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.
This is the detailed version of the reply letter submitted together with revised version of the manuscript.

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".

Additionally to the revision made according to the reviewer comments we re-structured the supplementary information in order to make it easier accessible. For example, in table S1 we deleted the column "water depth" and added a sentence to the table caption mentioning the sampling depth for total suspended matter was ca. 0.5m. This was done to avoid confusion with actual water depth at the sampling locations, which we did not determine.

Please note, in the following the page and line numbers of the changes we made according to the reviewer comments refer to the Word document (submitted as pdf), not the BGD typeset pdf file. In contrast, page and line number of the reviewer comments refer to the BGD typeset pdf file.

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.

Changes: Page 15 lines 9-13: new sentence added here.

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.

Changes: Page 9 line 27, page 17 lines 27 & 29, page 43 line 6, page 45 lines 6 & 7, and page 49 lines 18 & 19.

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.

Changes: Page 15 lines 24-34 and page 16 lines 1-14. Here we extended the discussion on possible phytoplankton contribution including data from paper #2. This paragraph was also changed according to comments by the second anonymous reviewer.

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.

Changes: Page 17 lines 16-22: dissolved and particulate lignin differences explained.

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.

Changes: Page 17 lines 34 and page 18 lines 1-9.

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.

Changes: Page 19 lines 30-32.

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.

Changes: Page 20 lines 18-33 and page 21 lines 1-3.

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.

Changes: Page 21 lines 11-16.

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.

Changes: Page 22 lines 21-32.

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.

Changes: Page 22 lines 21-32. Changes were made in line with changes of the above comment.

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.

Changes: Page 23 lines 17-21, page 25 lines 7-10 and lines 32-34 as well as page 26 line 1 and lines 6-8.

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.

Changes: Page 5 lines 9-10.

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.

Changes: Page 16 lines 26-30.

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.

Changes: Page 8 lines 26-29.

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.

Changes: Page 9 lines 10-19.

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.

Changes: Page 12 line 31.

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.

Changes: Page 13 lines 13-18: Sentences added to clarify high $Ad/Al_{V,S}$ ratios in fresh plant tissue. Page 49 lines 12-13: Fig. 4B caption changed to clarify ranges on "fresh tissue" box.

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.

Changes: Page 23 lines 26-32 and page 24 lines 1-2.

Page 49 lines 12-13: Changed figure caption of Fig. 4B.

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.

Changes/Update: Page 11 lines 27-31 and page 12 lines1-2: When we look closer into the respective paragraph in section 3.2.1 there is only one sentence on sigma 8 of TSM samples (lines 27-28) and we cannot make this any shorter. The lines the reviewer refers to deal explicitly with the problem of sigma 8 for the TSM samples. It does not affect the sigma 8 of soil and sediment samples.

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.

Changes: Page 15 lines 24-34 and page 16 lines 1-14. Here we extended the discussion on possible phytoplankton contribution including data from paper #2. This paragraph was also changed according to comments by T. 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.

Changes: Page 16 lines 25-26.

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.

Changes/Update: Page 20 section 4.2.2: This paragraph was already modified according to comments from T. Tesi, which extended the discussion to include coastal erosion as possible source for angiosperm OM. In our opinion, discussing the ^{14}C data of our Lena Delta TSM from paper #2 here would add no new information to OM source appointment in the Buor Khaya Bay and go beyond the scope of this paper as we focus on vegetation sources in the Lena watershed.

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.

Changes: Page 23 lines 25-26 and page 25 lines 3-6.

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.

Changes/Updates: Page 25 lines 15-18. Sentence added. Further, we reconsidered adding ^{14}C data from paper #2 for the same reasons mentioned above.

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.

Changes: Page 41 lines 2-5. Table caption changed.

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.

Changes: Page 23 lines 26-32 and page 24 lines 1-2.

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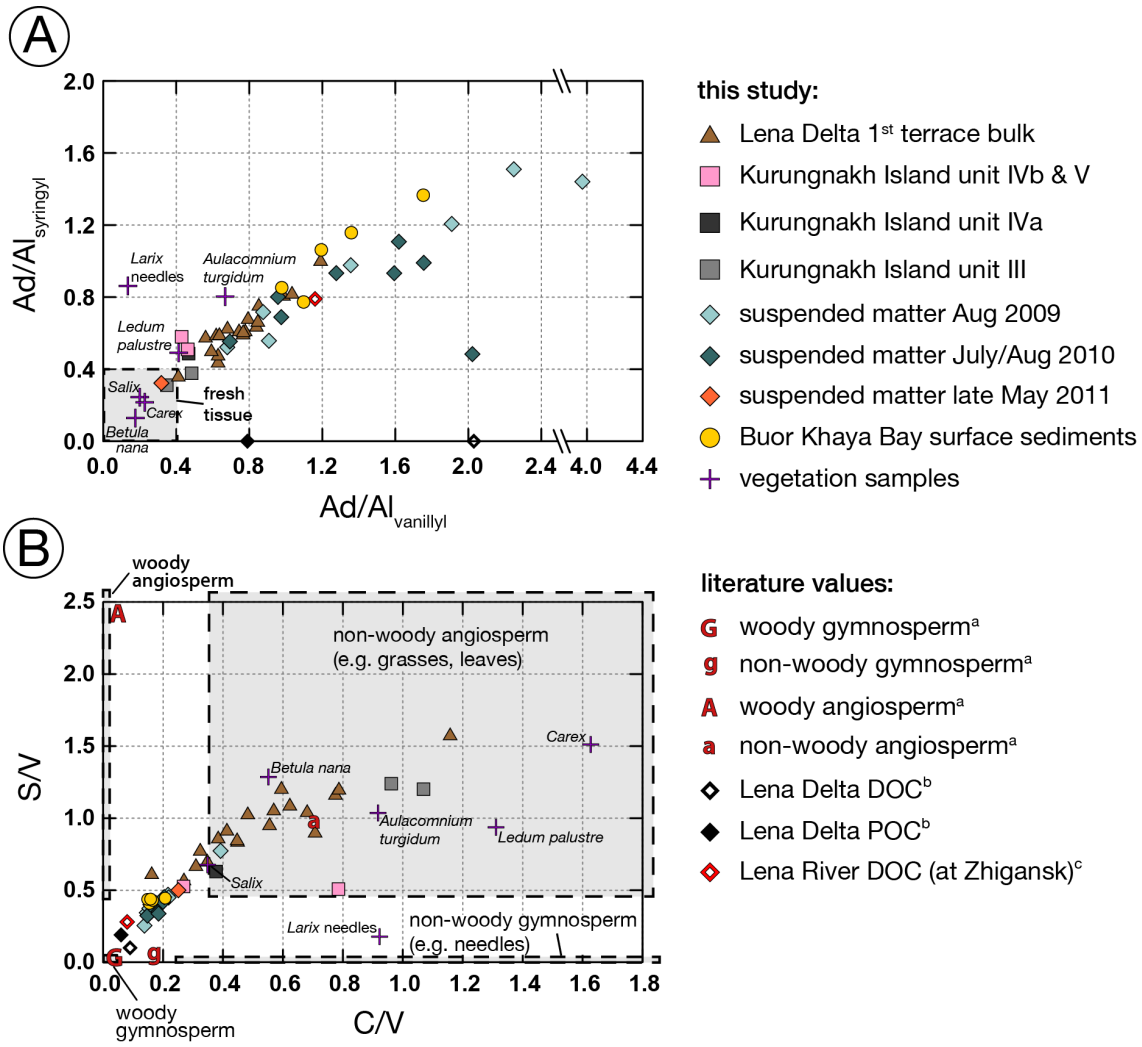
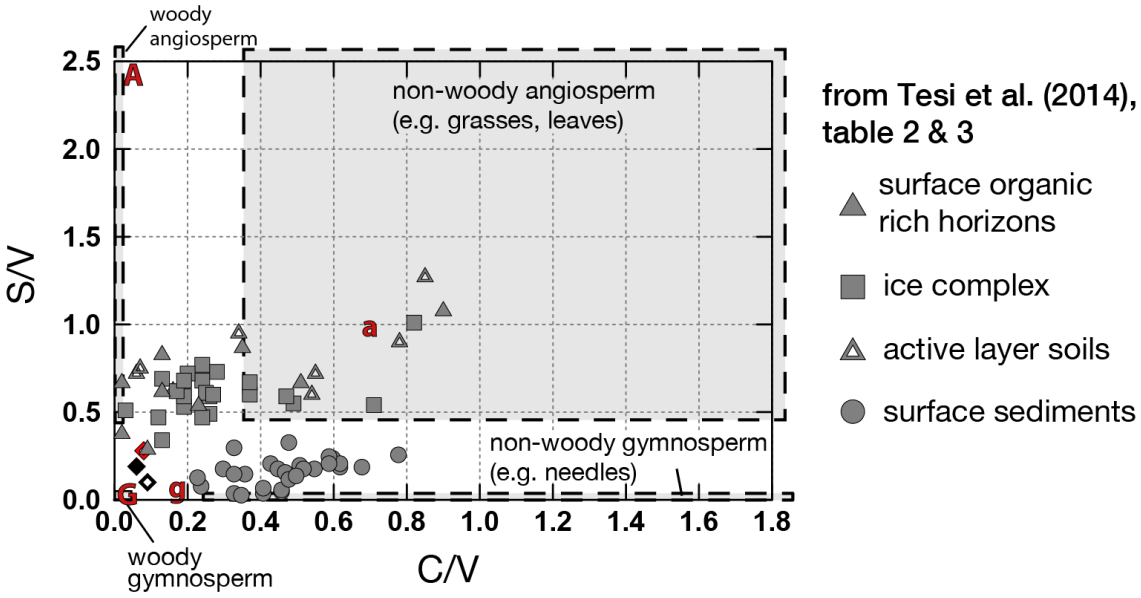


Updated version of Fig. 4. The woody and non-woody gymno-and angiosperm end-member symbols (A, a, G, g) are bigger and red to be more visible.

New figure caption: Lignin degradation indices (Al/Ad$_V$ vs. Al/Ad$_S$) and B) vegetation source parameters (C/V vs. S/V). For abbreviations see Fig. 3. Note the different scales. Literature values: [a]end-member values used in this study taken from table 4 in Amon et al. (2012); [b]Lobbes et al. (2000); [c]Amon et al. (2012). Note in A) the two values on the Ad/Al$_V$ axis where Ad/Al$_S$ is zero, because there were no values given in Lobbes et al. (2000).



Data from Tesi et al. (2014) to show the spectrum of possible lignin phenol compositions in the study region. (As information for the editors and reviewers).

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

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Abstract

The Lena River in central Siberia is one of the major pathways translocating terrestrial organic matter (OM) from its vast catchment area to the coastal zone of the Laptev Sea and the Arctic Ocean. The permafrost soils of its far south stretching catchment, which store huge amounts of OM, will most likely respond differently to climate warming and remobilize previously frozen OM with distinct properties specific for the source vegetation and soil. To characterize the material discharged by the Lena River, we analyzed the lignin phenol composition in total suspended matter (TSM) from surface water collected in spring and summer, surface sediments from the Buor Khaya Bay along with soils from the Lena Delta's first (Holocene) and third terraces (Pleistocene ice complex), and plant samples. Our results show that lignin-derived cinnamyl:vanillyl (C/V) and syringyl:vanillyl (S/V) ratios are >0.14 and 0.25, respectively, in TSM and surface sediments, whereas in delta soils they are >0.16 and >0.51, respectively. These lignin compositions are consistent with significant inputs of

organic matter from non-woody angiosperm sources mixed with organic matter derived from woody gymnosperm sources. We applied a simple linear mixing model based on the C/V and S/V ratios and the results indicate the organic matter in delta TSM samples and Buor Khaya Bay surface sediments contain comparable contributions from gymnosperm material, which is primarily derived from the taiga forests south of the delta, and angiosperm material typical for tundra vegetation. Considering the small catchment area covered by tundra (~12%), the input is substantial and tundra-derived OM input is likely to increase in a warming Arctic. The similar and high acid to aldehyde ratios of vanillyl and syringyl ($Ad/Al_{V,S}$) in Lena Delta summer TSM (>0.7 and >0.5, respectively) and Buor Khaya Bay surface sediments (>1.0 and >0.9, respectively) suggest that the OM is highly degraded and Lena River summer TSM could be a possible source for the surface sediments. The $Ad/Al_{V,S}$ ratios of the first and third delta terraces were generally lower (mean ratios >0.4 and >0.4, respectively) than summer TSM and surface sediments. This implies that TSM contains additional contributions from a more degraded OM source (southern catchment and/or finer more degraded particle size). Alternatively, OM degradation on land after permafrost thawing and subaqueously during transport and sedimentation could be considerable. Despite the high natural heterogeneity of OM stored in delta soils and exported by the Lena River, the catchment characteristic vegetation is reflected by the lignin biomarker composition. Climate warming related changes in the Lena River catchment may be detectable in changing lignin biomarker composition and diagenetic alteration.

