Author responses to referee 1 comments, and planned edits to BG ms "*Contrasting composition of terrigenous organic matter in the dissolved, particulate and sedimentary organic carbon pools on the outer East Siberian Arctic Shelf*" (doi:10.5194/bg-2016-260, 2016)

by Salvadó, Tesi, Sundbom, Karlsson, Kruså, Semiletov, Panova and Gustafsson

We thank the reviewer for her/his careful reading of our manuscript. The constructive reviews and suggestions contribute to improve the paper further during our revisions. All referee comments and our responses, as well as the planned edits, are detailed below, organized such that first the reviewer comments are given in italic, directly followed by our response and outline of planned edits in regular font.

Reviewer Comments

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 CO_2 and CH_4 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.

We appreciate this positive overall assessment of the value and suitability of our paper.

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.

We understand the review point and have now clarified these points. We do not mean to base conclusions only on this Pn/P ratio. We have thus removed Figure 9A to prevent misunderstandings. Throughout the manuscript we have now edited to state that POC in surface waters may have a preferential marine origin, mainly inferred from its very low lignin concentrations, compared to DOC and SOC pools (Figures 2B and 4). Further, we have also corrected that the Pn/P ratios observed in DOC (0.08-0.37), SOC (0.06-0.17) and POC (0.02-0.14) suggest that the OC in the dissolved pool is more terrestrial than in the particulate and sediment pools (Tables 1, 2 and 3; Figure 9A).

Nevertheless, these proxies should be interpreted carefully as P products account for less than 0.1% of the bulk OC so care should be placed when extrapolating the biomarker data..

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?

We agree and have now clarified these matters. The bulk proxies and the lignin yield are telling us that there is a significant decoupling of terrestrial OC sources and pathways. While higher lignin values in "young" DOC are related to the fluvial discharge of fresh OC from the Lena River, enhanced lignin yields in "old" POC, from near-bottom waters, most likely reflect the off-shelf transport of permafrost-derived OC in the nepheloid layer (Figures 2B, 3 and 4).

We have now included in the manuscript that some surface POC samples, the ones in the Kara Sea, had more lignin than in the DOC, but those concentrations were relatively low compared to the higher lignin yields observed in the dissolved and sedimentary OC pools from the ESAS. We also explain in many parts of the manuscript that the enhanced lignin values in near-bottom waters may be due to the off-shelf transport of permafrost-derived OC in the nepheloid layer, through repeated cycles of deposition and resuspension across the shelf.

We agree that the Pn/P ratio is not following the same trend as the lignin yield in the particulate and sedimentary OC pools. We have thus clarified that this proxy should be interpreted carefully and removed Figure 9A to prevent misunderstandings. On the other hand, we are confident stating that POC in surface waters of the outer-shelf of the ESAS is composed preferentially of marine OC mainly due to its very low lignin concentrations, compared to DOC and SOC pools (Figures 2 and 4), and its no-correlations with $\delta^{13}C$ and lignin values.

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?

We understand the review point; however, we cannot assume that higher 3,5Bd/V necessarily correlates with lower %OC. For example, OC can be affected by several other factors which include grain-size and dilution with marine OC. Therefore, the OC content itself does not necessarily reflect the extent of degradation as the 3,5Bd/V ratio does.

Nevertheless, we agree and have now included in the text that 3,5Bd/V could support the role of a source change as observed with S/V and C/V proxies. In this data set pCd/Fd ratios, another ratio that has been used as a diagenetic indicator (Amon et al., 2012; Houel et al., 2006), followed the same pattern as the ones observed in 3,5-Bd/V ratios with higher values in POC and SOC (Tables 1, 2 and 3; Figure 9C). This would strengthen the hypothesis that POC and SOC are more degraded than DOC.

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.

We have now strengthened the discussion of these aspects in the manuscript.

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).

We agree with this assessment and have now deleted this sentence here in the abstract. Moreover, we have now clarified throughout the manuscript that POC in surface waters may have a preferential marine origin mainly due to its very low lignin values. We also state now in many parts of the manuscript that the higher lignin values in younger DOC samples are likely related to the fluvial discharge of fresh OC from the Lena River, while the higher lignin yields in older POC samples, from near-bottom waters, is bound to reflect the off-shelf transport of permafrost-derived OC in the nepheloid layer.

44: define ESS

We have now deleted this acronym as we have restructured the abstract.

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.

