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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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Dear Reviewer #2, Responding to your comments, the text has been revised. Please find below our detailed responses to your comments and suggestions.

- Comment: Arctic rivers and their estuaries are characterized by seasonal extremes; long ice cover, limited light conditions and a very strong seasonal signal in discharge, but also sediment, and POC/DOC fluxes. Even though many readers are probably familiar with this, it should be mentioned. It would be good to minimally add timing and amounts in discharge and delivered OM, and relate this to timing of sampling (August). Also, a description of prevailing currents in this region would be beneficial, and potential benthic boundary layer transport mechanisms.

- Answer: The study area paragraph was rewritten and the following text was added (page 3884, line 3) : 'This study was conducted in the southeast Beaufort Sea, with an emphasis on the MacKenzie delta outflow, during summer 2009 on board the Canadian Research Icebreaker "CCGS Amundsen" as a part of the international Malina Program. The physical, biological and sedimentological caracteristics of Malina study area will be detailed on the editorial of the present special issue. The area is dominated by coastal shelves with a maximum of 580 m water depth on the outer MacKenzie shelf. The major input of sediment and particulate organic carbon to Beaufort Sea comes from the Mackenzie River (O'Brien et al., 2006). The Mackenzie is the largest river draining into the Arctic Ocean in sediment and particulate organic carbon supply (127 106 tons y-1 of sediment and 2.1 106 tons y-1 of particulate organic carbon respectively, Macdonald et al., 1998, Holmes et al., 2002) and the fourth largest in terms of freshwater discharge (3.3 1011 m3 y-1, Milliman and Meade, 1983; Brunskill, 1986; Macdonald et al., 1998). Despite the coastal erosion may be locally important, particularly in the inner shelf, the contribution of the MacKenzie River is clearly much important (5.6 $\times$ 106 t a-1 vs. 64.45 $\times$ 106 t a-1; Hill et al., 1991, MacDonald et al., 1998; Rachold et al., 2000) and supplies about 95-99% of the sediment to the Beaufort Shelf (Rachold et al., 2004). The shelf is seasonally ice covered. The sea ice usually starts to form in October and reaches its maximum 2 m-thickness in March. The landfast ice covers the inner shelf (<20 m water depth). It is bounded offshore by an hummock, or Âń stamucki Âż, formed by the collision of the mobile offshore ice pack and the landfast ice edge. In winter, the stamucki retains the turbidity waters from the MacKenzie River under the landfast ice to the inner shelf. Sporadic polynya form at the edge of the landfast ice due to winter winds that push mobile ice pack away from the stamucki. Around June, the stamucki breaks and releases the Mackenzie River plume in the top 10 m of surface layer of the Shelf. This plume is pushed seaward by easterly winds (MacDonald and Yu, 2006). The sea ice break-up favors the formation of polynya and then marine organic matter production.'

- Comment: The authors devote one small paragraph (end of Section 3.2) to spatial variability of the results, which I think is insufficient, especially when comparing with the comprehensive description of lipid results. I do like, for example, the relation to oxygen penetration depths, but I would like to see a more elaborate discussion on spatial trends. For example: where do algal blooms typically occur (near which stations?); can more distinctive patterns in depth vs. lipid trends be observed?; where are the dominant outflow channels of the Mackenzie freshet plume, and does this relate to lipid (degradation) patterns observed?

- Answer: The main spatial variability observed concerned abiotic oxidation state of terrestrial OM (indeed, algal OM appeared to be practically always weakly degraded) and the degradation state of bacteria. We thus focused the discussion on these two points. The previous text (page 3897, line 7) was replaced by 'While algal OM appeared to be weakly degraded in all the sediments investigated (Fig. 4A), a strong spatial variability of the autoxidative degradation state of terrestrial OM was observed (Figs. 4B and 4C). This variability could be related to the position of the stations relative to the Mackenzie mouth. Indeed, a strong autoxidation of terrestrial OM in SPM was previously observed in the mixing zone of the Mackenzie (Rontani et al., submitted). The extent of autoxidation appeared to be well correlated with salinity, suggesting that these free radical oxidation processes are enhanced by contact with seawater. Consequently, the stations the more distant from the Mackenzie, where the residence time of terrestrial OM in seawater is expected to have been longest, should exhibit the highest autoxidation states. The results obtained well support this assumption. Indeed, the highest autoxidation states were observed at the stations 110, 235 and 345 (Figs. 4B and 4C), which are very distant from the Mackenzie, while the station 689 close to the mouth (Fig. 1) exhibited the weakest degradation state (Figs. 4B and 4C). It is interesting to note that Link et al. (this issue), which used chlorophyll-a/phaeopigment ratio as a proxy of the quality or "freshness" of the organic matter supply, also observed highest degradation states at the stations 110, 235 and 345. The biogeochemical fluxes measured at the same stations by Link et al. (this issue) showed highest oxygen demands for the inner

