To the editors and reviewers

We greatly appreciate the constructive and helpful comments and criticisms by Tommaso Tesi and one anonymous reviewer. All comments were carefully considered and most of the suggestions were incorporated in the revised version of the manuscript. We also thank the associate editor Naohiko Ohkouchi for handling the manuscript.
An overview of the changes made can be found in the attached pdf file (below). In those cases where we chose not to follow specific recommendations for alteration, we present further arguments supporting our approach.

Sincerely,
Maria Winterfeld

Biogeosciences Discussion, 11, 14359-14411, 2014

"Characterization of particulate organic matter in the Lena River Delta and adjacent nearshore zone, NE Siberia – Part 1: Lignin-derived phenol compositions"

by Winterfeld et al.

Overview of revisions to the manuscript, and response to reviewer comments

Both reviewers note that the carbon isotopic data ($\delta^{13}C$, $\Delta^{14}C$) presented in the companion paper ("Characterization of particulate organic matter in the Lena River Delta and adjacent nearshore zone, NE Siberia – Part 2: Radiocarbon inventories") would be a valuable addition to the interpretation of the lignin phenol data presented here and suggest a combination of the two manuscripts into one.
We agree that the interpretation of the lignin phenol data will benefit from discussing it also in the context of the carbon isotopic data and we will follow the suggestion and specific comments made by Tommaso Tesi to discuss the isotopic data and refer to it more precisely where it is needed. However, we decided to separate the data sets into two related but individual manuscripts and we argue to keep the manuscripts separated for the following reason: The two manuscripts have two different target audiences. The paper on lignin phenols elaborates on processes of fluvial transport of particulate organic matter (POM) from the river catchment to the coastal zone and possible POM degradation as well as on the sources contributing to the POM. Because the Lena River is not only a large Siberian river but one of the largest rivers in the world this manuscript will be interesting to researchers working in or offshore large river systems using POM and biomarkers to study fluvial POM transport processes and characterize vegetation changes in the catchment through time. The companion paper in contrast, focuses on carbon isotopes ($\delta^{13}C$, $\Delta^{14}C$) of surface water POM within the delta in order to characterizes the Lena-specific isotopic fingerprint of POM transported to near shore zone. The Lena catchment is characterized by permafrost soils, which are vulnerable to thawing and degradation in a warming Arctic. On the one hand our data serves as a baseline to detect increasing permafrost thaw depths and thus release of deeper, older organic matter in the future. On the other hand, it is an important attempt to define the Lena River transported POM more accurately. A more accurately defined Lena end-member would improve the dual-carbon isotope three end-member modeling approach, which seems to be useful to unravel organic matter sources to Laptev Sea sediments and thus estimate organic carbon fluxes from permafrost soils to the ocean (e.g. Karlsson et al. 2011; Vonk et al. 2012). Solely combining the carbon isotopic data to support the lignin phenol discussion would not give us the room to additionally address this important issue.

Further, we would like to ask the editors to consider a change of the order of the two submitted manuscripts and thus a change of the titles. As mentioned above, the paper on

lignin phenols benefits from including carbon isotopic data from the second paper in the discussion and we refer to paper #2 several times throughout the manuscript. While we do not refer to lignin phenol paper that much in the discussion of the carbon isotopic data. Therefore it seems only consequent to treat paper on carbon isotopes as the background data providing "Part I" and the paper on lignin phenols as the second paper, i.e. "Part II".

Reviewer 1 (Tommaso Tesi) specific comments:

Page 14377 line 25: *"... it is not possible to draw meaningful conclusion based on this one spring flood measurement". This statement sounds somewhat defensive. At the beginning of the discussion, the authors made a very good point highlighting the different transport conditions which characterize the spring freshet and the summer period. The difference in TSM between the summer time-series (this study and Fedorova et al., 2013) and the datum presented here still reveals that timing is crucial, especially because a significant fraction of TerrOC is supplied during the freshet. I think that our current understanding of TerrOC flux to the Arctic Ocean is biased by the sampling because the concentration and composition of the particulate material supplied during the freshet is poorly characterized. Indeed, I am not surprised that this spring sample (sample 37) has a distinct bulk composition (d13C and D14C) compared to the river end-member chosen in previous mixing model exercises (e.g. Karlsson et al., 2011). That said, one datum is clearly not enough to constrain the TerrOC flux to the Laptev Sea but the differences presented here should be discussed more in terms of lack of resolution in a system which is essentially event-driven. That's why I would replace the statement above and end the paragraph in line with the initial discussion about the seasonality of the river supply.*

Reply: We deleted the sentence and re-phrased the end of this paragraph.