1 Introduction

Within the permafrost affected soils of the high northern latitudes lies a huge organic carbon (OC) reservoir, estimated to be as big as 1400-1850 Pg carbon representing about 50% of the global soil OC (Tarnocai et al., 2009). Currently most of this OC pool remains frozen and is therefore excluded from biogeochemical cycles. Over the last decades mean annual air temperatures in the Arctic increased more strongly than the global mean and this trend is projected to continue (IPCC, 2013). As a result annual permafrost thaw depths and arctic river runoff increase (McClelland et al., 2012; Peterson et al., 2002) likely leading to enhanced mobilization and export of old, previously frozen soil-derived OC (e.g. Guo et al., 2004; Schuur et al., 2008; Vonk et al., 2010). Consequently, the great arctic rivers play an important role in global biogeochemical cycles by connecting the large permafrost carbon pool of their hinterlands with the arctic shelf seas and the Arctic Ocean.

Terrigenous sediments reaching the nearshore zone and shelves serve as archives recording changes in material derived from river catchments and from erosion of permafrost coasts. The particulate organic matter associated with these sediments consists of a complex mixture of compounds from different aquatic and terrigenous sources with different chemical/physical recalcitrance towards decomposition and mineralization. Determining the sources (e.g. phytoplankton, vegetation, surface soil, mineral-associated soil, peat, etc.) and quality of OC transported by arctic rivers is therefore important to understand the effects of climate change on the river watersheds as well as on the arctic coastal zone.

Recent studies using molecular organic compounds and their carbon isotopes have shown that there are great differences in the age, quality, and source of OM exported by individual rivers (Dickens et al., 2011; Drenzek et al., 2007; Feng et al., 2013; Goñi et al., 2013; 2000; Gustafsson et al., 2011; Karlsson et al., 2011; Kuzyk et al., 2008; Unger et al., 2005; Vonk et al., 2010). The catchments of the great arctic rivers in North America and Siberia cover several climate zones. Their response to climate change will most likely vary strongly between the temperate and high latitude regions affecting river biogeochemical carbon cycling in different ways. Knowing where the OM derives from (southern vs. northern part of the catchment), if and how the relative contributions of climatic zones to riverine POC may change with climate warming, is important to understand and evaluate different permafrost thawing scenarios and their projected effect on the global climate.

Research efforts on studying arctic rivers increased in the last decades and the spatial and temporal data resolution on dissolved and particulate organic matter has improved. Nonetheless, the resolution is still relatively low, especially for riverine POC. The main reasons for that are the great logistical difficulties of conducting fieldwork in these remote arctic regions under mainly severe climate conditions, especially for winter and spring campaigns.

This is the first of two papers (see same issue) dealing with particulate organic matter from the Lena River Delta and adjacent Buor Khaya Bay. The Lena River is one of the biggest Siberian rivers in terms of water and sediment discharge and an important source of sediment as well as dissolved and particulate organic matter to the Laptev Sea and Arctic Ocean (Holmes et al., 2002; 2012; Rachold, 1999). In recent years, several studies have investigated the input, composition, and transport mechanisms of sediments delivered by the Lena River and by erosion of permafrost coasts (e.g. Charkin et al., 2011; Günther et al., 2013; Karlsson et al., 2011; Rachold and Hubberten, 1999; Semiletov et al., 2011). However, it is still under

debate how OM from the two main sources (riverine vs. coastal erosion) affects the total carbon budget and cycling in the Laptev Sea. Our samples were taken during field campaigns in the summers of 2009 and 2010 as well as in spring 2011. Here, we present new data on particulate OC composition and quality from riverbank soil profiles of the eastern Holocene first delta terrace and the Pleistocene third terrace of Kurungnakh Island (e.g. Schwamborn et al., 2002), surface water particulate matter along the main delta channels, and surface sediments from the Buor Khaya Bay. We used the lignin phenol composition to distinguish the sources of OM transported by the river, namely the taiga forest in the southern catchment versus the tundra covering the northernmost part of the watershed including the delta. The alkaline cupric oxide (CuO) oxidation products are also used to characterize the degree of aerobic degradation of lignin in these samples.

Lignin is a biopolymer produced almost exclusively by terrestrial vascular plants. Through CuO oxidation it is possible to break up the polymer structure and analyze the main building blocks, the lignin-derived phenols, as well as other CuO oxidation products by gas chromatography mass spectrometry (GC-MS). This method has been successfully applied in numerous studies to a variety of environments including the Arctic to trace soil-derived OM and differentiate between gymnosperm and angiosperm plants as well as between woody and non-woody tissues as sources (see Bianchi et al., 2007; Goñi et al., 2000; Hedges and Mann, 1979; Kuzyk et al., 2008; Onstad et al., 2000; Opsahl et al., 1999; Prahl et al., 1994; Tesi et al., 2011). Furthermore, lignin is believed to be a rather recalcitrant fraction of soil organic matter, although this model is currently under debate (Feng et al., 2008).

Considering that, our study in the Lena Delta can serve as possible benchmark against which future changes in OM composition and quality associated with a warming Siberian Arctic could be assessed. Because of our sampling location in the delta covered by tundra vegetation we provide lignin compositional information from the Lena River including the whole catchment and compare these results with data from more southern Lena River sampling locations (e.g. Amon et al., 2012). Further, characterizing the riverine particulate organic matter can improve our understanding of organic matter delivery cycling in the near coastal zone of the Buor Khaya Bay and Laptev Sea.

2 Material and Methods

2.1 Study Area

The Lena River is one of the largest Russian Arctic rivers draining an area of ~2.46 × 10^6 km^2 in central Siberia (Fig. 1A). Its watershed stretches from 53°N near Lake Baikal to 71°N where the river discharges into the Laptev Sea and Arctic Ocean. Because of its huge extension, the Lena River basin comprises a diverse flora and fauna. In general, the basin can be divided into two major vegetation zones transitioning from south to north: 1) the boreal forest or taiga which covers about 72% of the watershed and 2) a small tundra zone in the north representing 12% of the basin area (the remaining area is categorized as water bodies, cropland, etc.; see Amon et al., 2012) consisting mainly of wet and dry dwarf-shrub tundra and sedge/grass wetland tundra (CAVM Team, 2003). About 90% of the Lena River catchment are characterized by continuous and discontinuous permafrost (72-80% and 6-10% of basin area, respectively; (Amon et al., 2012; Zhang et al., 2005). The permafrost table beneath the seasonally thawed layer (active layer) acts as water-impermeable layer and thus its distribution has a large impact on regional hydrology and hydrochemistry. Because of the extreme continental climate of central Siberia with average temperatures around -45°C in January and up to +35°C in August, the Lena River water discharge varies strongly throughout the seasons (e.g. Holmes et al., 2012). The river is covered by a thick ice layer (~2m) from October to late May/June and runoff is comparatively low during this time of the year (Yang et al., 2002). It reaches its maximum during the spring ice-breakup and snowmelt in late May to June when more than 50% of the annual freshwater, sediment, and dissolved and particulate organic matter discharge into the Laptev Sea take place (Rachold et al., 2004). With a mean annual water discharge of ~588 km^3 between 1999 and 2008 (Holmes et al., 2012) the Lena ranks second largest of the Russian rivers after the Yenisey. Corresponding annual sediment, dissolved organic carbon (DOC) and particulate organic carbon (POC) fluxes are 20.7 Tg/yr (Holmes et al., 2002), 5.7 Tg/yr (Holmes et al., 2012), and 1.2 Tg/yr respectively (Rachold and Hubberten, 1999). A second major source for terrestrial organic matter delivered to the Laptev Sea is the sediment input by thermal erosion of the ice-rich Pleistocene ice complex or Yedoma deposits along the coast (see Gustafsson et al., 2011; Mueller-Lupp et al., 2000; see Rachold and Hubberten, 1999). Annual supply of sedimentary material and total organic carbon to the Laptev Sea by coastal erosion is estimated to be ~58.4 Tg/yr and 1.8 Tg/yr, respectively (Stein and Fahl, 2004).

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The Lena River Delta is the largest arctic delta with an area of ~32,000 km^2. It can be divided into three geomorphological terraces (Grigoriev, 1993; Schwamborn et al., 2002). The first terrace includes the active floodplains that were formed during the Holocene and makes up about 55% of the total delta area (Morgenstern et al., 2008) covering the central and eastern part. Within the first delta terrace remains of a Pleistocene accumulation plain, also called ice complex or Yedoma deposits, form the third terrace. Covering about 6% of the total delta area (Morgenstern et al., 2008). Sandy islands forming the second terrace cover the rest of the delta area in the west. The first and third terraces formed under completely different conditions. Whereas, fluvial high energy depositional regime characterize the Holocene (e.g. Schwamborn et al., 2002), the Pleistocene terraces were formed under a comparatively low energy alluvial and proluvial depositional regime (e.g. Schirrmeister et al., 2011). These contrasts result in distinct differences in OC content and quality, extent of soil formation, composition of the soil matrix, and ice content. Erosion of exposed surfaces means that both terraces contribute to the suspended particulate matter in the Lena Delta surface water sampled for this study, as well as suspended matter transported by the river from the southern catchment area.

Lena River water and sediment discharge is not equally distributed through the different delta channels (Fig. 1B). Approximately 80-90% of the total water and up to 85% of the sediment discharge are delivered through the three main eastern channels to the Buor Khaya Bay east of the delta, i.e. through the Sardakhsko-Trofimovskaya channel system (60-75% water, 70% sediment) and the Bykovskaya channel (20-25% water, 15%sediment). Only a minor portion is discharged to the north and west through the Tumatskaya and Olenyokskaya channels (5-10% water, 10% sediment; (Ivanov and Piskun, 1999).

All riverbank bluffs sampled here belong to the first terrace, which is elevated (5 to 16 m) over the active floodplains. The bluff profiles vary strongly in sediment composition and organic matter content. Within the profiles sandy layers derived from extreme flooding events (Schwamborn et al., 2002) and aeolian input (Kutzbach et al., 2004; Sanders, 2011) alternate with buried surface soil layers and peat layers rich in fibrous plant and root detritus in different stages of decomposition. The peat layers are either of autochthonous or of allochthonous origin. Allochthonous material is eroded from river banks further upstream and re-deposited in the delta.

The first terrace is characterized by wet polygonal tundra with depressed polygon centers and elevated polygon rims. Phytologically, the polygon centers are dominated by hydrophilic

sedges like *Carex aquatilis*, *Carex chordorrhiza*, *Carex rariflora*, and mosses (e.g. *Drepanocladus revolvens*, *Aulacomnium turgidum*) and the rims by mesophilic dwarf shrubs (e.g. *salix glauca*) and mosses (e.g. *Hylocomnium splendens*, *Timmia austriaca*) (Boike et al., 2013; Kutzbach et al., 2004; Sachs et al., 2010).

2.2 Sampling

The sampling sites presented in this study are located in the eastern part of the Lena Delta and adjacent Buor Khaya Bay (Fig. 1B). Permafrost soil samples, total suspended matter (TSM) from surface waters, and surface sediments were collected during two expeditions in August 2009 and July/August 2010. Additional TSM samples were collected during the Lena River freshet in late May 2011. Four Holocene permafrost peat bluffs of different heights (3 to 8 m above river level in August 2009 and July/August 2010) were sampled along the main channels of the first delta terrace (all sampling sites in Fig. 1B and Table 1). In order to obtain samples that reflect the original state of the frozen permafrost soils, thawed material was removed with a spade for the total height of each bluff. Frozen pieces of peat were excavated at different depths using hatchet and hammer.

Suspended particulate matter of Lena River surface water was sampled at different stations in the main river channels of the delta on the Russian vessel Puteyski 405 (Fig. 1B, Table 1). Between 1 and 30 L of water were filtered on pre-combusted (4.5h at 450°C) and pre-weighed glass fiber filters (GF/F Whatman, 0.7µm membrane, Ø142mm) for biomarker analysis. Additionally, water samples of 15 and 20 L from the spring freshet in 2011 were stored cooled in opaque canisters for several days to allow for the suspended matter to settle. Before decanting the supernatant water it was filtered on pre-combusted and pre-weighed GF/F filters to check for the TSM remaining in suspension. For the sample presented here (sample ID 37) the TSM of the supernatant water represented 0.1% of the settled material on a dry weight basis and therefore the loss of material in suspension can be neglected.

Surface sediment samples from the Lena riverbed and off Muostakh Island were taken 2009 using a grab sampler on board the Russian vessel Puteyski 405. Surface sediments from the Buor Khaya Bay were taken in 2010 with the Russian vessel PTS using a steel tube (Ø 5cm) connected to a rope. Penetration depths into sediment were between 3 and 6cm.

The peat and sediment samples were stored in pre-combusted glass jars (4.5h at 450°C) and GF/F filters were wrapped in pre-combusted aluminum foil. All samples were kept frozen at –20°C during storage and transport until analysis.

