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Biogeosciences Discussions

Interactive comment on "Contrasting composition of terrigenous organic matter in the dissolved, particulate and sedimentary organic carbon pools on the outer East Siberian Arctic Shelf" *by* Joan A. Salvadó et al.

Anonymous Referee #1

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Review of Biogeosciences Discussion bg-2016-260 "Contrasting composition of terrigenous organic matter in the dissolved, particulate and sedimentary organic carbon pools on the outer East Siberian Arctic Shelf" by Salvado et al.,

The manuscript of Salvado et al., provides new data to examine organic carbon cycling in the East Siberian Arctic Shelf. This is an important issue. The Arctic Ocean is undergoing significant warming, and this is projected to increase over the coming century. The impact of this warming on carbon pools remains an important question – i.e. are the carbon pools stable, or could they degrade and release gaseous carbon to

contribute to atmospheric CO2 and CH4 budgets. One of the key unknowns remains the source, age and nature of organic carbon in the water column and at the seafloor (and how these are linked). Despite a large amount of recent work in the study area (involving some of the authors), we are still sample limited, and this paper delivers an impressive new dataset.

A strength of the study is that they examine dissolved and particulate phases in the surface water, and deep water, alongside the sedimentary organic matter. The paper presents bulk elemental and isotopic measurements (including radiocarbon) alongside a range of biomarker yields to help reveal patterns in the source and processing of OC. These aspects allow the authors to examine the contrasting source and age of the OC, and discussion what processes are responsible for these contrasts. Age contrasts between DOC and POC have been examined before, but not too my knowledge through the water column, and in relation to the lignin biomarkers. The decoupling of deep POC and DOC is very stark. The findings are new and should certainly interest the readership at Biogeosciences.

However, I have one main comment, which is comprised of a few parallel issues/observations which I feel the authors should work to clarify in revision:

1. How sensitive are the biomarker proxies (used to examine marine vs terrestrial, and evidence for degradation): a) The Pn/P (hydroxyacetophenone/p-hydroxybenzoic acids) ratio is discussed in the context of a marine versus terrestrial biomarker (Fig. 9a) and used to conclude (stated in the abstract and throughout) that POC is 'mainly composed' of marine OC, suggesting more than 50% of the TOC is marine in origin. However, I think the paper needs to be a little more cautious on this point. They discuss some of the caveats of this biomarker ratio in the text, but also remember this is an extracted component of the TOC. What are the bulk proxies (elemental, isotope) telling us?

Indeed, what is the lignin yield telling us? After two reads, to me, the lignin yield data

doesn't seem to line up with this conclusion. Some surface POC has more lignin yield than the DOC (and not significantly less) and the deep POC samples also have high Lignin yields. Have I missed something here? I don't follow how the lignin yield (a 'major' biomarker if you like) can show these patterns, but the bulk Pn/P ratio tell us something else about organic matter source? The POC is 13C-depleted (note – seems to correlate with DOC d13C looking at the maps) which could be marine organic matter soured from DIC with a remineralisation signature (as the authors explain somewhere). Or it could be the 'top soil' end member identified by Vonk et al., 2012, Nature, at -26 to -30 per mil (see the supplement). Added to this, the 14C-depleted nature of the bulk, deep water POC is easier to explain if a 'permafrost' terrestrial OC signature, so again, how can this be material dominated by marine OC?

b) I have a related comment on the degradation proxies. I think these are important to pursue, so they should certainly be in here and discussed. But, there are some key questions. Do we know the starting compositions of organic matter? The authors acknowledge we have no POC samples from terrestrial materials to compare too. Second, if the biomarkers suggest 'significant' degradation (or as the authors put it, more than we have seen before), should we not also see this in the bulk %OC too? Is there a link in this dataset, or is the %OC too variable due to other factors (sorting, heterogeneity). Indeed, for the SOC samples, a quick look in Table 3 reveals those with high 3,5Bd/V (1.87, 1.89, 2.38) appear to have relatively high %OC (1.7%, 1.3%, 1,7% respectively), while those with lower %OC (0.4%, 0.5%) have lower 3,5Bd/V (0.72, 0.59). This is the opposite of what you might expect for degradation, i.e. higher 3,5Bd/V should indicate more degradation and lower %OC. Does this suggest a strong role of a source change, rather than a degradation signal, to explain the 3,5Bd/V ratios?

More discussion on these issues, and awareness of the caveats would benefit the manuscript. I wonder if a combined results/discussion is helping this. It could be wise to separate these sections to clarify some of these points.

Other comments (by line numbers)

37: based on my reading of the manuscript and the data, a key contrast is that the lignin is highest in the oldest POC samples, whereas the lignin is highest in the youngest DOC samples, suggesting a significant decoupling of terrestrial OC sources and pathways. I was less convinced by the evidence for 'preferential' (implies >50% ?) marine origin of the POC (especially at the seafloor).