Page 14370 line 24: *be consistent with the terminology of P products in the text. The authors use para-hydroxybenzenes in the method and p-hydroxy phenols in the discussion.*

Reply: We changed it to *p*-hydroxybenzenes throughout the whole manuscript.

Page 14378 line 8-12: *here it would be interesting to compare the results from paper #2 with the lignin concentrations. If the lower lignin content is indeed the result of the dilution of soil OC with river phytoplankton, I would show some numbers in the text to illustrate the relative proportion of phytoplankton in these samples (i.e., F_plankton, equation#1 paper#2). Also, differences in C/N ratio and lignin content can be simply driven by the*

relative proportion between vascular plant debris and mineral soil (e.g. Goni et al 2003 ECSS). This part of the discussion should either include this possibility or argue against it.

Reply: Here we indeed could have used the data from paper #2 to discuss this aspect. Consequently, we changed the paragraph to compare the lignin contents with the C/N and plankton fraction data from paper #2 and discussed the possibility of vascular plant debris versus mineral soil being responsible for C/N changes.

Page 14379 line 14: *be careful when comparing data by Amon et al 2012 and this dataset. Amon et al characterized the composition of dissolved TerrOC which has modern 14C age reflecting therefore a different source compared to the particulate material in suspension which is up to a few thousand years old. Despite the fact that there is potential exchange between the dissolved and particulate phases, the relationship between the two carbon pools is not so obvious to me. When comparing the two datasets, make sure that the reader understands that you are comparing modern TerrOC with pre-aged material old material (refer to paper #2).*

Reply: We acknowledge the concerns about comparability of dissolved and particulate lignin phenol compositions. Indeed, we did not make the differences between the data sets and possible implications clear for the reader. We followed the recommendation and changed the paragraph to explain the characteristics of dissolved OM (as in Amon et al. 2012) and particulate OM in the Lena River in more detail. Yet, we still think that a comparison of our data with Amon et al. (2012) is worthwhile for the following reasons: 1) Both sample sets were taken from the modern system, and the POM and DOM are part of a continuum of material, artificially separated by a defined filter pore size. 2) It is unknown what the radiocarbon composition of dissolved lignin is – only bulk radiocarbon data are available. We do not contest the assumption that it is likely rather young, but this may also be true for part of the particulate lignin.

Page 14379 line 24-34: *if the suspended material in summer is affected by phyto-plankton as previously stated by the authors, the relatively increase of the P/V ratio would simply reflect the increase of the proteinaceous fraction rather than a change in vegetation. See for example the P yields in marine phytoplankton (Goni and Hedges 1995, GCA).*

Reply: The P yields being a marker for phytoplankton in our riverine samples did slip our attention and indeed could be due a protineaceous contribution. We included this possibility in the line of discussion here.

Chapter 4.2.1: *I might be missing something but I cannot find the sample ID 21 in tables or figures. This surface sediment was apparently was collected off the Muostakh island. Based on the map, this sample should be L09-34 instead. In addition, this sample doesn't*

display low lignin content compared to the rest of the samples as stated by the authors. Please revise.

Reply: The sample ID 21 is wrong. The sample name is L09-34 as given in the map. The OC-normalized lignin phenol yield of this sample is slightly lower than the two samples closest to the river outlets (L10-23 and L10-36), but higher than two samples farthest away from the river outlets (L10-24, L10-25). To avoid confusion we re-phrased the sentence.