Additionally to the samples taken for this study, we analyzed 5 samples (2 from the early Holocene, 3 from the Pleistocene) from a profile on Kurungnakh Island, which were taken in 2002 and provided by Lutz Schirrmeister from the AWI Potsdam, Germany. A detailed description of the study site and the paleoenvironmental interpretation was published by Wetterich et al. (2008). Furthermore, vegetation samples collected further south along the Lena River were provided by Ulrike Herzschuh and Juliane Klemm from the AWI Potsdam, Germany (for more information on the sampling sites see: Herzschuh et al. 2009; Klemm and Zubrzycki, 2009; Zubrzycki et al., 2012). Plant species analyzed here were *Aulacomnium turgidum* (moss), *Ledum palustre* (wild rosemary), *Carex spp.* (sedges), *Betula nana* (dwarf birch), *Salix* (willow), and *Larix* (larch).

2.3 Laboratory analyses

Peat and sediment samples were freeze-dried, homogenized, and subsampled for elemental and biomarker analysis.

All filters were oven-dried at 40°C for 24h. Due to expected problems with alkaline CuO oxidation of glass fiber filters in the microwave (dissolution of glass fiber), the particulate matter from samples selected for CuO oxidation was carefully scraped off the filter with a scalpel. During the filtering process a large portion of the particulate matter settles within the membrane structure. Therefore it was only possible to scrape off the material sitting directly on the filter surface. This material made up between 23-72 % (mean: 50%) of the total TSM on the filters. Because of this treatment the measured CuO oxidation products cannot accurately be related to the original water volume filtered and are rather treated like sediment samples normalized to the sample weight and weight of organic carbon.

2.3.1 Elemental analyses

Weight percent organic carbon (OC) and total nitrogen (TN) content of soil and sediment samples were determined by high temperature combustion after removal of carbonates as described by Goñi et al. (2003). The particulate organic carbon (POC) and particulate nitrogen (PN) content of TSM were analyzed on Ø25mm and Ø47mm GF/F obtained from the same water sample as the respective Ø142mm filters, which were scraped for lignin phenol analysis.

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2.3.2 CuO oxidation products

Alkaline CuO oxidation was performed at Oregon State University based on the method described by Goñi and Montgomery (2000). Alkaline oxidations were carried out with nitrogen-purged 2N NaOH at 150°C for 1.5h using a microwave digestion system. After the oxidation, recovery standards (ethyl vanillin, *trans*-cinnamic acid) were added and the solution was acidified to pH 1 with concentrated HCl. Subsequently, samples were extracted with ethyl acetate. Extracts were evaporated to dryness under a stream of nitrogen. CuO reaction products were re-dissolved in pyridine and derivatized with bis-trimethylsilyl trifluoroacetoamide (BSTFA)+1% trimethylchlorosilane (TCMS) to silylate exchangeable hydrogens prior to analysis by gas chromatography-mass spectrometry (GC-MS). Compounds were separated chromatographically in a 30m x 250µm DB1 (0.25µm film thickness) capillary GC column, using an initial temperature of 100°C, a temperature ramp 4°C/min and a final temperature of 300°C. Gas chromatography-mass spectrometry was used to identify and quantify individual biomarkers (e.g., Goñi et al., 2009). The GC-MS was set to scan from 50 to 650 amu and used to acquire full spectra of compounds of interest that were compared to those of standards to confirm identities. Individual compounds were quantified based on the intensities of selected ions using multi-level calibrations run routinely during the analysis period. Yields of non-lignin products were quantified using the detector response of *t*-cinnamic acid. External calibration standards were determined for individual compounds using ions specific to each chemical structure. The calibrations, which were performed on a weekly basis to test the response of the GC-MS, were highly linear (r^2>0.99) over the concentration ranges measured in the samples. A more detailed method description can be found in Goñi et al. (2009) and Hatten et al. (2012).

Quantified reaction products included eight lignin-derived compounds: vanillyl phenols (V = vanillin, acetovanillone, vanillic acid), syringyl phenols (S = syringealdehyde, acetosyringone, syringic acid), and cinnamyl phenols (C = *p*-coumaric acid, ferulic acid).

In addition, also non-lignin-derived phenols were quantified including *p*-hydroxybenzenes (P = *p*-hydroxybenzaldehyde, *p*-hydroxybenzophenone, *p*-hydroxybenzoic acid).

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2.4 End-member unmixing

The concentration of different lignin phenol groups of marine sediment samples and riverine suspended matter samples was used to infer the contribution of gymnosperms and angiosperms to the total lignin derived OM. The end-member (EM) properties from the

literature (as shown in Amon et al., 2012) in the form of C/V and S/V ratios were transformed into relative concentrations of the respective lignin compounds (see Table 7). The linear mixing system of lignin concentrations in the samples can be written in matrix notation as:

$$\boldsymbol{X}=\boldsymbol{A}\boldsymbol{S}+\boldsymbol{R}$$

$\boldsymbol{X}$ represents a n-by-m matrix of n samples and m of lignin compounds. $\boldsymbol{A}$ (n-by-l) denotes the mixing coefficients of l EMs for the n samples. The m EM properties (lignin concentrations) for the l EMs are represented by matrix $\boldsymbol{S}$ (l-by-m). $\boldsymbol{R}$ (n-by-m) denotes the residual matrix. This linear problem can be solved using non-negative least-squares fitting (NNLSQ, (Löfberg, 2004). Since the mixing coefficients must be positive and the abundances must add up to unity, a non-negativity-constraint ($\boldsymbol{A}$>=0) and sum-to-one constraint for the rows in $\boldsymbol{A}$ was defined. Because the relative abundances of lignin represent a closed data set, we performed the centered-log-ratio transformation (Aitchison, 1982) to bring the data $\boldsymbol{X}$ into real space. We implemented a Monte-Carlo simulation with 500 iterations, each with randomized first guess within the constraints formulated above. The resulting probability density function of possible solutions for each sample and EM contribution characterized by its median and interval containing 90 % of the possible solutions.

3 Results

3.1 General characteristics and elemental composition

The surface water TSM concentrations showed a strong spatial (within the delta) and temporal (seasonal/annual) variability (Table 2). The concentrations varied from 3.1 mg/L to 174.9 mg/L in 2009 and from 3.5 mg/L to 32.2 mg/L in 2010. The maximum value of 174.9 mg/L in 2009 of sample 17 (Fig. 1B, Table S2) was determined offshore Bykovsky Peninsula close to shore in shallow water depth. The particulate organic carbon (POC) concentrations and POC to particulate nitrogen (PN) ratios are from the companion paper (Winterfeld et al., 2015; submitted as companion paper) and additionally given in Table 2. The sample taken in 2011 shortly after the ice-breakup off Samoylov Island (sample ID 37) showed with 494 mg/L the highest TSM loads determined during this study.

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OC and TN contents of first terrace soil samples varied strongly within individual riverbank bluffs and between the bluffs. The OC contents ranged from 1.02 to 17.14 wt% and the TN

contents from 0.03 to 0.45 wt% (Table 3, Fig. S6). The highest values (>10 wt% OC) were not necessarily found in the topsoil layers, but also within bluff profiles associated with layers containing plant remains like twigs and leaves. Lower OC and TN contents (<2 wt% and <0.1 wt%, respectively) were found in layers with high sand contents. The atomic OC to TN ratios (OC:TN) of these samples show a similar distribution pattern. The ratios varied from 21.7 to 68 with the highest values (>40) in samples rich in plant remains.

Buor Khaya Bay surface sediments showed generally lower OC and TN contents than observed for the first and third delta terraces (Table 3) ranging from 1.67 to 2.47 wt% and from 0.09 to 0.18 wt%, respectively. The highest OC and TN contents (2.47 wt% OC and 0.18 wt% TN) were analyzed for sample L09-34 off Muostakh Island (see Fig. 1B). The island is mainly composed of Pleistocene Yedoma deposits and highly affected by coastal erosion providing a lot of particulate matter throughout the open water season. The highest OC:TN ratio of 20.9 was determined off the Sardakh-Trofimovskaya channel system (sample L10-36, see Fig. 1B, Table 3), where the majority of the Lena River water and sediment discharge occurs.

3.2 CuO oxidation products

Table 4 and 5 summarize the sediment- and OC-normalized CuO product yields of samples presented in this study. Yields of individual samples can be found in the supplementary material (Table S4 and S5).

3.2.1 Sediment- and carbon-normalized CuO oxidation yields

On average the plant samples exhibit the highest V, S, C, and P phenol yields per gram dried sediment/plant tissue (dws), i.e., Σ8 (sediment-normalized sum of V, S, and C phenols) ranging from 4.64 to 17.08 mg/g dws. Only a few soil samples of the first terrace reach similar yields. Generally first terrace Σ8 contents vary from 0.04 to 7.10 mg/g dws (mean Σ8 1.93 mg/g dws). Contents from the third terrace on Kurungnakh Island are generally lower (<2.0 mg/g dws) except for the two Pleistocene samples from unit III (Σ8 is 1.81 mg/g dws for both samples). Suspended matter from 2009 to 2011 and surface sediment samples have CuO product yields in a similar range from 0.04 to 0.47 mg/g dws over all phenol groups. In the Buor Khaya Bay the yields decrease with distance from the delta. Highest values were determined in front of the Sardakh-Trofimovskaya channel and offshore Muostakh Island. As already shown for the OC and TN contents above, also the V, S, C, and P phenol yields vary

strongly within the first delta terrace soils samples and TSM samples. In general, the P and V phenol groups were most abundant followed by the S and C phenol groups.

An overview of the CuO yield per 100 mg OC (Λ8) for the different locations and sample types is presented in Figure 2. The overall patterns described for the sediment-normalized yields are also true for the carbon-normalized yields. The highest Λ8 were analyzed in samples from the first and third delta terraces varying between 0.78 and 8.81 mg/100mg OC over all phenol groups (Table 5). The Λ8 were lower in TSM from the summers 2009 and 2010 (<1.5 mg/100mg OC) and notably higher for the spring flood sample from 2011 (5.16 mg/100 mg OC) as well as for the surface sediments of the Buor Khaya Bay (mean value 1.96 mg/100 mg OC). Also the amounts of individual phenol groups are different between the delta soil samples, the TSM, and the surface sediments samples. Generally the P and V phenols were most abundant followed by S and C phenols (Fig. 2). Again, the two samples from the third terrace from unit III were slightly different. Here, the S phenols were most abundant followed by the P, V, and C phenols. The distribution of V, S, C, and P phenols in the summer TSM samples of 2009 and 2010 were similar with the V and P phenols being most abundant. The spring flood sample from 2011 and the surface sediment samples were comparable with V and S phenols having the highest yields (Fig. 2).

3.2.2 Vegetation source parameters

The bulk samples of the first delta terrace show a broad range of C/V and S/V ratios (0.16 to 1.16 for C/V and 0.58 to 1.58 for S/V, Table 5 and S5 and Fig. S7). As shown in Fig. 4B the values fall on a mixing line between woody gymnosperm and non-woody angiosperm tissues. The P/V ratios show a similar range of variation. The samples from the third terrace have comparable ratios as those from the first terrace, with the highest C/V and S/V ratios determined for the two Pleistocene samples from unit III. The values of the TSM samples taken in summer and spring and in three consecutive years are within the same range. Mean C/V ratios were 0.21, 0.18, 0.25 and mean S/V ratios were 0.44, 0.38, 0.5 for the years 2009, 2010, and 2011, respectively. The P/V ratios were higher in the summers of 2009 and 2010 (0.65 to 1.25 and 0.62 to 0.89, respectively) than in spring 2011 (0.44). The C/V, S/V, and P/V ratios vary only slightly in the Buor Khaya surface sediments and are generally in the range of the TSM samples and lower than the mean of the first delta terrace and the third terrace soil samples. Except for the sample of larch needles, the C/V, S/V, and P/V ratios of the vegetation samples reflect their tissue and plant origin closely (Fig. 4B and 5).

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3.2.3 Degradation indicators

The acid to aldehyde ratios of vanillyl and syringyl phenols ($Ad/Al_{V,S}$) of the first delta terrace vary strongly from moderately degraded (0.5 to 0.6) to highly degraded (>0.6) (Figs. 4A and S7, Table 5). Ratios of the third terrace on Kurungnakh Island are generally lower (<0.6) than ratios from the first terrace. Notably, the lowest ratios were analyzed for the oldest sample S45 (<0.4, Table 5). $Ad/Al_{V,S}$ ratios of the summer TSM are in the range of the first delta terrace or higher, e.g. varying between 0.68 and 3.97 for Ad/Al_V in 2009 and between 0.69 and 2.02 in 2010. The spring flood sample from 2011 is characterized by one of the lowest ratios of all samples presented here (0.32 for both, Ad/Al_V and Ad/Al_S). Buor Khaya Bay surface sediments showed ratios >0.6, which are in the range of the first delta terrace and summer TSM samples (0.98-1.75 for Ad/Al_V and 0.77-1.37 for Ad/Al_S). The highest ratios were analyzed off Muostakh Island (sample L09-34). The vegetation samples have low $Ad/Al_{V,S}$ ratios (<0.4) except for the larix needles, the herb sample (*Ledum palustre*) and the moss sample (*Aulacomnium turgidum*), which have ratios >0.4. It is known that different plant species or even different parts of a plant (e.g. mosses and needles, respectively) can have naturally higher acid concentrations resulting in higher $Ad/Al_{V,S}$ (=more degraded) even when they are fresh (see Benner et al., 1990). This is most likely also the case for the vegetation samples presented here.