44: define ESS

36, 47 & 58: these are important observations, but they are repeated here. Consider restructuring the abstract to make the results and implications/discussion more distinct.

45: the sea ice observation (Fig. 4) seems important, but it is not well explained. Perhaps reorganise the abstract and add a sentence to more clearly make this point.

57: how much evidence for this is presented? Perhaps add a caveat about lignin yields not being that different, and %OC being not that different (more bulk indicators of net degradation?)?

60: ended on a rather generic note. The final sentences could do a better job of summing up the main findings.

87: there are two issues here. 1st the potential fate of OC at the seafloor due to warming (we know nothing about this?!) and 2nd the changing terrestrial inputs. The text could be modified to make these points.

100: define acronyms at first use here.

109: Line 102 mentions the Arctic Ocean here, but I think these comments are linked to the Eurasian Shelf. Certainly, the POC does not appear to degrade faster than POC in the beaufort Sea/Mackenzie Delta studies, probably because of the much higher sediment input at this point. Anyhow, worth clarifying.

116: another issue worth flagging is that the POC in the Eurasian rivers is not well characterised. Previous studies (Vonk et al and others) rely on estuarine samples.

127: could be useful to provide estimates of these OC fluxes.

137: I agree, this is cool, but could you better explain why it is important to do this.

153: how much? (% or Tg C yr-1)?

201: to what depth was the sediment sampled? I wasn't too clear on whether these were surface samples, or cores

221: HCl fumigation (vapour) or leach (liquid) method?

304: this DOC D14C is much older than reported in the study of Eurasian Arctic Rivers by Raymond et al., 2007, GBC, who have values D14C > +39 per mil in the Lena! Worth discussion.

322-327: This seems like an important observation and worth expanding on (certainly worth its own paragraph). To me, this is the key evidence for decoupling of the POC and DOC pools, and as the authors point out, the evidence for pre-aged OC in the system.

328-339: this discussion needs to be more clear on whether you are invoking mixing to explain the patterns, or processes, or both.

355: sentence could be clearer.

364-366: interesting. How does this work hydrodynamically? Lignin rich materials may contain more coarser woody particles, which should be buoyant/neutrally buoyant. This suggests not, and indicates waterlogged terr-OC which can sink. This is seen in the Mackenzie River (but we don't have samples from the Eurasian rivers to examine).

374: 'addition' rather than 'dilution'?

394: split the paragraph here. These are important observations which need to be better drawn out.

437-438: this sentence doesn't fit well with the discussion on 480, where V is noted to

be sensitive to degradation. So, could the shift in S/V space for the POC be due to this, and not changing source? Why is the sediment not V depleted?

454: I don't understand how this can be the case ('mainly composed' implies that >50% OC is marine) when the lignin yields (Fig 2) are higher in some POC samples than for DOC. Doesn't that suggest the same lignin loading, and similar contributions from terrestrial OC in POC and DOC?

455 & 526: role of sea ice and pacific inflow – when I read these bits of text, I thought it was not well supported by the data. After a second reading and closer look at Figure 4, I see your point. This needed to be better explained (why would sea ice do this?) and perhaps drawn out to give this its own paragraph in the discussion.

455: missing text

472: are these Arctic studies or global – clarify.

477- how sensitive are these ratios? are they a linear function of degradation? The second point is important when interpreting what a change from 1-3 actually means.

519-: Overall I found the conclusions didn't map as well onto the discussion and data as they could have done.

527: seemed to be a somewhat misleading statement based on the available data. It would be better to explain the key findings first, and discussion what they indicate, with caveats.

531: the S/V ratios show a mixture in fig. 8a? not a dominant source from one end member??

541: what do you mean by 'less' burial and 'more' mineralisation. Vonk et al., (and others) already indicate this is going on. So, do you mean the numbers could be wrong by a lot (i.e. 50%) or a little (1-5%), or we don't know.

Fig 2b – my comment about lignin yields is contained here (1a above). Subwater and

surface POC can have higher lignin yields than DOC, but the main text then concludes a mainly marine composition for POC – I don't follow that logic.

Fig 5- nice data. Could you plot (a) and (b), with DOC one lot, and POC on the other, just to help see the surface-depth contrast in the POC.

Fig 6 – why exponential functions?

Fig. 8. Plot the surface/subsurface distinction here.

Fig. 9. Do we know how sensitive are these proxies are? What are their expected compositions for marine and terrestrial OC, and how much do they vary. In other words, when we have +ve, are we talking about change of a few % of the total OC, or a lot more? And/or can the source of the OC impact the ratios. This is discussed in the main text, but the abstract and conclusions make quite assertive points based on these data. See comment 1b above.

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