Page 14383 line 1-5: *this part reads as if the material depositing in surface sediment entirely derives from the watershed while it's well known that the Buor-Khaya bay is affected by intense erosion of ice complex deposits (Vonk et al 2010, Karlsson et al 2011, and many more) as also mentioned in the first part of the manuscript. It confuses me that this aspect is completely ignored from here on. For example, in discussing the C/V and S/V ratios the authors bypassed the importance of coastal erosion. For a comparison with soil profiles from erosional spots in the Buor-Khaya bay please see Tesi et al 2014 (GCA). Here we analyzed the composition of different soil samples from Muostakh island and Buor-Khaya Cape using alkaline CuO oxidations. I am sure that the interpretation of the lignin results in surface sediments will benefit from a discussion that encompasses both river and coastal erosion input. See also my next comments about this.*

Reply: We agree that this paragraph does not clearly state the possible sources for non-woody angiosperm material to the Buor Khaya Bay surface sediments, such as Lena transported material and the erosion of permafrost coasts. We focused here on the woody gymnosperm material, which is predominantly provided by the Lena River fluvial input and derived from its taiga zone in the southern catchment. Gymnosperm plants are basically absent within the tundra zone and are therefore indicative of fluvially transported material as it cannot be derived from coastal erosion.
We follow the reviewer's suggestion and modified the paragraph to present a more comprehensive discussion of the possible terrestrial OM sources.

Page 14383 line 6-15: *see my previous comments on the proteinaceous source of P products and the limitations of the P/V ratio as vegetation proxy in marine and fresh-water environments. These P/V trends observed might be driven by the TerrOC source as stated by the authors but the potential input by phytoplankton cannot be entirely excluded. Please modify the text accordingly.*

Reply: According to earlier comment about possible phytoplankton sources of P phenols we included the possibility of plankton-derived P phenols to the discussion.

Page 14384 line 28: *". . .assuming that the ice complex deposit of Muostakh island. . .". Lignin data from Muostakh island are available in Tesi et al 2014.*

Reply: We included the data on ice complex deposits from Tesi et al. (2014) and extended the discussion.

Page 14385 line 9: *"More data on lignin composition of the ice complex deposit at various location is necessary. . .". See comment above.*

Reply: We deleted the sentence mentioned here and as for the above comment we modified the discussion here to include the recent results on lignin phenols in ice complex deposits.

Chapter 4.3.1 and conclusions. *Here again the input of TerrOC via coastal erosion was ignored. The authors argue that the small tundra domain (about 10%) exerts first order control in the supply of angiosperm tissues. However, the ice complex deposit which is being eroded in Muostakh island and Buor-Khaya Cape (Tesi et al 2014) display S/V and C/V ratios (about 0.6 and 0.2, respectively) consistent with the lignin fingerprint observed in Buor-Khaya bay sediments. Therefore, in addition to trapping gymnosperm material in the floodplain (which can potentially occur), it's clear that the composition of surface sediments is also affected by coastal erosion processes which result in diluting the original gymnosperm signal from the watershed.*

Reply: We agree that the discussion of the surface sediments presented here is not comprehensive. The coastal erosion of mainly ice complex deposits indeed contributes an angiosperm signal to the sediments diluting the gymnosperm signal. We modified the paragraph accordingly.

Reviewer 2 (anonymous) specific comments

P14365 L10-11: *72+12 = 84%. What about the remaining 16%?*

Reply: The remaining 16% are categorized for example as water bodies, cropland, wetlands, etc. as given in Amon et al. (2012), table 1. We changed the sentence to make this clear.

P14369 L14: *23-72% (mean 50%): that is really low (also not really surprising as it is notoriously difficult to recover particles from GFF filters). Please comment on potential sediment fractionation effects and their implications for the chemical composition of the organic matter.*

Reply: The reviewer makes an interesting point here, which we did not consider for the interpretation of our TSM data. We can only speculate about the possible implications, because we have no means in analyzing the trapped/remaining material. The material left in the GF/Fs might have a smaller grain size than the material sitting on the filter. Usually finer soil and sediment material is associated with more degraded lignin phenols. In this case our TSM samples would appear less degraded than they actually are. The lignin phenols of TSM samples presented in this study display a broad range of values for the degradation indices ($Ad/Al_{V,S}$) with many samples being more degraded than the soil samples. If we loose this information due to sediment fractionation, the TSM samples could be much more degraded. If a possible sediment fractionation could also impact the C/V and S/V ratios used to infer vegetation sources is difficult, actually impossible, to assess. However, the C/V and S/V ratios of the TSM samples are similar to the analyzed soil and surface sediment samples (Fig. 4B). Some C/V and S/V ratios are lower, which we interpret as a likely contribution of woody gymnosperm material from the southern Lena catchment. This gives us confidence to say that the source parameters (C/V & S/V ratios) are not or only minor affected by a possible sediment fractionation.
Yet, we cannot exclude that our data is biased by these fractionation processes as result of scraping off the material from the GF/F filters. We added this source of uncertainty introduced through our sample preparation to the interpretation of the TSM samples to chapter 4.1.2.

