Author responses to referee 2 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 have contributed 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 presented study provides a new and exciting data set from the outer East Siberian shelf investigating the sources and cycling of different organic carbon pools. The ongoing warming in the Arctic will likely increase the amounts of organic matter exported from land (trough rivers & coastal erosion) and our knowledge about the fate of the different terrigenous organic matter pools in the ocean and across the Siberian shelves is still surprisingly small despite recent publications trying to fill this gap. The combination of bulk dissolved, suspended particulate and sedimentary organic carbon (DOC, POC, and SOC) parameters including stable and radiocarbon isotopes as well as biomarker data (lignin phenols) from surface and bottom waters offers highly needed insights into the sources, quality, and age of the different terrigenous organic matter pools transported across the East Siberian shelf and their relationship with each other. The strong contrast between relatively young terrigenous surface water DOC and old terrigenous bottom water POC and SOC and the fact that they seem to be completely decoupled from each other are the most interesting outcomes of this study.

I recommend this manuscript for publication in Biogeosciences.

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

In the following, you can find my questions and remarks.

Lines 42-45: *How does the sea ice cover and Pacific inflow relate to the older and more enriched $\delta^{13}C$? Can you please elaborate here shortly?*

It is known that the Pacific inflow brings older and more enriched $\delta^{13}C$ signatures (Semiletov et al., 2005; Stein and Macdonald, 2004). In this study we also suggest that this inflow has a stronger influence under the sea ice extent, which could work as a barrier preventing the input of "young" DOC and POC.

We agree that this point may benefit from some further clarification. We have therefore now included that "the Pacific inflow and the sea ice coverage, which works as a barrier preventing the input of "young" DOC and POC, seem to have a strong influence on these carbon pools, presenting older and more enriched $\delta^{13}C$ signatures under the sea ice extent." (lines 40-43).

Line 174: *What is the pore size of the Teflon filters? Is it different from the GF/F filters and if so how could that influence the lignin yields and source as well degradation ratios in comparison to the DOC samples (filtrate from GF/F filters?)?*

We have now included that the pore size of the Teflon filters is 1 μm. (line 178).

We had to use Teflon filters to be able to analyse lignin-derived phenols in POC samples, as GF/F filters are not compatible with the alkaline hydrolysis of the CuO oxidation protocol. The cut-offs of Teflon and GF/F filters are as close/similar as possible and the results should be comparable. We do

not think that the Teflon filters could have influenced the different lignin yields and the degradation ratios between DOC and POC.

Lines 183-186: *Do you have any data or reference for the fact that GF/F filters are not compatible? As far as I understand the problem is that the silica of the GF/F filters could react with the NaOH and use it up, which would change the pH and the needed alkaline conditions for the CuO oxidation. Did you ever try it? If you would use a higher concentration of NaOH, it could keep the solution in alkaline conditions despite some of the silica reacting with the NaOH.*

As far as we know, there are not studies that specifically focus on how to circumvent the problem by changing the molar concentration of the NaOH solution. Winterfield et al (2015) used GF/F filters for river suspended sediments but they only used what they could scrap off the GF/F. Lobbes et al (2000) used a rotary evaporator to concentrate the POC of the Lena River. This is of course extremely time consuming and logistically impossible for our samples (i.e. much larger volumes).

Maybe changing the molarity of NaOH could work, but it was probably safer to use an inert PTFE filter that does not dissolve or interact with the analyses.

Lines 206-209: *Is there any estimate about the approximate age of the surface sediment slices (0.5cm and 1cm) analyzed here? The sedimentation rates are generally lower on the outer shelf than on the inner and they can vary quite strongly. Therefore, it would be important to know how much time is integrated in these samples when comparing them.*

The precise age of the surface sediment slices are not known. The 8-10 ^{210}Pb-dated sediment cores available from ESAS indicate linear sed rates on the order of 0.5-2 mm/yr (e.g. Vonk et al., 2012; Bröder et al., 2016). Naturally, there is also some mixing in the top several centimeters. A rough estimate is that the surf sediment samples represent material sedimented over the past years to several decades.

Also, can you please add the information on the sediment depth of each sample in Table 3 for easier readability?

We have now also marked the three cores sectioned on high resolution (0.5 cm intervals) in Table 3.

Lines 330-335: *Is there some information/words missing here? What "processes of terrigenous DOC along the offshore transport" are reflected here? Do you want to suggest that "processes such as hydrodynamic sorting, deposition, resuspension and uptake by primary production influence the DOC $\delta^{13}C$ and $\Delta^{14}C$ concentrations? Please clarify.*

We have now clarified that both mixing and processing such as sorting and degradation of the terrigenous DOC along the off-shelf transport explain the correlation between $\delta^{13}C$ and DOC (r^2=0.68). Processes such as hydrodynamic sorting, deposition, resuspension and uptake by primary production may contribute to the dispersal and further fate of the OC in the ESAS. On the other hand, the relationship between $\Delta^{14}C$ and DOC (r^2=0.87) represents both the source of the terrigenous DOC and mixing between components. (lines 339-347).

