooted in both multivariate data analysis and the dominant role that sitosterol plays in the Mackenzie River at freshet, and as such reflects one of the most important trends in the data, but it does not preclude other sources. Sitosterol and campesterol are primarily associated with the particulate phase (>0.7 μm) in river and nearshore suspended particulate and sediment samples (Yunker et al., 1994; 1995), which is consistent with an association with coarse plant debris. However, higher proportions of sitosterol are observed in the dissolved (<0.7 μm) fraction than in the particulate phase in the water column of the offshore Mackenzie shelf (Yunker et al., 1994), suggesting the presence of sitosterol either as a free sterol or in association with finer particulate, and indicating that marine production is highly likely as well. 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.

In both the Beaufort and Chukchi seas, sterols decrease from shelf to basin in both concentration and proportion of the lipid (Yunker et al., 2005). This trend is observed throughout the sediment cores, suggesting that the lipid composition is delivered "preformed" to the sediments, with the most likely removal mechanism being the removal of coarse plant material during transport (see Yunker et al., 2005 for a full discussion). Lipids which are delivered offshore from the shelves are either predominantly associated with fine particles (higher n-alkanes/alcohols/alkanoic acids) or are capable of atmospheric transport (higher n-alkanes)(Yunker et al., 2005; 2011). The plant-associated sterols that are present in offshore sediments (Belicka et al., 2004) appear to be delivered primarily on fine particulate, a fraction that is more likely to contain marine sterols (Yunker et al., 1994).

The conclusion is made on page 3898: "In contrast, autoxidation, photooxidation and biodegradation processes acted intensively on sitosterol and campesterol (mainly arising from terrestrial higher plants), while these compounds appeared to be only weakly affected by these degradation processes in particulate matter delivered by the Mackenzie River (Rontani, 2012)". I do not have access to this new paper by Rontani et al., but it seems that if sitosterol and campesterol are not being degraded in the Mackenzie River, where the sterols definitely have a terrestrial source and are predominantly associated with coarse particulate (Yunker et al., 1994; 1995), but they are being degraded in shelf sediments where marine sources of sitosterol and campesterol also contribute (Yunker et al., 1994), 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 of the findings of Yunker et al. (1994; 1995; 2005).

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Minor comments

Abstract. 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.

Page 3890, line 15. 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 warranted. The three fatty acids were all major constituents, with 16:1omega5 as the major fatty acid in most cases (Belicka et al., 2004).

Page 3890, line 20. Yunker et al. (2005) observed the degradation order campesterol > sitosterol > brassicasterol.

Page 3891, line 4. 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).

Page 3895. Equations (1-3) add length but really do not enhance the discussion.

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