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3.3 End-member unmixing

The EM unmixing was performed for the TSM and surface sediment samples. The EM properties of moss and peat contribution in this model do not represent the range of values observed in our samples. Fig. 5 shows our Pn/P and P/V ratios in relation to several published values, amongst others the end-members used for moss, soil, and peat.

Therefore, we applied an unmixing model distinguishing between the four major vegetation sources for OM: woody and no-woody gymnosperm and angiosperm tissues. We used C/V and S/V ratios and took the EMs (Table 6) from Amon et al. (2012) and references therein, which covered the complete range measured in TSM and surface sediment samples (Fig. 4B).

The median values of the unmixing solutions (obtained by Monte-Carlo simulation) of angiosperms (woody + non-woody) and gymnosperms (woody + non-woody) are shown in Table 7. The relative contributions show a broad range for the summer TSM samples of 2009 and 2010, i.e. gymnosperm contribution varies from 0.24 to 0.69 and from 0.49 to 0.63, respectively. The low gymnosperm contribution of 0.24 is inferred for sample 17, located off

Bykovsky Peninsula (Fig. 1B). The contributions to the Buor Khaya Bay surface sediments vary to a lesser extent from 0.49 to 0.56 for gymnosperms.

4 Discussion

4.1 Spatial and temporal patterns of Lena Delta total suspended matter

4.1.1 Suspended sediment distribution and particulate lignin biomarker abundances

Surface water suspended particulate matter sampled in highly dynamic systems like a river delta can only provide very local snapshots of the suspended matter properties. The Lena Delta is characterized by a dynamic hydrology and fast changes of local conditions of erosion and accumulation, which are related to changes in water velocity and turbidity leading to channel migration and branching (Fedorova et al., 2013). Longer time series covering several years and seasons are needed to observe catchment related changes in these properties independent of the natural variability. Further, it is important to consider the season of TSM sampling: In the summer season in July and August the active layer depth is deepest, riverbank erosion along the delta channels is very pronounced, and streams draining ice complex deposits and thermokarst lakes transport more sediment providing local delta-derived sediment to the river surface water. During the ice break-up and associated spring flood in late May to early June the soils in the delta and northern catchment are still frozen. Riverbanks and bluffs are eroded by ice jamming against the riverbank and by thermal abrasion by relatively warmer Lena River water. The eroded material mixes with sediment transported from the south and is exported with the flood to the Laptev Sea coastal zone.

Our TSM concentrations from July/Aug 2009 and 2010 (mean values are 28.5 and 19.85 mg/L, respectively) showed a high spatial and inter-annual variability (Fig. 3A-C). Surface water TSM from the Lena Delta has been sampled during several expeditions in the past, mainly during the summer season, and by the Federal Service of Hydrometeorology and Environmental Monitoring of Russia (Roshydromet) at several stations throughout the delta (see Fedorova et al., 2013). All concentrations measured in this study were well within the range of published values of samples taken in July to early September between 1989 and 2003 (16.5 to >30 mg/L) (Cauwet and Sidorov, 1996; Rachold and Hubberten, 1999). Our single measurement from the spring flood in late May 2011 taken offshore Samoylov Island (72.37°N, 126.47°E) was more than 10 times higher (494 mg/L) than the summer values. It

clearly reflects the distinct seasonality of the hydrograph of the Lena River, where more than 50% of the annual TSM export happen during the spring freshet (Cauwet and Sidorov, 1996; Rachold et al., 2004). The only additional spring flood values from the Lena River we are aware of are provided by the Arctic Great Rivers Observatory Project (A-GRO, www. www.arcticgreatrivers.org) and are taken at Zhigansk gauging station (66.77°N, 123.37°E) approximately 900 km south of the Lena Delta. The TSM concentrations reported by Arctic GRO for late May/early June 2004 to 2010 are lower than our measurement varying from 28.8 to 221 mg/L. The higher Lena Delta value from 2011 could be a result of the flood wave eroding and entraining more sedimentary material on its way to the north. Despite the low sample resolution for the time of the spring flood, our single delta sample and the few samples from Zhigansk (A-GRO) highlight the strong seasonal differences in river supply suspended sediments and the need for more sampling campaigns during the spring freshet to improve flux estimates of terrestrial OM to Laptev Sea.

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Gelöscht: Because of the high spatial variability, particularly in the delta, and high interannual sediment discharge variability it is not possible to draw a meaningful conclusion based on this one spring flood measurement from the delta.

We chose to only discuss the carbon-normalized (Λ8) yields instead of sediment-normalized (Σ8) results of our TSM samples, because during sample preparation some glass fiber filter material was included in the analyzed sample, thus biasing the sediment-normalized calculation (described above in Sect. 2.3). Like the TSM concentrations discussed above, the Λ8 concentrations reflect the strong seasonality of the Lena River hydrograph. Λ8 concentrations were similar in the summers 2009 and 2010 (mean Λ8 1.03 and 1.09 mg/100mg OC, respectively; Table 5) and about five times higher in spring 2011 (Λ8 of 5.16 mg/100 mg OC). The normalization to the total organic carbon measured in our TSM samples, which is a mixture of terrestrial- and plankton-derived organic matter, most likely alters the ratio of Λ8 to organic carbon in the sample. The presence of aquatic plankton-derived OM dilutes carbon-normalized lignin concentrations lowering Λ8 values relative to those from terrestrial source material. The particulate organic carbon to nitrogen ratios (POC:PN) from 2009 to 2011 (Table 2, from Winterfeld et al., 2015 companion paper) suggest a considerable amount of nitrogen-rich plankton-derived OM is present in our TSM samples. This is further supported by lower $\delta^{13}C$ values determined for the bulk POM taken in summer 2009 and 2010 (mean $\delta^{13}C$ of –30.6‰ and –29.2‰, respectively; Winterfeld et al., companion paper), which suggests a considerable fraction of freshwater plankton utilizing dissolved inorganic carbon depleted in $\delta^{13}C$ is present in the surface water as has been shown for the Lena and Yenisey Rivers (e.g. Alling et al., 2012; Galimov et al., 2006; Rachold and Hubberten, 1999). Furthermore, Winterfeld et al. (2015, companion paper) estimated fractions of phytoplankton OM contributing to the bulk POM of the same water samples analyzed here

for lignin phenol composition using two simple binary mixing models between phytoplankton- and soil-derived POM based on the POC:PN ratios and based on the $\delta^{13}C$ values. For the lignin phenol samples presented here the phytoplankton fractions ranged form 47% to 77% and 23% to 53% based on POC:PN ratios and $\delta^{13}C$ values, respectively (Winterfeld et al, companion paper). However, low POC:PN ratios in combination with elevated Λ8 values were also found in a river-dominated estuary in the US (Goñi et al., 2003). Here, the authors suggested that contributions of bacterial nitrogen-rich exudation products generated during vascular plant decomposition (Rice and Hanson, 1984), could be responsible for the lower POC:PN ratios (Goñi et al., 2003). Yet, OC:TN ratios from Lena Delta soils presented in this study are >20 (Table 3) and from soils along a North-South transect in the Lena watershed (73.5° – 69.5°N) are >13.5 (Zubrzycki et al., 2012), which points to less degraded soil OM and together with the low POM $\delta^{13}C$ values (Winterfeld et al., 2015, companion paper) supports the idea of higher phytoplankton OM contributions to our TSM samples instead of highly degraded mineral soil.

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Gelöscht: mayfromthey thus diluting Λ8 values relative to those from terrestrial source material.

4.1.2 Tracers of vegetation sources from the Lena River catchment

The C/V and S/V ratios allow to distinguish different vegetation sources, such as woody and non-woody tissues as well as gymnosperm and angiosperm tissues, respectively, (e.g. Hedges and Mann, 1979; Hedges et al., 1982; Kuzyk et al., 2008). As shown in Fig. 4B, the TSM values of 2009-2011 reflect a mixture of woody gymnosperm and non-woody angiosperm vegetation sources. However, cinnamyl phenols are known to degrade relatively fast during early diagenesis resulting in decreased C/V ratios, while S/V ratios seem to be only moderately altered (Benner et al., 1990; Opsahl and Benner, 1995). That implies our low C/V ratios do not unambiguously reflect high woody gymnosperm contribution. As a result, any estimate of woody gymnosperm contribution based on C/V ratios alone must be considered a maximum value. But this process seems to be less important here, because our data do not deviate from a linear trend in the C/V vs. S/V diagram. Furthermore, note that the sample preparation of filters was done by scraping off supernatant material (section 2.3) resulting in some kind of sediment fractionation, which could affect the lignin phenol compositions. Yet, our TSM samples lie within the range of soils and sediments presented here and we suggest this effect to be negligible for the OM source and degradation interpretation below.

Our C/V and S/V values are slightly higher than values measured for particulate and dissolved lignin sampled in the Lena Delta in 1994 (Lobbes et al., 2000) and dissolved lignin sampled from the Lena River at Zhigansk (Amon et al., 2012). This could either be because the

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contribution of non-woody angiosperm sources, most likely tundra vegetation to Lena Delta TSM increased since 1994 due to active layer deepening and increased riverbank abrasion. Alternatively, a detectable difference in contribution of non-woody angiosperm OM to delta samples compared to the southern sample location at Zhigansk is simply due to the fact that the latter location lies in the taiga-tundra transition zone, where higher woody gymnosperm contributions would be expected. Thirdly, a large fraction of the particulate river load might be trapped in floodplains and/or the lower reaches of the Lena River. Particularly material from the distal parts of the watershed carrying the predominantly woody gymnosperm signal would not be transported efficiently to the delta. This inefficient transport mechanism of riverine particulate load is characteristic for large river system and has for instance been reported for the Amazon River and the Fly River, Papua New Guinea (e.g. Alin et al., 2008; Aufdenkampe et al., 2007; 2011; Blair and Aller, 2012; Goñi et al., 2014; Moreira-Turcq et al., 2013; Zocatelli et al., 2013). The slightly lower C/V and S/V values from Lobbes et al. (2000) and Amon et al. (2012) could also be well within the range of the natural variability of Lena River TSM composition, which was not covered by samples from 2009 and 2010 in this study. However, it should be noted that dissolved and particulate lignin might be derived from different terrigenous sources, i.e. from a modern OM pool and a pre-aged OM pool, respectively. In general, dissolved organic matter in Arctic rivers is of modern age while POM is much older (10^2-10^3 years; e.g. Guo and Macdonald 2006; Guo et al., 2007; Raymond et al., 2007), which could result in differences of the lignin phenol composition and hence be an additional explanation for the differences of C/V and S/V values between our particulate lignin values and the dissolved lignin of Amon et al. (2012). Nonetheless, our C/V and S/V ratios clearly depict the catchment vegetation characteristics of the Lena River being a mixture of taiga forest in the south and tundra in the north. They therefore distinguish the Lena River catchment from other arctic river catchments like the Ob' River (Dickens et al., 2011) or Mackenzie River (Goñi et al., 2000).

Although *p*-hydroxybenzenes (P) have multiple sources, the CuO oxidation of fresh Sphagnum and other mosses, which do not produce the typical lignin phenols, release considerable amounts of *p*-hydroxybenzenes and the P/V and *p*-hydroxyacetophenone to P ratios (Pn/P) have been used as tracer for Sphagnum-derived OC in peats (Dickens et al., 2011; Tsutsuki and Kondo, 1995; Williams et al., 1998). The higher P/V ratios of summer TSM from 2009 and 2010 (mean ratios 0.9 and 0.8, respectively) compared to spring 2011 (0.4; Fig. 5, Table 5) might indicate a higher contribution of mosses to Lena Delta TSM in the summer season, presumably derived from local tundra vegetation. Alternatively, the rather

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high fraction of phytoplankton-derived OM contributing to our summer samples (see Winterfeld et al., 2015 companion paper) could also result in higher P/V ratios as phytoplankton has been shown to contain elevated amounts of P (e.g. Goñi and Hedges, 1995). Overall, the summer and spring P/V ratios in TSM were lower than the mean bulk P/V ratio of the first and third terrace (1.1 and 1.0, respectively), the moss sample (*Aulacomnium turgidum*) analyzed here (P/V ratio of 2.3) and other values from the literature for Sphagnum moss and peat (see Fig. 5). The relatively lower P/V ratios in TSM samples thus indicate that moss contribution is minor compared to a dominant non-woody angiosperm source, particularly when considering possible P contributions from phytoplankton to TSM.

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4.1.3 State of diagenetic alteration of suspended particulate lignin biomarkers

Lignin phenol composition has been widely used to identify sources of terrigenous OM in aquatic and soil systems and characterize the degree of aerobic degradation (e.g. Benner et al., 1990; Goñi and Hedges, 1992; Hedges and Mann, 1979; Hernes and Benner, 2002; Tesi et al., 2007). The acid to aldehyde ratios of vanillyl and syringyl ($Ad/Al_{V,S}$) usually increase with increasing OM oxidation. In general, values <0.4 for both ratios are considered fresh and samples with values >0.4 have undergone some degree of degradation (Goñi et al., 1993; Hedges et al., 1988).