Lines 338-339: *I generally agree with the statement made here that "large proportions the DOC exported to the outer shelf comes from young vascular plant material".*

Although "young" is a relative term. Based on the fact that the DOC is younger than the underlying sediment (and deep ocean DOC in the Atlantic for example), you could call it young. However, it is important to mention in this context that the DOC-$\Delta^{14}C$ values of Eurasian rivers, such as the Lena, are much more enriched in $\Delta^{14}C$ with values >0‰ (containing bomb-14C, see Raymond et al. 2007, Glob Biogeochem Cycl) and are therefore much younger than the samples presented here. That implies that there is either a considerable change in composition (and age) within the DOC pool

during the crossshelf transport likely affecting the young and labile fraction of DOC or mixing with older marine DOC.
Please include this aspect into your discussion.

We agree with this assessment and have now included that "The radiocarbon signatures in the DOC pool of the outer-shelf of the ESAS are older than those observed in the Lena River (>39‰) (Raymond et al., 2007), but younger or similar (in the outer and eastern stations) than those reported in surface waters of the Canada Basin (<-216‰) (Arctic Ocean) (Griffith et al., 2012), likely reflecting the inputs of Pacific waters. The considerable change in age within the DOC pool during the cross-shelf transport is likely due to mixing with older marine DOC." (lines 320-325).

Lines 399-401: Here it would be helpful to add information on for example the concentration of the hexadocenoic acid (C16FA:1), which is also a product of the CuO oxidation used here, in the POC and SOC samples. As Tesi et al. (2014) have shown, the C16FA:1 is a good indicator for marine organic carbon on the East Siberian shelf. Additionally, the dual-isotope ($\delta^{13}C$, $\Delta^{14}C$) three-endmember Monte Carlo simulation (see e.g. Vonk et al., 2012) could give an estimate about the contribution of marine, ice complex and surface soil organic carbon to these samples, which would improve discussion on the fraction of terrigenous and marine OC present in these samples.

We agree that the C16FA:1 proxy and the Monte Carlo simulations could be also useful to unravel the sources of the OC present in these samples. Unfortunately, we did not quantify that compound and we decided not to do statistical modelling in this study. We think that the extensive data presented here from the DOC and POC and SOC pools in the outer ESAS is valuable enough to elucidate interesting new issues and conclusions. Nevertheless, we agree that further studies should analyse more proxies and develop Monte Carlo simulations to strengthen some of the hypothesis and suggestions we are inferring in this study, particularly regarding sources and degradation of the DOC, POC and SOC pools in the outer ESAS.

Lines 401-403: Please clarify that the young Terr-OC is transported mainly in the surface water DOC, because the statement made here does not hold true for the bottom water DOC (3 out of 4 samples are older or as old as the respective bottom water POC samples).

We agree and have now clarified this issue with "whereas "young" Terr-OC is transported mainly within the surface dissolved fraction, near-bottom POC and SOC carries off-shelf preferentially old OC from remobilized permafrost." (lines 417-421)

Lines 431-433: Please mention in which ways to these processes alter the original composition (e.g. degradation causing a shift to towards woody lignin).

We agree and have now included that "degradation lowers both S/V and C/V ratio but largely C/V. If degradation was indeed the main process we would expect a correlation between S/V and C/V. Therefore, while some degradation cannot be excluded, the observed differences in lignin phenols between carbon pools likely reflect a different source." (lines 449-452).

Lines 436-438: Please explain in more detail here. Are you talking about the surface water or bottom water POC? These two POC pools seem to be influenced by different transport processes (more buoyant surface transport versus nepheloid layer transport, resuspension) working on different time scales (shorter at the surface versus longer, likely thousands of years, in nepheloid layer).

We agree with the review point; however, here we only want to differentiate the DOC, POC and SOC pools, without considering locations and water masses, as they depict clear different clustering between OC pools.

How would you explain the distinct clustering seen in the C/V versus S/V plot? Does selective degradation, hydrodynamic sorting, leaching/adsorption influence the source signal in the different

OC pools? Bröder et al. 2016, Biogeosciences Discussion (in your reference list still Bröder et al. submitted – please change), observed an increasing S/V ratio with increasing distance from the coast and suggested that this is rather a result of hydrodynamic sorting or selective degradation than a change in source.

The distinct clustering between DOC, POC and SOC pools suggests that small amounts of non-woody angiosperm tissues are mixing with large amounts of gymnosperm woods in these samples. It also suggests that angiosperms are mainly transported by SOC and gymnosperms by POC.