P14369 L19-21: *were C and N measured on total filters or scrapped sediments?*

Reply: The C and N contents were measured on different filters, i.e. on GF/Fs with Ø25mm and Ø47mm using the same water samples as for the respective Ø142mm filter, which were scraped for lignin phenol analysis. See also method description of paper #2.

P14370: *at first you tell us that the GC-MS was run in SIM mode then a few lines later that you scanned from 50-650 amu. Which is correct?*

Reply: We clarified this part of the method section explaining that both modes were used. We used the scan range from 50-650 amu to acquire full spectra of compounds of interest that were compared to those of standards and confirmed identities. Individual compounds wee quantified based on intensities of selected ions using multi-level calibrations runs routinely during the analysis period.

P14374 L27-28: *to the exception of the needles which fall outside the expected range of S/V values . . .*

Reply: Yes, the needles sample does not plot within the expected range, but we considered it to be close to it. To avoid misunderstanding, we changed the sentence to clarify this.

Section 3.2.3: *3 out of 6 (i.e. 50%) of the plants you measured fall outside the "fresh tissue" box drawn on fig 4A. This seems inconsistent to me. Either re-draw the "fresh tissue" box or provide a rationale explanation.*

Reply: The "fresh-tissue" box serves as an orientation not as an absolute range. We changed the solid line of the box into a dashed line in Fig. 4A and clarified this also in the figure caption. The last sentence of this paragraph (p14375, lines 13-16) was supposed to give a possible explanation for the higher $Ad/Al_{V,S}$ ratios of some of the vegetation samples. It is known that different plant species or even parts of a plant (e.g. mosses and needles, respectively) can have naturally higher acid concentrations resulting in higher $Ad/Al_{V,S}$ ratios (= more degraded) even when they are fresh (e.g. Benner et al., 1990). We re-phrased the sentence to make clarify this.

Section 3.3: *Mixing model: 1) Given that the data fall on a binary mixing line between woody gymnosperms and non woody angiosperms it would make more sense to narrow the mixing down to these 2 end members (instead of angiosperm vs gymnosperms as do P14376 L1-2). This would also make the system a lot less underdetermined. You could even use the trend displayed by the data (looks like a linear trend to me, i.e. binary mixing) to inform your choice of the possible range of endmember composition. 2) You assigned S/V and C/V to the endmembers but don't tell us what are the uncertainties on these. For instance the non-woody angiosperm field is very broad (in both S/V and C/V) and makes no sense to use a single value from the literature for its composition. Instead you should assign a range of values and propagate the uncertainties throughout the unmixing routine.*

Reply: 1) We cannot deny the fact that our data points more or less fall on a line between woody gymnosperms and non-woody angiosperms. However, we would like to maintain the four end-member approach as presented in the manuscript for several reasons. Firstly, this allows our approach to be comparable with the modeling approach used by Amon et al. (2012). These authors worked on samples close to our study area and for comparison we need to use the same end-members they did. Secondly, the two-source-mixing of our data set could be coincidental, i.e. just be a result due to the specific fractions/components/particles that are actually transported by the river and not reflect the actual natural variability of either soils in the catchment or surface sediments on the Siberian shelves. For example, the lignin phenol results of soil samples from northern Siberian (tundra and taiga zone) and surface sediments on the Laptev and East Siberian shelves by Tesi et al. (2014) do not plot on a line between woody gymnosperm and non-woody angiosperm, but also contain woody angiosperm as well as non-woody gymnosperm tissues (see figure attached to this reply letter with data by Tesi et al., 2014 plotted in a C/V versus S/V diagram). Considering a more comprehensive