The TSM $Ad/Al_{V,S}$ ratios vary annually and with the hydrograph. The spring flood value from 2011 appears to be derived mainly from fresh plant litter and/or surface soils (Fig. 4A) in agreement with the dissolved organic matter (DOM) exported during the flood, which was also found to be younger than summer DOM (Amon et al., 2012). In contrast, the $Ad/Al_{V,S}$ ratios of our TSM collected in summer, indicate a more degraded OM source presumably from deeper soil horizons that thawed during the summer months. The deeper soil OM could partly originate from the first and third delta terraces. However, most of the $Ad/Al_{V,S}$ ratios we determined for the TSM were higher than the bulk soil $Ad/Al_{V,S}$ ratios of the first and third terraces. Such finding points to either an additional more degraded source, most likely from south of the Lena Delta, or a more degraded fraction of soil present in suspended matter, most likely the fine fraction. The fine grain-size fraction of soils and riverine suspended matter are generally associated with higher $Ad/Al_{V,S}$ ratios (Carrington et al., 2012; Guggenberger et al., 1994; Hedges et al., 1986) and the fine fraction is also most likely to be held in suspension during lower summer flows compared to coarser grain sizes. Similarly degraded terrigenous OM was found in the surface waters of the Mackenzie River Delta also draining a permafrost affected watershed (Goñi et al., 2000).

Additionally, sorption of dissolved lignin to mineral surfaces could have an effect on the $Ad/Al_{V,S}$ ratios. Dissolved lignin in the Lena River has high $Ad/Al_{V,S}$ ratios of ~0.9 to 1.6 during the peak flow and ~0.6 to 1.3 during mid and base flow (Amon et al., 2012). Higher $Ad/Al_{V,S}$ ratios of dissolved lignin are not necessarily associated with highly degraded lignin, but are also observed when dissolved lignin is derived from leaching of litter or soil (Hernes et al., 2007). The Lena Delta summer TSM ratios from 2009 and 2010 were higher than any other values reported for particulate lignin in the Lena Delta or other arctic rivers (Dickens et al., 2011; Goñi et al., 2000; Lobbes et al., 2000), and to a large fraction also higher than values in dissolved lignin. Thus, they cannot be explained by sorption of dissolved lignin, but potentially reflect input from a highly degraded source, e.g., from greater soils depths of the southern catchment.

4.2 Spatial patterns in Buor Khaya Bay surface sediments

4.2.1 Lignin biomarker abundances

In contrast to the surface water TSM snapshots, the surface sediments from the Buor Khaya Bay integrate the sedimentary OM and associated lignin phenol signal over a certain period of time depending on the local accumulation rates and the sediment re-working by waves and land-fast ice affecting the shallow coastal zone. The surface sediments therefore reflect an average of the OM transported to the coastal zone and smooth the seasonal and interannual differences in OM properties as well as the differences between OM sources. Buor Khaya Bay sedimentary OM is mainly derived from three sources, i.e. terrigenous OM transported by the Lena River, terrigenous OM derived from coastal erosion of the Buor Khaya coast predominantly consisting of Pleistocene ice complex deposits, and aquatic (riverine and marine) primary production. The latter source is negligible when discussing lignin phenols.

The sediment-normalized (Σ8) and carbon-normalized (Λ8) lignin phenol concentrations of Buor Khaya Bay surface sediments are high in front of the two main delta outlets, the Sardakh-Trofimovskaya channel and the Bykovskaya channel (Fig. 3G, Table 4 and 5), and decrease offshore. That points to the Lena River as the dominant source of lignin phenols with decreasing influence offshore, presumably as a result of hydrodynamic sorting where a less lignin phenol-rich finer sediment fraction is transported further offshore. Highest Σ8 contributions from coastal erosion are evident at the site off Muostakh Island (L09-34), while the carbon-normalized yield (Λ8) at this location was slightly smaller than at the river outlets (samples L10-23 and L10-36).

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High lignin phenol concentrations are generally associated with the coarse particulate OM fraction in soils and suspended material and they decrease with decreasing grain size (Carrington et al., 2012; Guggenberger et al., 1994; Hedges et al., 1986). An offshore gradient of decreasing grain size off the delta coast and towards greater water depths has been reported for the Buor Khaya Bay (Charkin et al., 2011). The spring flood could play a major role in transporting coarser lignin bearing OM to the coastal zone, which is in agreement with the high spring flood Σ8 and Λ8 concentrations from 2011. In contrast, slower current velocities during summer would transport fine particulate material to the delta edge or further offshore, carrying a lower Λ8 signature. Alternatively, the increased sedimentation of particulate and dissolved material through flocculation in the mixing zone of fresh and salt water in the prodelta area (marginal filter; cf. Lisitsyn, 1995) could be an additional reason for increased lignin phenol concentrations at these sample locations. Unfortunately, there is not much known about transport of sediment along the delta channels to the coastal zone.

4.2.2 Vegetation sources contributing to sedimentary organic matter

We observed a generally high contribution of terrestrial organic matter to the Buor Khaya Bay sediments based on the OC:TN ratios (Table 3). An offshore trend of decreasing OC:TN ratios likely reflects the increasing marine contributions by plankton as well as decreasing amounts of terrigenous material reaching offshore locations, which supports similar findings on OM sources in Buor Khaya Bay surface sediments (e.g. Karlsson et al., 2011; Tesi et al. 2014).

The contribution of woody and non-woody gymnosperm and angiosperm tissues based on C/V and S/V ratios as well as the contribution from mosses based on the P/V ratios was rather similar for all surface sediment samples. The C/V and S/V ratios were notably lower than in the delta soil samples in this study (Fig. 3L-S and 4B) and the surface soil and ice complex samples taken in the Lena watershed and along the Buor Khaya coast by Tesi et al. (2014). This suggests a considerable contribution of woody gymnosperm tissues from the southern Lena catchment to Buor Khaya Bay sediments. Additional angiosperm-derived OM contributed by coastal erosion of Pleistocene ice complex deposits (Tesi et al., 2014) seems to dilute the gymnosperm signal from the Lena River with distance to the delta (slight increase in C/V and S/V ratios offshore, Table 5). The angiosperm-derived OM originating from the Lena catchment and from coastal erosion of ice complex, respectively, contribute to the Buor Khaya Bay sediments and these two sources cannot unambiguously be distinguished based on the their C/V and S/V ratios. Here, the use of bulk as well as lignin-specific ^{14}C

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concentrations might be helpful as the Pleistocene ice complex deposits are more depleted in ^{14}C than the soil-derived OM from the Lena catchment (e.g. Karlsson et al., 2011; Vonk et al., 2012; Winterfeld et al., 2015 companion paper).

Further, sedimentary P/V ratios (0.4 to 0.5) suggest the fraction of moss-derived OM in the sediments is smaller than in the summer TSM samples (0.62 to 1.25) and bulk soils from the first and third delta terrace (Fig. 5, Table 5). Instead, the sedimentary P/V ratios were similar to the spring TSM sample from 2011 (value of 0.4) pointing to a considerable contribution of spring flood TSM to Buor Khaya Bay sediments. However, we cannot exclude that lower P/V ratios could be partially the result of selective degradation of more labile P phenols compared to V phenols resulting in lower P/V ratios than carried by the original OM source (Hedges and Weliky, 1989; Williams et al., 1998). And as discussed above for the TSM samples we also cannot exclude possible contributions from phytoplankton containing elevated P concentrations to sedimentary OM. The slight increase in P/V ratios further offshore (samples L10-23 to L10-25, Table 5) might point to higher phytoplankton OM contributions with larger distance to the coast. The estimated relative contributions of the different vegetation zones in the Lena catchment will be discussed in section 4.3.1.

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4.2.3 Degradation of terrigenous organic matter

The relatively high $Ad/Al_{V,S}$ ratios (0.77 to 1.75, Table 5, Fig. 3K) imply a rather strong degradation of lignin phenols in the surface sediments. There is a small gradient towards less degraded material along the offshore transect (Fig. 3K) of progressively finer sediments (Charkin et al., 2011). This in contrast to analysis of soils and Amazon River suspended material, where $Ad/Al_{V,S}$ ratios increased with decreasing particle size (Amelung et al., 1999; Carrington et al., 2012; Hedges et al., 1986). As summer TSM in our samples is predominantly strongly degraded (see section 4.1), and as discussed above inferred to be more fine grained than the less degraded spring flood material, this observation argues against a dominant control of hydrodynamic sorting on the lignin monomer distribution. An additional OM source with a less degraded $Ad/Al_{V,S}$ signature contributing to Buor Khaya Bay sediments, e.g. Lena River spring flood TSM or material derived from erosion of ice complex deposits along the Buor Khaya coast, could explain the offset. Efficient sediment redistributing processes such as bottom erosion and nepheloid layer bottom transport of sediments in the Buor Khaya Bay have been identified by Charkin et al. (2011).

It is difficult to assess where the lignin degradation occurred. Oxidative degradation of the lignin macromolecule in soils by fungi is known to increase $Ad/Al_{V,S}$ ratios severely (e.g.

Goñi et al., 1993). Subaqueous decay of lignin has also been shown to increase the Ad/Al ratios (e.g. Opsahl and Benner, 1995). We favor the explanation of aerobic degradation on land, because $Ad/Al_{V,S}$ ratios of the sediment samples are in the upper range of values found in the bulk first terrace soils and well within the range of summer TSM samples from the delta, suggesting that river-transported material is the dominant source of OM deposited in surface sediments. The one spring flood sample from 2011 appears to be relatively fresh. If the majority of particle discharge to the Laptev Sea occurs during spring, we would expect that similarly low $Ad/Al_{V,S}$ ratios would be observed in the sediments. The fact that we do not observe such a signal might be either due to insufficient information about the heterogeneity of material transported during the spring flood, or due to efficient degradation of lignin during transport and/or early diagenesis. Karlsson et al. (2011) studied bulk parameters and lipid biomarker contents of surface sediments in the Buor Khaya Bay. Using a three EM and dual isotope ($\delta^{13}C$ and $\Delta^{14}C$) Monte Carlo simulation, these authors suggested that about 60% of the sedimentary OM is derived from ice complex deposits and roughly 20% each from surface soils and primary production. Further, using lipid biomarker indicators for OM degradation and ^{14}C dating, they found marked differences between river-derived POC that was younger and more degraded and sedimentary OM that was older but less degraded. These lipid-based findings are in contrast to our lignin data, which suggest similar states of degradation for both, river-derived OM and surface sediments.

Notably, the highest Ad/Al_V ratio of 1.75 was measured offshore Muostakh Island (Fig. 3K, Table 5), which consists of Pleistocene ice complex deposits. In contrast, the Ad/Al_V ratios of ice complex deposits on Muostakh Island were much lower varying between 0.16 and 0.95 (see Tesi et al., 2014). Additionally, other ice complex deposits from the Buor Khaya Cape and along the Lena channel (Tesi et al., 2014) as well as from Kurungnakh (this study) showed similar low Ad/Al_V ratios supporting the idea of relatively fresh ice complex OM (e.g. Karlsson et al., 2011; Vonk et al., 2012). Therefore, the lignin fraction of the OM must have been strongly degraded between erosion and deposition in surface sediments. This could have happened after thawing on land and/or post-depositional under subaqueous conditions. Vonk et al. (2012) suggested that substantial degradation of Muostakh Island ice complex material occurs rapidly and immediately after thawing. Sanchez-García et al. (2011) determined rapid particulate OM degradation rates to occur subaqueously in shallow Laptev Sea waters.

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Gelöscht: Assuming that the ice complex of Muostakh Island is similar to the ice complex deposits on Kurungnakh Island analyzed in this study (mean Ad/Al_V ratios of 0.4 to 0.5),

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Gelöscht: On the other hand, it is well known that ice-complex deposits are extremely heterogeneous (e.g. Schirrmeister et al., 2011; Strauss et al., 2013). More data on lignin composition of ice complex deposits at various locations is necessary to further assess the fate of ice complex material.