Bröder et al., 2016 presented a complete shelf transect in the Laptev Sea in surface sediment samples that could suggest that increasing S/V ratios were due to hydrodynamic sorting or selective degradation; however, she could not compare it with the DOC and POC pools. In this study, we are presenting samples along the outer shelf of the ESAS and we are focusing on comparing the DOC, POC and SOC pools. The classical source plot of S/V versus C/V depicts distinct clustering between DOC, POC and SOC, suggesting that SOC mainly carries angiosperms while POC is more resembling gymnosperms.

Furthermore, when I looked into the data of Bröder et al. 2016 I realized that the sediment samples presented here with the IDs 1, 4, 6, 14, 23, and 24 are the same as presented there. Only here the prefix SW is missing, but the Longitude and Latitude match and as both studies are based on samples from the SWERUS-Expedition in summer 2014 I assume these are the same samples. At first, I thought you forgot to put a reference in here for the $\delta^{13}C$ and lignin data of these samples. And for the $d^{13}C$ SOC data you should do that, because Bröder et al. published it first in Biogeosciences Discussion. However, the lignin data presented here by Salvadó et al. (S/V; C/V; Sd/Sl; Vd/Vl; 3,5-Bd/V) is considerably different from the data in Bröder et al. 2016 for these samples, e.g. in the C/V vs. S/V plot the data from Bröder et al. 2016 for these particular samples would plot much more in the direction of woody angiosperm material. So, maybe I got it all wrong and you used different samples than Bröder et al. 2016 or something got mixed up. Please check your data again and clarify.

We appreciate this assessment and understand the review point. It is right that these are the same samples; however, Lisa Bröder decided to inject them later altogether with the rest of her samples to minimize differences between all her samples. It is know that different injections and calibrations can affect the results a little, therefore, as the objective was to have a good comparison with DOC, POC and SOC pools, all samples presented in this manuscript were injected together. These small differences may be due to the different injections and the different calibrations used. For this reason, we did not put a reference for this data. We have now included in the manuscript that "Some sediment samples (SWE-1, SWE-4, SWE-6, SWE-14, SWE-23, SWE-24) were also analysed by Bröder et al. (2016). The small differences in lignin phenols results may stem from the different injections and calibrations used" (lines 252-255).

Lines 439-455: *First of all, the Pn/P and P/V data is missing in Tables 1, 2, and 3. Further, I'm not convinced that the Pn/P ratio is a good proxy for marine versus terrestrial OC contribution here. In Tesi et al. (2014) active layer permafrost soil samples from the Indigirka, Lena, and Kolyma watersheds yielded Pn/P ratios <0.1, which could be a possible source for the low POC values here.*
As mentioned above, you could use the C16FA:1 concentrations or the dual-isotope three-endmember Monte Carlo simulation the assess the relative contributions of terrigenous and marine organic carbon in these samples.

Sorry, we have now included Pn/P and P/V data in Tables 1, 2 and 3. We have also clarified in the manuscript that this proxy should be interpreted carefully and have now removed Figure 9A to prevent misunderstandings (line 470). As mentioned above, we did not quantify the C16FA:1 proxy and we decided not to do statistical modelling in this study.

Line 455: *Sentence missing in the end.*

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

Tables 1-3: *Pn/P and P/V ratios missing.*

We have now added Pn/P and P/V ratios in Tables 1, 2 and 3.

Tables 1 and 2: *Please explain swi in DOC-swi and POC-swi.*

We have now described -swi, seawater intake samples (surface water samples at 8 m depth); and -sub, samples obtained by submersible pump (near-bottom water samples, 5 m above bottom) in Tables 1 and 2.

Fig. 2A: *The second y-axis on the right shows a different maximum value and different intervals. Is one of the axes for POC and one for DOC? Please clarify.*

We have now clarified in the figure caption that the left y-axis is for DOC and the right y-axis for POC.

Fig. 8A: *Where do the boxes for angiosperm leaves, etc. come from? Can you give a reference?*

We have now added in the figure caption that "Typical ranges for woody and non-woody tissues of both angiosperm and gymnosperm vegetation are indicated as boxes in the graph (Goñi et al., 2000)."

Fig. 9C: *It is hard to see in this figure, but is there a slight trend in SOC pCd/Fd ratio with Longitude? And if so, how would you explain that?*

We agree that there is also a slight trend in SOC pCd/Fd, the same observed in 3,5-Bd/V ratios. Previous studies in sediments and the colloidal fraction from the ESAS also reported the same trend (Karlsson et al., 2016; Tesi et al., 2014) reflecting the Pacific inflow from the east of more marine and degraded OC. We have now included it in the manuscript "In this data set pCd/Fd ratios follow the same pattern as the ones observed in 3,5-Bd/V ratios with higher values in POC and SOC and a slightly increasing tendency in the eastern SOC samples" (lines 526-529).