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shelf sediments (stations 689, 680, 390, and 260). These oxygen demands, which were associated with high production rates of metabolites (e.g. NO2-, PO43-, NH4+), are indicative of an intense biodegradation activity in these sediments. These results are in good agreement with the weak degradation state and cis/trans ratio of vaccenic acid measured at these stations (Fig. 5) attesting to the presence of non-stressed bacteria in good healthy state and thus very active.'

- Comment: Only in the conclusions (page 3898, lines # 8-14) do the authors mention that "In the Arctic, global warming may induce changes in vegetation from tundra toward leaf-bearing plants: : :". In my opinion this statement comes too late, and is also oversimplified; the Arctic landscape is very heterogeneous and warming trends will lead to different vegetation, ecological, and hydrological changes. It would be more valuable to speculate on more specific (predicted) changes in the Mackenzie drainage basin/Beaufort shelf region and how this study can improve our insights in these potential changes, and highlight this earlier in the manuscript (i.e. Introduction).

- Answer: The following text was added in the introduction (page 3883, line 12) 'Recent studies predicted that in next decades significant changes in the arctic zone will occur (McGuire et al., 2009, Griffith et al., 2012). These changes should result in a river flow increase coupled to a permafrost thaws and a highest coastal erosion modifying the organic and inorganic terrestrial inputs. The longer free sea ice period in summer will modify light availability and thus the primary productivity and photochemical processes affecting both dissolved and particulate OM. In consequence, the relative importance of the fluxes of terrestrial and marine organic carbon to the seafloor will likely change, as will the processing and preservation of organic carbon in Arctic sediments (Katsev et al., 2006). A Thus a better knowledge of the degradation processes affecting sedimentary organic matter is essential to establish a baseline to understand the impact of global change in Arctic Ocean. To further investigate and confirm these previous results, we examined the lipid content of surface sediments from the Beaufort Shelf. Even though this shelf accounts for only a few percent of the total Arctic Ocean surface area it receives a large amount of freshwater from the Mackenzie River estimated at 330 km3 yr-1 (Stein and Macdonald, 2004). This flux contributes vast quantities of terrigeneous organic carbon to Beaufort Sea (O'Brien et al 2006).'

- Comment: The authors often refer to a manuscript that is submitted to GCA (e.g. "it was previously observed:" line #5, page 3891 and many more places). Since the readers do not have access to this manuscript, and it might not be accepted in GCA, I think the authors should tune down on referring to the results in that manuscript or, alternatively, include a brief summary and/or most relevant results of that paper (essentially a manuscript too) in this manuscript.

- Answer: The following text summarizing the main results of this paper was added in the introduction (page 3883, line 12): 'Lipids of terrestrial vascular plants, which are well preserved in SPM of the Mackenzie River, appeared to be extensively degraded by bacterial and especially autoxidative degradative processes on the Beaufort Shelf, while planktonic lipids were only weakly affected. A good correlation was observed between the extent of autoxidation and salinity, suggesting that these free radical oxidation processes are enhanced by contact with seawater. In order to explain the specific induction of autoxidative processes on vascular plant-derived material, a mechanism involving metal ion-catalyzed homolytic cleavage of photochemically produced hydroperoxides resulting from the senescence of higher plants on land was proposed.'

- Comment: Introduction Lines #3-16: in addition to the extra references suggested by Mark Yunker (Interactive comment June 4th), van Dongen et al. (Marine Chemistry, 2008) and Vonk et al. (Marine Chemistry, 2008) also report on lipid degradation patterns in (sub-arctic) surface POM versus sediments.

- Answer: These two references were added in the text and in the reference list.

- Comment: Results and discussion In my opinion, there is some basic information missing here, such as exact coordinates and sampling depth, and bulk geochemical characteristics of the sediment samples (i.e. % sediment OC, d13C). These data could easily be added as a Table. Interpretation of spatial trends would be much easier with this information at hand.

- Answer: Values of OC percentage, d13C, d15N were measured in these sediments (Link et al., this issue) but they are very close and not very informative.

- Comment: The manuscript does not contain any lipid concentrations nor distributions. This would also be of great value, and could be included as Supplementary Information.

- Answer: Two tables (Table 1 page 3890, line 16, Table 2 page 3891 line 26) given concentrations of the main sterols and fatty acids in the sediments investigated were added.