4.3 Terrigenous organic matter sources of Lena Delta suspended matter and Buor Khaya Bay surface sediments

4.3.1 Unmixing of taiga and tundra vegetation contributions

As in a first approximation, gymnosperm vegetation is restricted exclusively to the taiga part of the Lena River catchment, we use the gymnosperm to angiosperm ratio as estimate for the relative contributions of taiga and tundra. Therefore, we combined the model solutions for woody and non-woody contributions of gymnosperms and angiosperms, respectively. According to the model presented here, the fractions of gymnosperm and angiosperm-derived OM varied strongly in the summer TSM samples. However, the mean gymnosperm contributions for spring 2011 and the summers 2009 and 2010 were very similar (Table 7), i.e. 0.4 (n=1), 0.5 (n=7), and 0.6 (n=8), respectively. The Buor Khaya Bay surface sediment total gymnosperm fraction was in the range of the TSM values (mean fraction = 0.5, n=5). In summary the model suggests roughly equal contributions of total gymnosperm and total angiosperm-derived OM in suspended particulate OM and sediments based on the lignin monomer distribution. This implies that a large fraction of the gymnosperm POM derived from the taiga gets trapped in floodplains along the course of the Lena River and hence the contribution of angiosperm vegetation, mainly present in the tundra, to surface water TSM is relatively big. The Buor Khaya Bay surface sediments receive additional angiosperm-derived OM through coastal erosion of ice complex deposits (Tesi et al., 2014), which adds to the angiosperm-derived OM from the Lena catchment and dilutes the gymnosperm signal with distance to the delta. Moreover, we cannot distinguish and therefore exclude small angiosperm contributions from the taiga zone itself being a heterogeneous landscape with some amount of angiosperm vegetation and contributions from higher elevated areas, where bushes and grasslands are favored over trees. Thus, taiga-derived material might indeed account for more than 50% of the total lignin in our samples, which in turn implies that based on our model the maximum contribution by the tundra zone (angiosperm OM) is 50%. Also the C/V and S/V values we chose for the non-woody angiosperm source ("a" in Fig. 4B, see Hedges and Parker, 1976; Hedges and Mann, 1979) add some uncertainty to the model results that has to be considered when interpreting the data. As shown in Fig. 4B the end-member values lie well within most of the soil samples, but there are also several soil and vegetation samples with higher and lower C/V and S/V ratios. Using more representative end-member values including the natural variability of the different permafrost soil sources could reduce

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the model uncertainty here. Unfortunately, this kind of data is not available for Lena watershed, yet.

The comparison of C/V and S/V ratios between dissolved and particulate lignin can be complicated by fractionation processes occurring during leaching of lignin phenols from plant tissues and soils as well as sorption of dissolved lignin to minerals in soils or sediments (Hernes et al., 2007). However, Lobbes et al. (2000) and Amon et al. (2012) have shown that C/V and S/V ratios of dissolved lignin in arctic rivers, including the Lena River, reflect the vegetation signal of the individual catchments and are not significantly altered by degradation or fractionation. Therefore, we feel confident to compare our Lena Delta data with C/V and S/V ratios generated by Amon et al. (2012).

We compared the gymnosperm fractions in our samples with the results from Amon et al. (2012), who estimated a total gymnosperm contribution of 70 % to Lena River dissolved lignin. Despite a broad range of ratios in our summer TSM and surface sediments, we infer a substantially lower gymnosperm contribution to particulate OM in the delta surface water and Buor Khaya Bay surface sediments than further upstream at Zhigansk. This finding clearly indicates the overprint of TSM signatures by higher contributions of angiosperm OM contributing to the total TSM load between Zhigansk, located at the taiga-tundra transition zone, and our sampling sites in the delta. As mentioned above this might be due to the inefficient transport of POM from distal catchment areas to the delta and its intermediate storage on floodplains (e.g. Aufdenkampe et al., 2007; 2011; Moreira-Turcq et al., 2013; Zocatelli et al., 2013). In contrast, dissolved organic matter including dissolved lignin is transported with the flow of the water, which might lead to a more efficient transport of taiga-derived DOM to the delta, thus explaining the difference of modeled gymnosperm contributions by Amon et al. (2012) and our study. The resulting considerable impact of the northern part of the catchment area to the POM composition is disproportional to its small spatial extent within the Lena River drainage area. It further implies environmental changes associated with above average climate warming expected for the high northern latitudes will most likely increase the disproportional OM input by enhanced permafrost thawing in the north compared to the southern catchment.

5 Conclusions

Despite the annual, seasonal, and spatial variability, the distribution of lignin phenols in our Lena delta surface water TSM samples clearly reflects the main vegetation characteristics of

the Lena River catchment. The gymnosperm fraction derived from the taiga covering most of the catchment and the angiosperm fraction derived predominantly from the northern tundra zone contribute about equally to the spring and summer TSM samples. However, because of possible contributions of angiosperm OM from the taiga zone, for example from elevated treeless areas, the 50% angiosperm vegetation have to be interpreted as the maximum contribution from tundra zone. Considering the relatively small area covered by tundra (~12%; e.g. Amon et al., 2012) this still relatively high angiosperm contribution emphasizes the importance of this small area as organic matter source to the Lena Delta surface water TSM and Laptev Sea coastal zone, where it adds to the angiosperm OM contributed by coastal erosion.

Based on the low acid to aldehyde ratios of vanillyl and syringyl phenols ($Ad/Al_{V,S}$), the spring flood sample seems to have organic matter that has undergone a relatively low extent of degradation and most likely originates from surface soils and fresh vegetation. This could be due to the fact that particularly in the northern part of the catchment the soils are still frozen at the time of the spring freshet, which may favors surface erosion by the flood wave. On the other hand, less degraded OM with low $Ad/Al_{V,S}$ ratios is also found in ice complex deposits of Pleistocene age (e.g. Tesi et al., 2014) and does not necessarily have to be derived from surface soils. The summer TSM samples displayed compositions ($Ad/Al_{V,S}$) consistent with higher degrees of degradation, and presumably originated from greater soil depths thawed during the summer months. As the first and third delta terrace bulk soil samples analyzed here had generally lower $Ad/Al_{V,S}$ ratios than the summer TSM, we speculate that there must be an additional more degraded organic matter source. This source could be organic matter derived from the southern catchment, where annual permafrost thaw depths are greater than in the Lena Delta. Because these materials are transported to the delta during lower flow conditions, it is likely they are predominantly composed of finer particles, which usually contain more highly altered lignin and may have been affected by sorptive processes with DOM, all of which can contribute to the higher $Ad/Al_{V,S}$ ratios.

The marginal filter leading to flocculation of dissolved and particulate organic matter and rapid sedimentation seems to be the dominant reason for high lignin contents off the major delta outlets. Similar to the TSM samples, the lignin distribution within the surface sediments of the Buor Khaya Bay points to a mixed gymnosperm and angiosperm vegetation source for organic matter and the modeled contributions are as well about equal for both sources. The additional contribution of angiosperm-derived OM to Buor Khaya Bay sediments through coastal erosion makes it difficult to unambiguously distinguish between angiosperm-derived

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OM from the Lena watershed and from coastal erosion of ice complex deposits. However, as gymnosperm vegetation is not present in the Lena Delta and along the Buor Khaya coast today and their respective Holocene and Pleistocene deposits but covers the southern part of the Lena River catchment, the fact that we find gymnosperm-derived OM in surface sediments suggests that a substantial amount of sedimentary organic matter in the Buor Khaya Bay originates from Lena River catchment. The additional source of angiosperm OM contributed by coastal erosion results in dilution of the gymnosperm signal with distance to the delta.

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The surface sediments were strongly degraded resembling the Lena Delta summer samples and implying at least some summer TSM is transported from the delta to the coastal zone. However, the strong degradation of sedimentary organic matter close to Muostakh Island consisting of Pleistocene ice complex and being affected by coastal erosion, which most likely happened after thawing on land, makes it complicated to distinguish between degraded ice complex and degraded summer TSM derived organic matter.

In the future more severe warming is expected for the high northern latitudes (IPCC, 2013), which will presumably influence the northernmost part of the Lena River catchment, i.e. the tundra zone with the delta, stronger than the southern part. On the basis of our data it should be possible to trace changes in OM contribution and quality from different parts of the Lena River catchment area. Additionally, more research is needed to investigate the fate of Lena River and ice complex organic matter, particularly their degradability on land, in the water column, and post-depositionally to understand their potential for possible increase in greenhouse gas release from the Arctic.

Additional data on individual CuO oxidation products for the samples presented here can be found in PANGAEA (www.pangaea.de).

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Table 1. Samples presented in this study and analyzed for lignin phenol composition. Bluff height is given in meters above river level [m a.r.l.] measured in Aug 2009 and Jul/Aug 2010. All total suspended matter samples 2009-2011 were taken from the surface water layer with a sampling depth of ca. 0.5m. Additional surface water samples used for total suspended matter determination can be found in table S1 in the supplement. Not applicable denoted by n.a.

Sample code	Sample & site description	Date of sampling	Latitude N [dec]	Longitude E [dec]	Bluff height [m a.r.l.]	Water depth [m]
Lena Delta first terrace bluff profiles						
L09-08	Gorgolevsky Island, 3 depths sampled	17-Aug-2009	72.6158	127.2627	3.4	n.a.
L09-12	Samoylov Island, 5 depths sampled	18-Aug-2009	72.3775	126.4954	7.5	n.a.
L09-28-2	Bykovskaya Channel, 2 depths sampled	21-Aug-2009	72.0586	128.6309	1.7	n.a.
L10-04	Baron Belkey Island, 6 depths sampled	31-Jul-2010	72.5378	126.8608	6.5	n.a.
Kurungnakh Island third terrace[a]						
S29	unit V, middle Holocene	Aug-2002	72.3447	126.3092	37.0	n.a.
S17	unit IVb, early Holocene	Aug-2002	72.3447	126.3092	37.0	n.a.
S13	unit IVa, Pleistocene ice complex	Aug-2002	72.3447	126.3092	37.0	n.a.
S22D	unit III, Pleistocene ice complex	Aug-2002	72.3447	126.3092	37.0	n.a.
S45	unit III, Pleistocene ice complex	Aug-2002	72.3431	126.3056	37.0	n.a.
Lena River total suspended matter						
4	Lena River main channel south of Tit Ari Island	16-Aug-2009	71.9040	127.2544	n.a.	n.a.
10	Lena River main channel	19-Aug-2009	72.2760	126.9041	n.a.	n.a.
11	Lena River main channel	19-Aug-2009	72.5159	126.7142	n.a.	n.a.
13	Lena River Bykovskaya Channel	20-Aug-2009	72.2352	127.9619	n.a.	n.a.
14	Lena River Bykovskaya Channel	20-Aug-2009	72.0341	128.5232	n.a.	n.a.
16	Lena River Bykovskaya Channel	21-Aug-2009	72.0586	128.6309	n.a.	n.a.
17	offshore Bykovsky Peninsula	22-Aug-2009	71.7889	129.4189	n.a.	n.a.
25	Lena River Trofimoskaya Channel	31-Jul-2010	72.4764	126.6250	n.a.	n.a.
26	Lena River Trofimoskaya Channel	31-Jul-2010	72.4764	126.8588	n.a.	n.a.
27	Lena River main channel south of Samoylov	1-Aug-2010	72.3776	126.7478	n.a.	n.a.
28	Lena River main channel north of Tit Ari Island	1-Aug-2010	72.2102	126.9423	n.a.	n.a.
29	Lena River main channel south of Tit Ari Island	1-Aug-2010	71.9514	127.2582	n.a.	n.a.
30	Lena River main channel off Kurungnakh	2-Aug-2010	72.2808	126.2091	n.a.	n.a.
31	Lena River main channel	2-Aug-2010	72.3567	126.3521	n.a.	n.a.
32	Lena River Bykovskaya Channel	3-Aug-2010	72.3604	127.6761	n.a.	n.a.
37	Lena River main channel off Samoylov Island	29-May-2011	72.3651	126.4757	n.a.	n.a.
Buor Khaya Bay surface sediments						
L09-34	surface sediment (grab sampler) off Muostakh Island	23-Aug-2009	71.5750	129.8200	n.a.	10.5
L10-23	surface sediment (steel tube)	4-Aug-2010	71.7778	130.0872	n.a.	11.5
L10-24	surface sediment (steel tube)	4-Aug-2010	71.9250	130.8227	n.a.	17.0
L10-25	surface sediment (steel tube)	4-Aug-2010	72.0725	131.5896	n.a.	17.0
L10-36	surface sediment (steel tube)	6-Aug-2010	72.7411	130.1324	n.a.	5.8

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Vegetation samples[b]						
09-TIK-04	*Aulacomnium turgidum*	Jul/Aug 2009	72.8087	124.9121	n.a.	n.a.
09-TIK-01	*Carex spp.*	Jul/Aug 2009	73.1731	124.5757	n.a.	n.a.
09-TIK-13	*Ledum palustre*	Jul/Aug 2009	69.3991	123.8261	n.a.	n.a.
09-TIK-13	*Betula nana*	Jul/Aug 2009	69.3991	123.8261	n.a.	n.a.
09-TIK-13	*Salix spp.*	Jul/Aug 2009	69.3991	123.8261	n.a.	n.a.
09-TIK-13	*Larix* (mostly needles)	Jul/Aug 2009	69.3991	123.8261	n.a.	n.a.

[a] samples provided by L. Schirrmeister (Alfred Wegener Institute Potsdam, Germany), data from Wetterich et al. (2008)

[b] samples provided by U. Herzschuh (Alfred Wegener Institute Potsdam, Germany), expedition field reports by Herzschuh et al. (2009) and Klemm and Zubrzycki (2009)

Table 2. Total suspended matter (TSM) concentrations in Lena Delta surface waters (2009 to 2011) and atomic particulate organic carbon (POC) to particulate total nitrogen (PN) ratios. Note that there is one sample less for the TSM [mg/L] calculation (n=20) of the TSM August 2009 data than for POC and POC:PN (both n=21), because one filter weight was missing while the volume filtered was known and thus POC:PN could be calculated.