modeling approach that includes a broader data set as well as literature data, the model should be comparable when using the four end-members for estimating the contribution by each source.
2) The point made here about the end-member uncertainties and error propagation is a very important one. Unfortunately, we cannot give any uncertainties for the used end-members. The boxes given for the expected range of woody and non-woody gymno- and angiosperm tissues are not meant to absolute ranges for these vegetation classes. We agree that Fig. 4B might be misleading in that case. We changed the solid lines of these boxes to dashed lines and stated careful interpretation of these boxes more clearly in the figure caption as well as the text dealing with the interpretation of this data (sections 4.1.2 and 4.2.2). The end-members that we used are compilations of literature values from different woody and non-woody gymnosperm and angiosperm tissues as stated in table 4 in Amon et al. (2012), mainly from the two studies of Hedges and Parker (1976) and Hedges and Mann (1979). Here, particularly North American plants, such as different conifer and deciduous trees (e.g. pine, oak, maple, cedar, alder), grasses as well as different algae were analyzed. To our knowledge there is no comprehensive data on plants representing the tundra and/or taiga zone. Different phenol extraction methods used in the 1970s compared to today as well as the fact that sometimes only the C/V and S/V ratios are given and not the individual phenol concentrations or vice versa make it difficult to assign an error to these end-member values. The few vegetation samples we analyzed ourselves are not representative of the plant communities in the tundra or taiga. Furthermore, we only analyzed one sample per species and cannot say anything about the variability of lignin phenol compositions within each species or family. We analyzed these vegetation samples to get an idea of the lignin phenol composition and how they compare to the soils for example.
We are aware that the end-member model could be greatly improved if more representative data, including a natural spread of end-member properties would be available. For now we can acknowledge this problem by clarifying this issue in more detail in section 4.3.1.

P14377 L27-29: *then why do you bother describing the sigma 8 data at length in the result section?*

Reply: We condensed the respective paragraph on sigma 8.

P14378 L 5-12: *this is a good illustration of why you need to rope the isotopes into the mix (so to speak).*

Reply: That is right, the isotope data are helpful here to clarify the discussion on TSM samples. We re-phrased the sentences and added isotopic data from paper #2. This paragraph has also been modified to implement suggestions made by Tommaso Tesi.

P14378 L 18-20: *it seems to me that preferential degradation of cinnamyl phenols would make the data deviate from a linear trend in the C/V vs. S/V diagram, which they don't. You can thus probably rule that out.*

Reply: Good point, we don't want to completely rule out selective degradation, but for our data set it indeed looks like this is not playing an important role. We changed the sentence to make this clear.

Section 4.2.1 and 4.2.2: *C/N ratios in Buor Khaya Bay sediments are much higher (on average almost double) than in Lena River TSM!! Please tell us what this means. That's another very good example of how the isotopes would help making sense out of the data.*

Reply: As already suggested by the first reviewer that we should refer to paper #2 more often where it can be beneficial for the discussion of this manuscript. The paragraphs referred to in this comment were restructured to include more information on the C/N ratios and $\delta^{13}C$ ratios of TSM samples from paper #2. Additionally, the paragraphs were modified following the suggestions by Tommaso Tesi regarding lignin phenol composition of ice complex deposits and a possible phytoplankton source of P phenols.

P14386 L1-6: *that's a key limitation to your quantitative apportionment of Taiga and Tundra derived OM. Please reflect this in your conclusion (e.g. stating that "a maximum" of xx% of the OM derives from the tundra).*

Reply: We added a sentence to section 4.3.1 and the conclusions chapter clarifying that the 50% angiosperm vegetation fraction in our model can be interpreted as the maximum contribution by the tundra zone.

P14387 L17: *then why is the 2011 freshet sample the second most 14C depleted TSM sample? Again please discuss both datasets together, this will make for a much stronger paper.*

Reply: The sentence referred to here can indeed be misunderstood and more explanation is needed, not only at this point of the concluding chapter, but also earlier in the discussion of the TSM samples (sections 4.1.2 and 4.1.3).
Yes, the bulk POM age of the freshet sample from 2011 is the oldest (2880 ± 30 ^{14}C years, see paper #2). However, in a permafrost environment it is not necessarily a contradiction to have "fresh" organic matter, in this case based on lignin phenol parameters, which is quite old, because the frozen state of the soil preserved the organic matter (e.g. Karlsson et al., 2011; Vonk et al., 2012 using lipid biomarkers in permafrost soils and permafrost-derived sediments). Furthermore, the surface soil and active layer have been shown to contain organic matter which can be up to 3000 ^{14}C years old within the upper 30cm of the soil (Höfle et al., 2012). That means it is possible to have a "fresh" lignin phenol signature and relatively old bulk ^{14}C age. Because we only measured the bulk age of the suspended POM we cannot distinguish between the possibilities of