- Comment: Also, could Brassicasterol not (partly) originate in freshwaters as is the case, for example, in the Yenisey River (Fahl et al. 2003)?

- The sentence (page 3890, line 23) 'Brassicasterol (mainly arising from phytoplankton, Volkman, 1986: 2003) appeared to . . .' was replaced by 'Brassicasterol (mainly arising from marine or freshwater phytoplankton, Volkman, 1986: 2003; Fahl et al., 2003) appeared to . . .'

- Comment: Line # 10-13, page 3891: An alternative explanation to this statement could be lateral sediment transport, i.e. lipid patterns in the surface sediment do not need to be representative of the water column POM directly above (in fact, they probably are not). The sediment could consist of particles that have settled much closer to land (and as such have spent less time in degradative environments?) and have been transported over the bottom instead.

- Answer: We agree with this comment. The following sentence was added in the text (page 3891 line 13): 'Lateral transport of sediments that already have known degradation and diagenetic processes could be another explanation. Indeed, in this case sediment would consist in part of particles that have settled closer to land and have thus spent less time in water column where degradation is more efficient.'

- Comment: Regarding the extra sentences that were added based on the comment of Mark Yunker (Interactive comment by Rontani et al. 11 June, page C1867, end of first paragraph): Where on the shelf where the sterols by Belicka et al. measured? If the "quick degradation" happens in the "second cm of sediments", it would be worth comparing it with spatial patterns of oxygen penetration depth that are mentioned in the manuscript (page 3897, line #16-19), to see if this can indeed be the case.

- Answer: Two of the stations investigated by Belicka et al. are closed to our stations 110 and 140. At these stations oxygen penetration may reach 2-4 cm. This relatively high oxygen penetration well supports our hypothesis of intensive degradation of zooplanktonic material in the second cm of sediment. The following sentence was added in the text (page 3890 line 16): '. This assumption is supported by the penetration depth of oxygen, which may reach 2-4 cm in this zone (Magen, 2007) and which may contribute to oxic degradation of the settled organic matter well deeper than the sediment-water interface.'

- Comment: Another note regarding the Interactive comments of Yunker: he states that "Sitosterol and campesterol are primarily associated with the particulate phase [ ] However, higher proportions of sitosterol are observed in the dissolved (<0.7um) fraction than in the particulate phase". The authors do not answer to this specific comment, but I think this is an interesting and valid remark and worth a response.

- Answer: The presence of sitosterol in the dissolved fraction does not imply necessarily a marine origin, indeed a contribution of very fine higher plant debris to this fraction is also possible.

- Comment: Section 3.2 Lines # 21-23, page 3894: the authors write multiple times that a "very high trans/cis ratio" was observed, and only here relate this to the 0.1 value (>0.1 indicator of oxidative stress). Readers that are not familiar with this could be confused (any ratios <1 still mean more cis than trans!), so I suggest to move this more forward, and/or also include this in the Figure captions.

- Answer: The following sentence was added at the beginning of the discussion concerning cis/trans ratio of monounsaturated fatty acids. (page 3893 :line 16) 'While trans/cis ratio of monounsaturated fatty acids is usually 0.05 or less in healthy non stressed bacterial populations (Navarrete et al., 2000), unusually high proportions of monounsaturated fatty acids with a trans double bond could be detected in the sediments analyzed.'

- Comment: Line # 20, page 3896: "(see above)", where exactly do you refer to? In Section 3.1 you report that autoxidation processes appear only minor in sediments (lines #7-10, page 3891)? That seems contradictory.

- Answer: The sentence (page 3894 line 23) 'The very high trans/cis ratio observed in the sediments analyzed () could thus be attributed to an adaptive reaction of sedimentary bacteria to the presence of high amounts of photochemically and autoxidatively-produced hydroperoxides (see above)' was replaced by 'The very high trans/cis ratio observed in the sediments analyzed () could be attributed to an adaptive reaction of sedimentary bacteria to the presence of significant amounts of intact hydroperoxides in sinking particles (Rontani et al., this issue) reaching these sediments.' And the sentence 'Due to the strong oxidative stress observed in the sediments investigated (see above), an induction of cis-trans isomerization by thiyl radicals resulting from the reaction of thiols with hydroperoxides (Fig. 9) seems thus very likely.' was replaced by 'Due to the presence of significant amounts of intact hydroperoxides in sinking particles reaching these sediments (Rontani et al., This issue), an induction of cis-trans isomerization by thiyl radicals resulting from the reaction of thiols with hydroperoxides (Fig. 9) seems thus very likely.'.

- All the minor corrections required were carried out.

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