	TSM [mg/L]	POC[a] [mg/L]	POC[a] [wt%]	atomic POC:PN[a]
TSM Aug 2009	*n=20*	*n=21*	*n=20*	*n=21*
mean	28.50	1.21	7.2	9.6
median	14.94	0.83	4.7	9.2
min	3.10	0.35	1.9	6.8
max	174.92	7.24	37.7	19.3
TSM July/Aug 2010	*n=15*	*n=13*	*n=13*	*n=13*
mean	19.85	0.57	3.05	7.6
median	19.88	0.47	3.05	7.8
min	3.52	0.15	1.42	3.7
max	32.23	1.30	4.74	10.3
TSM late May 2011				
sample 37	494.00	8.20	1.66	7.5

[a] from Winterfeld et al. (2015, submitted as companion paper)

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Table 3. Organic carbon (OC), total nitrogen (TN), and atomic OC:TN ratios of the Lena Delta soil samples (first and third terrace) and Buor Khaya Bay surface sediments

Sample code	OC [wt%]	TN [wt%]	atomic OC:TN
Lena Delta first terrace bulk, n=19			
mean	7.48	0.21	38.5
median	7.61	0.24	35.1
min	1.02	0.03	21.7
max	17.14	0.45	68.0
Lena Delta third terrace (Kurungnakh Island)[a]			
S29 (unit V)	3.76	0.19	19.4
S17 (unit IVb)	1.97	0.38	5.2
S13 (unit IVa)	1.69	0.19	9.1
S22D (unit III)	6.91	0.54	12.8
S45 (unit III)	3.72	0.31	12.1
Buor Khaya Bay surface sediments			
L09-34	2.47	0.18	15.7
L10-23	2.33	0.17	16.4
L10-24	1.88	0.15	14.7
L10-25	1.93	0.16	11.7
L10-36	1.67	0.09	20.9

[a] from Wetterich et al. (2008)

Table 4. Sediment-normalized yields of CuO oxidations products of Lena Delta soils, total suspended matter (TSM), surface sediments, and vegetation samples in milligram per gram dry weight sediment (mg/g dws). Trivial names of analyzed plant species in brackets. V = vanillyl phenols (sum of vanillin, acetovanillone, vanillic acid), S = syringyl phenols (sum of syringealdehyde, acetosyringone, syringic acid), C = cinnamyl phenols (sum of *p*-coumaric acid, ferulic acid), Σ8 = sum of V, S, and C phenols, P = *p*-hydroxybenzenes (sum of *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, *p*-hydroxybenzoic acid), Pn = *p*-hydroxyacetophenone.

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	V	S	C	Σ8	P	Pn
	[mg/g dws]					
Lena Delta first terrace bulk, n=19						
mean	0.75	0.74	0.43	1.93	0.84	0.13
median	0.73	0.66	0.31	1.60	0.69	0.10
min	0.04	0.04	0.02	0.09	0.05	0.00
max	2.41	2.82	1.87	7.10	3.68	0.42
Lena Delta third terrace (Kurungnakh Island)						
S29 (unit V)	0.24	0.17	0.21	0.63	0.13	0.04
S17 (unit IVb)	0.17	0.14	0.06	0.37	0.15	0.02
S13 (unit IVa)	0.13	0.11	0.06	0.29	0.12	0.02
S22D (unit III)	0.53	0.69	0.59	1.81	0.97	0.13
S45 (unit III)	0.54	0.73	0.54	1.81	0.62	0.09
TSM Aug 2009, n=7						
mean	0.16	0.07	0.04	0.27	0.14	0.05
median	0.17	0.07	0.03	0.27	0.15	0.05
min	0.10	0.04	0.02	0.17	0.07	0.04
max	0.22	0.17	0.08	0.47	0.21	0.07
TSM July/Aug 2010, n=8						
mean	0.21	0.08	0.04	0.32	0.16	0.04
median	0.20	0.08	0.03	0.31	0.15	0.05
min	0.08	0.03	0.01	0.12	0.07	0.02
max	0.34	0.14	0.06	0.53	0.30	0.06
TSM late May 2011, n=1						
	0.47	0.24	0.12	0.83	0.21	0.24
Buor Khaya Bay surface sediments						

L09-34	0.33	0.14	0.05	0.52	0.13	0.07
L10-23	0.41	0.18	0.06	0.64	0.15	0.08
L10-24	0.16	0.07	0.03	0.25	0.07	0.05
L10-25	0.11	0.05	0.02	0.18	0.05	0.05
L10-36	0.28	0.12	0.04	0.45	0.12	0.07
Vegetation samples						
Aulacomnium turgidum (moss)	1.57	1.63	1.44	4.64	3.64	1.74
Carex spp. (sedge)	4.13	6.24	6.71	17.08	3.58	0.70
Ledum palustre (wild rosemary)	2.76	2.59	3.62	8.97	3.51	0.82
Betula nana (dwarf birch)	5.78	7.43	3.19	16.40	1.27	0.34
Salix (willow)	6.22	4.21	2.17	12.59	2.19	0.75
Larix needles (larch)	7.93	1.41	7.32	16.66	5.48	1.46

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Table 5. Carbon-normalized yields of CuO oxidation products of Lena Delta soils, surface water total suspended matter (TSM), and surface sediments in milligram per 100 milligram organic carbon [mg/100mg OC] and related lignin parameters. Abbreviations for phenol groups are the same as in table 4. Ad/Al_V = acid to aldehyde ratio of vanillyl phenols, Ad/Al_S = acid to aldehyde ratios of syringyl phenols, C/V = cinnamyl to vanillyl phenols, S/V = syringyl to vanillyl phenols, P/V = *p*-hydroxybenzenes to vanillyl phenols, Pn/P = *p*-hydroxyacetophenone to *p*-hydroxybenzenes. Not determined denoted by n.d.

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Gelöscht: phenols

	V	S	C	Λ8	P	Pn	Ad/Al_V	Ad/Al_S	C/V	S/V	P/V	Pn/P
				[mg/100 mg OC]								
Lena Delta first terrace bulk, n=19												
mean	1.08	1.02	0.54	2.64	0.99	0.14	0.76	0.64	0.53	0.96	1.05	0.14
median	0.91	0.88	0.47	2.18	0.95	0.13	0.77	0.62	0.48	0.92	1.08	0.14
min	0.30	0.31	0.14	0.78	0.33	0.03	0.41	0.37	0.16	0.58	0.24	0.07
max	3.50	3.62	1.69	8.81	2.38	0.27	1.19	1.01	1.16	1.58	1.53	0.22
Lena Delta third terrace (Kurungnakh Island)												
S29 (unit V)	0.73	0.37	0.57	1.66	0.35	0.10	0.43	0.58	0.79	0.51	0.49	0.28
S17 (unit IVb)	1.05	0.55	0.28	1.89	0.75	0.11	0.46	0.51	0.27	0.53	0.71	0.15
S13 (unit IVa)	0.87	0.55	0.33	1.74	0.74	0.12	0.47	0.49	0.38	0.63	0.85	0.16
S22D (unit III)	0.80	0.96	0.86	2.62	1.40	0.18	0.48	0.38	1.07	1.20	1.75	0.13
S45 (unit III)	1.52	1.88	1.46	4.87	1.68	0.24	0.35	0.31	0.96	1.24	1.10	0.14
TSM Aug 2009, n=7												
mean	0.63	0.27	0.13	1.03	0.54	0.05	1.71	0.99	0.21	0.44	0.85	0.10
median	0.62	0.26	0.11	0.99	0.58	0.05	1.36	0.98	0.19	0.41	0.81	0.09
min	0.43	0.17	0.09	0.73	0.29	0.04	0.68	0.52	0.14	0.25	0.65	0.07
max	0.80	0.48	0.24	1.35	0.71	0.07	3.97	1.51	0.39	0.77	1.25	0.13
TSM July/Aug 2010, n=8												
mean	0.70	0.27	0.12	1.09	0.53	0.05	1.36	0.81	0.18	0.38	0.77	0.09
median	0.74	0.30	0.14	1.19	0.51	0.05	1.44	0.87	0.18	0.39	0.81	0.09
min	0.28	0.09	0.05	0.42	0.25	0.02	0.69	0.48	0.15	0.32	0.62	0.07
max	0.93	0.37	0.16	1.44	0.81	0.06	2.02	1.11	0.20	0.45	0.89	0.11
TSM late May 2011, n=1												
	2.94	1.47	0.74	5.16	1.29	0.24	0.32	0.32	0.25	0.50	0.44	0.19
Buor Khaya Bay surface sediments												
L09-34	1.34	0.55	0.21	2.09	0.52	0.07	1.75	1.37	0.15	0.41	0.39	0.13
L10-23	1.74	0.76	0.26	2.76	0.65	0.08	1.36	1.16	0.15	0.44	0.37	0.12
L10-24	0.84	0.36	0.14	1.33	0.37	0.05	1.19	1.06	0.16	0.43	0.44	0.14
L10-25	0.57	0.25	0.12	0.94	0.28	0.05	0.98	0.85	0.21	0.45	0.50	0.16
L10-36	1.68	0.74	0.27	2.68	0.72	0.07	1.10	0.77	0.16	0.44	0.43	0.10

Vegetation samples												
Aulacomnium turgidum (moss)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.67	0.80	0.92	1.04	2.32	0.48
Carex spp. (sedges)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.23	0.22	1.63	1.51	0.87	0.20
Ledum palustre (wild rosemary)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.41	0.49	1.31	0.94	1.27	0.23
Betula nana (dwarf birch)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.18	0.13	0.55	1.29	0.22	0.27
Salix (willow)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.20	0.24	0.35	0.68	0.35	0.34
Larix needles (larch)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14	0.87	0.92	0.18	0.69	0.27

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Table 6. Endmember ratios taken from the literature used for the unmixing model here and our calculated relative amounts of V, S, and C phenols. For abbreviations see description in table 4 and 5.

Endmember	C/V	S/V	V	S	C
				[%]	
woody gymnosperm	0.04*	0.03*	0.93	0.03	0.04
non-woody gymnosperm (needles)	0.17*	0.04*	0.83	0.03	0.14
woody angiosperm	0.05*	2.42*	0.29	0.70	0.01
non-woody angiosperm (leaves, grasses)	0.7*	0.98*	0.37	0.37	0.26

*endmember ratios from table 4 in Amon et al. (2011) including Hedges and Mann (1979), Hedges and Parker (1976), Prokushkin et al. (in preparation), Williams et al. (1998)

Table 7. Results of unmixing model including relative abundances of V, S, and C phenols, median mixing coefficients and gymnosperm to angiosperm ratio. See tables 4 and 5 for abbreviations.

				median (500 iterations) mixing coefficients						
sample code	rel. V [%]	rel. S [%]	rel. C [%]	woody gymnosperm	non-woody gymnosperm	woody angiosperm	non-woody angiosperm	median total gymno-sperm	median total angio-sperm	proportion of median gymnosperm/ angiosperm
TSM Aug 2009										
4	0.67	0.23	0.10	0.34	0.27	0.21	0.17	0.61	0.38	1.6
10	0.65	0.24	0.10	0.31	0.27	0.23	0.18	0.58	0.41	1.4
11	0.72	0.18	0.10	0.37	0.31	0.15	0.14	0.69	0.29	2.4
13	0.59	0.28	0.13	0.22	0.26	0.21	0.31	0.47	0.53	0.9
14	0.60	0.27	0.13	0.22	0.26	0.20	0.32	0.48	0.51	0.9
16	0.63	0.25	0.12	0.26	0.28	0.21	0.26	0.53	0.46	1.2
17	0.46	0.36	0.18	0.02	0.22	0.21	0.57	0.24	0.78	0.3
TSM July/Aug 2010										
25	0.64	0.25	0.12	0.27	0.28	0.20	0.25	0.55	0.44	1.2
26	0.64	0.25	0.11	0.29	0.27	0.22	0.20	0.56	0.43	1.3
27	0.62	0.26	0.12	0.24	0.27	0.20	0.28	0.52	0.48	1.1
28	0.65	0.24	0.11	0.30	0.27	0.20	0.22	0.57	0.42	1.4
29	0.68	0.22	0.10	0.33	0.30	0.20	0.16	0.63	0.36	1.8
30	0.64	0.26	0.10	0.30	0.26	0.24	0.19	0.56	0.43	1.3
31	0.60	0.27	0.12	0.24	0.25	0.22	0.29	0.49	0.51	1.0
32	0.66	0.22	0.12	0.28	0.30	0.16	0.25	0.58	0.41	1.4
TSM late May 2011										
37	0.57	0.29	0.14	0.17	0.25	0.19	0.37	0.43	0.57	0.8
Buor Khaya Bay surface sediments										
L09-34	0.64	0.26	0.10	0.31	0.25	0.25	0.18	0.56	0.44	1.3
L10-23	0.63	0.28	0.09	0.30	0.25	0.28	0.17	0.55	0.45	1.2
L10-24	0.63	0.27	0.10	0.28	0.26	0.26	0.20	0.54	0.46	1.2
L10-25	0.61	0.27	0.13	0.23	0.26	0.21	0.29	0.49	0.50	1.0
L10-36	0.63	0.27	0.10	0.29	0.25	0.27	0.19	0.54	0.46	1.2

Figure captions

Figure 1. A) Lena River catchment area with approximate tundra and taiga forest distribution, B) Lena Delta and Buor Khaya Bay sampling sites from 2009 to 2011 and associated sample codes.