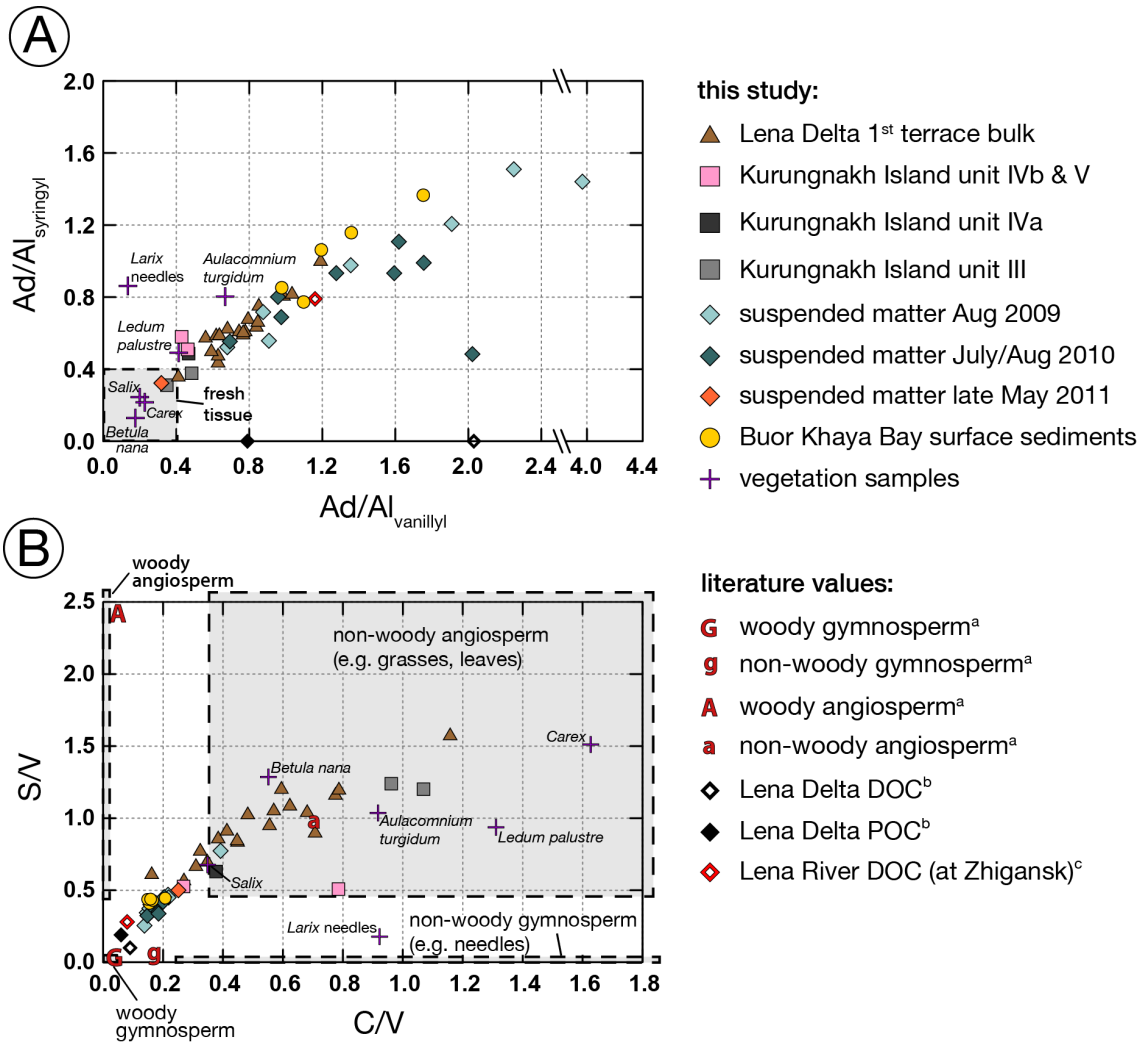
having young and fresh lignin phenols derived from fresh vegetation mixed with very old soil organic matter resulting in the determined bulk POM ^{14}C age and relatively old lignin phenols appearing to be fresh. It seems we did not make this difference clear enough to reader. Therefore we added ^{14}C results from paper #2 to the TSM discussion in section 4.1.3 and changed the sentence in the conclusions chapter to hopefully avoid this confusion.