We agree and have now restructured the abstract. We have now deleted the sentences "Depleted $\delta^{13}C$, modern $\Delta^{14}C$ and lignin phenols concentrations were all well correlated with DOC levels indicating a relatively young terrestrial contribution. In contrast, POC may have a preferential marine origin, as its concentrations were not correlated with isotope and terrestrial biomarker proxies" and "Overall, DOC is strongly affected by the Lena River plume transporting young Terr-OC from topsoil and/or recently produced vascular pant material, while near-bottom POC and SOC preferentially carries off-shelf old OC released from thawing permafrost". Further, we have now included the sentence "Overall, the key contrast between enhanced lignin yields both in the youngest DOC and the oldest POC samples suggest a significant decoupling of terrestrial OC sources and pathways."

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.

We have now restructured the abstract and rewritten this sentence "Further, the sea ice coverage and the Pacific inflow from the east seem to have a strong influence on those carbon pools, which present older and more enriched δ13C signatures under the sea ice extent."

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?)?

We agree that there in not a strong evidence for this; therefore, we have now deleted this sentence "This suggests that the remobilized old OC from thawing permafrost, which is mainly transported within these pools, could experience less burial and more mineralization than believed earlier." Moreover, we have included the sentence "suggesting more degradation within these pools".

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

We have now rewritten this sentence "Overall, the key contrast between enhanced lignin yields both in the youngest DOC and the oldest POC samples reflects a significant decoupling of terrestrial OC sources and pathways."

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.

We have now included these points: "The sources and the inputs of Terr-OC are likely to vary in the northern shelf margin due to the changing climate".

100: define acronyms at first use here.

We have now defined DOC, POC and SOC 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.

This appears to be a misunderstanding. Here we are referring to studies in different places of the Arctic Ocean that indicated a conservative behavior of DOC.

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.

We have now clarified this and state that POC in the Eurasian rivers is not well characterised.

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

We have now included an estimate of Terr-OC input in the ESAS "(22±8 Tg OC/yr; Vonk et al., 2012)".

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

We have now explained why it is important to do this study "…seeking to test the hypothesis that carbon pools may carry different types of OC with different propensity toward off-shelf transport and degradation".

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

We have now included the percentage of ICD-PF that enters the Laptev Sea (53±5%; Vonk et al., 2012).

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

We have now clarified that "Sediment cores were collected from 40 to 3120 m water depth" and that "This study focused on surface sediments (0-1 cm)."

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

We have now clarified that "surface sediment samples were subsampled and subject to aqueous acidification with HCl (1.5M)"

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.

We agree and have now included "The radiocarbon signatures in the DOC pool of the outer-shelf of the ESAS are much older than those observed in the Lena River (>39‰) (Raymond et al., 2007), but similar and even younger than those reported in surface waters of the Canada Basin (<-216‰) (Arctic Ocean), likely reflecting the inputs of Pacific waters."

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.

We have now expanded these statements "It is important to point out that near-bottom waters presented more depleted and similar $\Delta^{14}C$ signatures in both DOC_{SPE} and POC (-258±94‰ and -250±83‰, respectively) than in surface waters (-213±93‰ and -57±86‰, respectively) (Figure 5; Tables 1 and 2), suggesting the same older and terrigenous source of OC in both pools. Those contrasting age offsets between surface and near-bottom waters, particularly for the POC fraction, may reflect the off-shelf transport of OC translocated over long distances from thawing permafrost."

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

We have now clarified this discussion stating that both mixing and processes of the terrigenous DOC along the off-shelf transport explain the correlation between $\delta^{13}C$ and DOC (r^2=0.68). Further, the relationship between $\Delta^{14}C$ and DOC (r^2=0.87) represents both the source of the terrigenous DOC and mixing between components.

355: sentence could be clearer.

We have now clarified this sentence "Lignin concentrations exhibited contrasting offsets between surface and near-bottom waters, particularly in the POC pool."

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).

We appreciate this assessment; however, vascular plant debris does not float when vascular plant gets old. Actually, it has a high settling velocity because of its dimension (i.e. coarse) (see Tesi et al., 2016). Wood floats because of its air inside that fills all the conducts (e.g., xylem and floem vessels). An old debris floats until its vessels are replaced with water, then it sinks and behaves hydraulically as sandy material. The lignin we see in the outer-shelf is adsorbed on the fine fraction traveling across the margin (see Tesi et al, 2016).

374: 'addition' rather than 'dilution'?

We think it is better to state "concentrations in DOC, POC and SOC pools may be interpreted to result from dilution with marine organic during transport".