Table 2: *for the August 2009 data set, how can you have n=20 for TSM and n=21 for POC and POC/PN?*

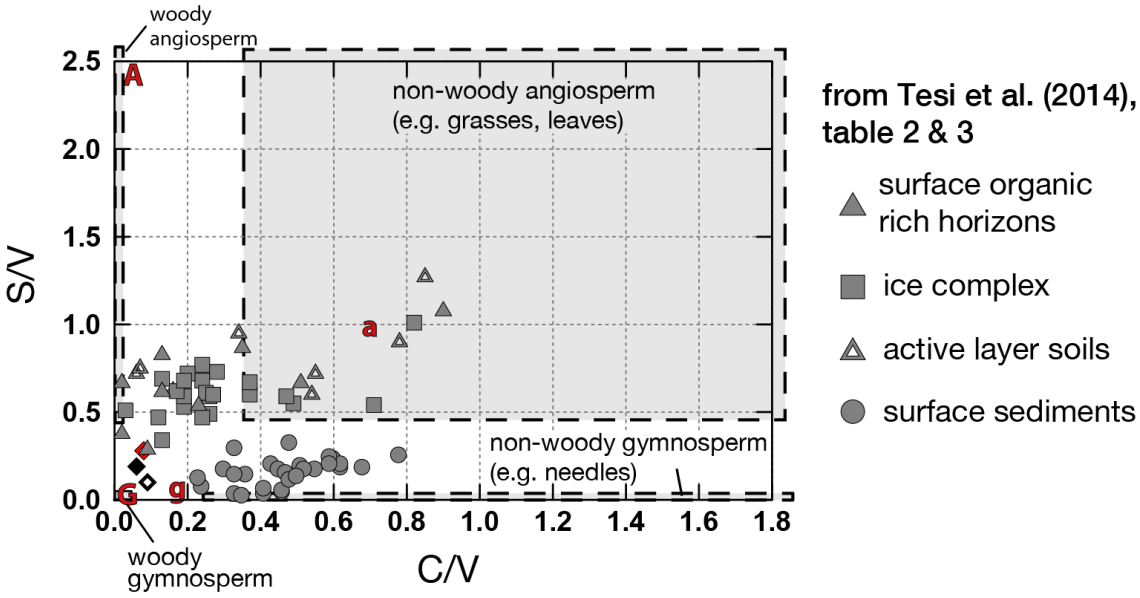
Reply: There is no sample weight for sample 19 (see table S2) and hence we could not calculate the TSM concentration or POC content in wt% for this sample. But the water volume filtered is known and the POC and PN measurements could be normalized to µg/L, which we then used to calculate the POC/PN ratio. We added a short remark to the table caption.

Table 6: *how does the C/V and S/V values you choose for non woody angiosperms compare with the average of your own measurements of plant composition?*

Reply: The values used for the end-member mixing model are displayed as letters "A" for woody angiosperm, "a" for non-woody angiosperm, "G" for woody gymnosperm, and "g" for non-woody gymnosperm in Fig. 4B. We changed the color of the letters to red to make them more visible (please see updated figure below).
The C/V and S/V values of "a" end-member are in our opinion a fairly good representation of the soil samples found in the delta. It is true that the samples of *Carex*, *Ledum palustre,* and *Aulacomnium turgidum* analyzed in this study have higher C/V and/or S/V values than the "a" end-member. That could imply our "a" end-member is not representative of the vegetation in the studied region. However, we analyzed only one sample per plant species and we don't know the range of C/V and S/V values within one species. We decided to analyze the plant samples to get an idea of their lignin phenol compositions, as there are hardly any lignin phenol analyses of plants representative of tundra vegetation available. Please see also our comment above on the end-member model referring to this problem.
To clarify and discuss the uncertainties associated with our model approach in more detail, we modified parts of section 4.3.1.



Updated version of Fig. 4. The woody and non-woody gymno-and angiosperm end-member symbols (A, a, G, g) are bigger and red to be more visible.



Data from Tesi et al. (2014) to show the spectrum of possible lignin phenol compositions in the study region.