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

We have now split the paragraph into two.

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?

We understand the review point; however, the ratio cinnamyl over vanillyl (C/V) is just used to distinguish woody lignin from other sources (Goni and Hedges, 1992; Hedges and Mann, 1979). Degradation lowers both S/V and C/V ratio but largely C/V. If degradation was indeed the main process I would expect a sort of linear correlation between S/V and C/V. Therefore, while some degradation cannot be denied, differences in lignin phenols between carbon pools likely reflect a different source.

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?

We agree and have now rewritten these statements: "These ratios are in agreement with the relationships of DOC and $\Delta^{14}C$ and $\delta^{13}C$ presented above, which indicate that the DOC exported off-shelf is mainly "young" and terrestrial. Nevertheless, it is important to note that these proxies should be interpreted carefully as P products account for less than 0.1-0.2% of the bulk OC, and in some samples the particulate and sedimentary pools have more lignin yield than the dissolved OC".

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.

We have now better explained the role of the sea ice and the pacific inflow: "The older and enriched $\delta^{13}C$ signatures in the outer-shelf of the ESS may reflect the influence of sea ice coverage and the Pacific inflow from the East. We suggest that the sea ice would work as a barrier preventing the direct terrigenous input from land and reinforcing the influence of Pacific waters". The influence of the Pacific inflow from the East has also been observed in several other studies (i.e. Semiletov et al., 2005; Stein and Macdonald, 2004; Karlsson et al., 2015).

455: missing text

We have now removed this text "Overall, these proxies"

472: are these Arctic studies or global – clarify.

We have now clarified that these are global studies.

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.

We use these ratios just to estimate which carbon pool is more degraded. They are not a linear function of degradation. Further, these ratios should be interpreted carefully as these products account for less than 0.1% of the bulk OC.

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

We have now rewritten some parts of the conclusions section:

"Near-bottom waters present more depleted $\Delta^{14}C$ signatures and higher concentrations of lignin, particularly within the POC pool. This reflects the off-shelf transport of thawed-out permafrost OC in the nepheloid layer, through repeated cycles of deposition and resuspension across the shelf."

"Moreover, the opposite trends in the Pn/P and P/V ratios also indicate the terrigenous source of DOC".

"If this hypothesis is true, the remobilized OC from permafrost, which is mainly transported within these carbon pools, could experience less burial and more mineralization than the DOC pool."

"The high abundance of Terr-OC in the outer ESAS, particularly in the dissolved and sedimentary carbon pools, is a clear indicator of the magnitude of shelf to basin transport. Overall, the results are a key evidence for decoupling of the DOC, POC and SOC pools in the ESAS and elucidate the off-shelf transport of permafrost-derived OC in the particulate pool of near-bottom waters."

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.

We agree and have now removed this statement. We have also rewritten the following sentences to "Near-bottom waters present more depleted $\Delta^{14}C$ signatures and higher concentrations of lignin, particularly within the POC pool. This is a key evidence for decoupling of the POC and DOC pools and reflects the off-shelf transport of permafrost-derived OC in the nepheloid layer, through repeated cycles of deposition and resuspension across the shelf."

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

The ratios of S/V indicate gymnosperm vegetation as the most important source of lignin (Figure 8A), and increasing S/V ratios in the easternmost samples reflect a relatively higher source contribution of tundra plants.

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.

We have now clarified that regarding 3,5-Bd/V and pCd/Fd ratios, which are higher in the SOC and POC pools, the remobilized OC from permafrost (mainly transported within these carbon pools) could experience less burial and more mineralization than the DOC pool.

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.

We have now clarified throughout the manuscript that some surface POC samples, the ones in the Kara Sea, had a larger lignin fraction than that in the DOC, but those Kara Sea lignin concentrations were relatively low compared to the higher lignin yields observed in the dissolved and sedimentary OC pools from the ESAS.

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.
We have now plotted $\Delta^{14}C$ of POC and SOC in Figure 5A and DOC and SOC in Figure 5B.

Fig 6 – why exponential functions?
We observed that our points followed exponential functions.

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

We prefer not to modify these figures. We only want to differentiate the DOC, POC and SOC pools and we do not want the figures to be too crowded.

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.

We have now clarified throughout the manuscript that these proxies should be interpreted carefully as these products account for less than 0.1% of the bulk OC. We have also removed Figure 9A, which was representing Pn/P ratios, to prevent misunderstandings.