Figure 2. Carbon-normalized yields of phenols groups shown as Whisker plots when the number of samples was large enough and as individual samples for smaller numbers.

Figure 3. Spatial distribution of carbon-normalized lignin concentrations (Λ8) and lignin parameters of Lena Delta total suspended matter (TSM) and Buor Khaya Bay surface sediments. $Ad/Al_{vanillyl}$ = acid to aldehyde ratio of the vanillyl phenols, C/V = ratio of cinnamyl to vanillyl phenols, and S/V = ratio of syringyl to vanillyl phenols.

Figure 4. A) Lignin degradation indices (Ad/Al_V vs. Ad/Al_S) and B) vegetation source parameters (C/V vs. S/V) including compositional ranges of major vascular plant types (Goñi et al., 1998; Goñi and Hedges, 1992; Hedges and Mann, 1979; Hu et al., 1999). For abbreviations see Fig. 3. Note the different scales. Literature values: [a] end-member values used in this study taken from table 4 in Amon et al. (2012) and references therein, [b]Lobbes et al. (2000), [c]Amon et al. (2012). Note in A) the two values on the Ad/Al_V axis where Ad/Al_S is zero, because there were no values given in Lobbes et al. (2000).

Figure 5. The ratios of *p*-hydroxyacetophenone to *p*-hydroxybenzenes (Pn/P) versus *p*-hydroxybenzenes to vanillyl phenols (P/V) of samples analyzed in this study and values from the literature used as indicator for moss contributions. [a]Amon et al. (2012), [b]table 4 in Amon et al. (2012) and references therein, [c]Williams et al. (1998).

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Supplementary information for:

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

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Table S1. Additional total suspended matter (TSM) samples, which were included into the mean TSM calculation, but not analyzed for CuO oxidation products. The TSM samples were taken from the surface water layer with a sampling depth of ca. 0.5m.

Sample code	Sample & site description	Date of sampling	Latitude N [dec]	Longitude E [dec]
Lena River total suspended matter				
1	Olenyokskaya Channel	14-Aug-2009	72.4771	125.2856
2	Olenyokskaya Channel	14-Aug-2009	72.3598	125.6728
3	Lena River main channel	16-Aug-2009	72.1526	126.9139
5	Sardakhskaya/Trofimovskaya Channel	17-Aug-2009	72.5825	127.1891
6	Sardakhskaya Channel	17-Aug-2009	72.7002	127.4922
7	Sardakhskaya/Trofimovskaya Channel	17-Aug-2009	72.6268	127.3860
8	near Kurungnakh Island	18-Aug-2009	72.2904	126.0909
9	Lena River mai channel	19-Aug-2009	72.2987	126.7080
12	Bykovskaya Channel	20-Aug-2009	72.4140	126.9124
18	NE of Muostakh Island	22-Aug-2009	71.6761	130.1728
20	W of Muostakh Island	23-Aug-2009	71.6088	129.9393
21	close to Muostakh Island shoreline	23-Aug-2009	71.5750	129.8269
22	off Samoylov Island	30-July-2010	72.3650	126.4628
23	off Kurungnakh Island	30-July-2010	72.3392	126.3125
24	Trofimovskaya Channel	31-July-2010	72.5343	126.8725
33	Bykovskaya Channel	4-Aug-2010	72.3604	127.6765

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Table S2. Total suspended matter concentration of individual TSM samples from 2009 and 2010. Not determined denoted by n.d.

Sample code	TSM [mg/L]
July/Aug 2009	
1	3.10
2	14.17
3	6.33
4	29.01
5	11.65
6	14.09
7	7.45
8	8.82
9	66.39
10	38.97
11	52.51
12	20.20
13	29.26
14	33.32
15	15.72
16	19.56
17	174.92
18	6.72
19	n.d.
20	10.52
21	7.33
July/Aug 2010	
22	14.89
23	16.26
24	11.83
25	32.23
26	28.94
27	25.28
28	22.56
29	26.57
30	25.81
31	31.11

32	19.88
33	19.07
34	3.52
35	9.30
36	10.54

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Table S3. Organic carbon (OC), total nitrogen (TN), and atomic OC to TN ratio (OC:TN) for individual soil samples of the Lena Delta first terrace bulk samples. Bulk samples include the >2mm fraction. Sample depth is given in meter below surface [m b.s.].

	Depth	OC	TN	Atomic OC:TN
	[m b.s.]	[wt%]		
Lena Delta first terrace bulk				
Gorgolevsky Island (L09-08)				
	0.02	5.39	0.18	35.1
	1.70	8.95	0.28	37.0
	3.40	7.91	0.28	33.6
Samoylov Island (L09-12)				
	0.45	9.24	0.45	23.7
	1.35	15.49	0.32	56.3
	2.50	17.14	0.39	51.5
	4.70	13.58	0.23	68.0
	5.80	11.69	0.24	56.5
Bykovsky Channel (L09-28)				
	0.30	6.14	0.19	33.1
	1.70	2.69	0.12	21.7
Baron Belkey Island (L10-04)				
	0.05	1.82	0.06	34.6
	0.28	1.13	0.03	38.1
	0.93	1.68	0.08	24.6
	1.25	5.48	0.26	24.5
	1.43	1.02	0.04	29.4
	2.15	4.59	0.16	32.8
	3.58	10.45	0.25	49.1
	4.70	7.61	0.24	37.7
	6.00	10.05	0.26	44.8

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Table S4. Sediment-normalized CuO oxidation products and parameters of individual bulk soil samples from the first delta terrace and total suspended matter samples from 2009 and 2010. Bulk samples include >2mm fraction and sample depth is given in meters below surface [m b.s.]. When sample material was not sufficient for analysis, not determined is denoted by n.d. Not applicable denoted by n.a.

	Depth	V	S	C	Σ8	P	Pn
	[m b.s.]		[mg/g dws]				
Lena Delta first terrace bulk							
Gorgolevsky Island (L09-08)							
	0.02	0.47	0.49	0.32	1.28	0.69	0.13
	1.70	0.85	0.72	0.38	1.95	1.14	0.20
	3.40	0.89	0.55	0.14	1.58	0.82	0.06
Samoylov Island (L09-12)							
	0.45	0.94	0.74	0.30	1.98	1.01	0.22
	1.35	2.41	2.82	1.87	7.10	3.68	0.42
	2.50	1.55	2.46	1.80	5.81	2.14	0.42
	4.70	0.73	0.42	0.20	1.35	0.45	0.04
	5.80	0.78	0.71	0.71	2.04	0.65	0.13
Bykovsky Channel (L09-28)							
	0.30	0.88	0.77	0.34	1.99	0.87	0.10
	1.70	0.47	0.33	0.16	0.96	0.21	0.03
Baron Belkey Island (L10-04)							
	0.05	0.64	0.66	0.31	1.61	0.16	0.02
	0.28	0.04	0.04	0.02	0.1	0.05	0.00
	0.93	0.05	0.05	0.03	0.13	0.06	0.01
	1.25	0.31	0.37	0.24	0.92	0.37	0.04
	1.43	0.07	0.09	0.04	0.20	0.09	0.01
	2.15	0.69	0.47	0.21	1.37	0.47	0.04
	3.58	0.79	0.76	0.44	1.99	0.86	0.18
	4.70	0.68	0.75	0.42	1.85	0.72	0.10
	6.00	1.08	0.92	0.48	2.48	1.53	0.23
TSM Aug 2009							
sample code							
4	n.a.	0.18	0.06	0.03	0.27	0.15	0.05
10	n.a.	0.19	0.07	0.03	0.29	0.17	0.06

11	n.a.	0.15	0.04	0.02	0.21	0.11	0.05
13	n.a.	0.14	0.07	0.03	0.24	0.09	0.05
14	n.a.	0.10	0.05	0.02	0.17	0.07	0.04
16	n.a.	0.17	0.07	0.03	0.27	0.21	0.05
17	n.a.	0.22	0.17	0.08	0.47	0.20	0.07
TSM July/Aug 2010							
25	n.a.	0.20	0.08	0.04	0.32	0.13	0.05
26	n.a.	0.20	0.08	0.03	0.31	0.17	0.06
27	n.a.	0.18	0.08	0.04	0.29	0.11	0.05
28	n.a.	0.17	0.06	0.03	0.26	0.13	0.05
29	n.a.	0.21	0.07	0.03	0.31	0.17	0.05
30	n.a.	0.34	0.14	0.05	0.53	0.30	0.06
31	n.a.	0.28	0.13	0.06	0.46	0.18	0.05
32	n.a.	0.08	0.03	0.01	0.12	0.07	0.02

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Table S5. CuO oxidation products and parameters of individual bulk soil samples from the first delta terrace and total suspended matter from 2009-2011. Bulk samples include >2mm fraction and sample depth is given in meters below surface [m b.s.]. When sample material was not sufficient for analysis, not determined is denoted by n.d. Not applicable is denoted by n.a. Abbreviations like in table 4 and 5 of the manuscript.

Depth	V	S	C	Λ8	P	Pn	Ad/Al_V	Ad/Al_S	C/V	S/V	P/V	Pn/P
[m b.s.]	[mg/100 mg OC]											
Lena Delta first terrace bulk												
Gorgolevsky Island (L09-08)												
0.02	0.87	0.91	0.59	2.37	1.28	0.23	0.63	0.44	0.68	1.05	1.48	0.18
1.70	0.95	0.80	0.43	2.18	1.28	0.22	0.68	0.63	0.45	0.85	1.34	0.18
3.40	1.13	0.70	0.18	2.01	1.04	0.07	0.74	0.62	0.16	0.62	0.92	0.07
Samoylov Island (L09-12)												
0.45	1.02	0.80	0.33	2.15	1.09	0.24	0.99	0.82	0.32	0.78	1.07	0.22
1.35	1.55	1.82	1.21	4.58	2.38	0.27	0.56	0.58	0.78	1.17	1.53	0.11
2.50	0.91	1.44	1.05	3.40	1.25	0.25	0.63	0.48	1.16	1.58	1.38	0.20
4.70	0.54	0.31	0.14	0.99	0.33	0.03	0.84	0.64	0.27	0.58	0.62	0.09
5.80	0.67	0.61	0.47	1.75	0.56	0.11	0.62	0.60	0.71	0.91	0.84	0.20
Bykovsky Channnel (L09-28)												
0.30	1.44	1.25	0.55	3.24	1.41	0.16	0.79	0.69	0.38	0.87	0.98	0.11
1.70	1.74	1.23	0.60	3.57	0.76	0.11	0.64	0.60	0.35	0.71	0.44	0.15
Baron Belsky Island (L10-04)												
0.05	3.50	3.62	1.69	8.81	0.85	0.13	0.41	0.37	0.48	1.04	0.24	0.15
0.28	0.34	0.31	0.14	0.79	0.41	0.04	0.85	0.67	0.41	0.92	1.19	0.09
0.93	0.30	0.31	0.17	0.78	0.35	0.05	0.78	0.62	0.57	1.06	1.17	0.14
1.25	0.57	0.68	0.45	1.70	0.67	0.08	0.77	0.60	0.79	1.21	1.19	0.11
1.43	0.73	0.88	0.43	2.05	0.91	0.10	0.77	0.61	0.59	1.21	1.25	0.11
2.15	1.51	1.02	0.47	3.00	1.02	0.08	1.03	0.83	0.31	0.68	0.67	0.08
3.58	0.76	0.73	0.42	1.91	0.82	0.17	0.85	0.76	0.56	0.96	1.08	0.21
4.70	0.89	0.98	0.56	2.43	0.95	0.13	0.59	0.51	0.62	1.10	1.06	0.14
6.00	1.07	0.92	0.48	2.47	1.52	0.23	1.19	1.01	0.45	0.86	1.41	0.15
TSM Aug 2009												
sample code												
4	0.76	0.26	0.11	1.13	0.61	0.05	2.25	1.51	0.15	0.34	0.81	0.08
10	0.80	0.30	0.12	1.22	0.71	0.05	1.91	1.21	0.15	0.37	0.89	0.08

11	0.68	0.17	0.09	0.94	0.52	0.05	3.97	1.44	0.14	0.25	0.76	0.09
13	0.59	0.27	0.13	0.99	0.38	0.05	0.91	0.56	0.22	0.47	0.65	0.12
14	0.43	0.20	0.09	0.72	0.29	0.04	0.68	0.52	0.22	0.45	0.66	0.13
16	0.55	0.23	0.10	0.88	0.69	0.05	1.36	0.98	0.19	0.41	1.25	0.07
17	0.62	0.48	0.24	1.34	0.58	0.07	0.88	0.72	0.39	0.77	0.93	0.11
TSM July/Aug 2010												
25	0.77	0.30	0.14	1.21	0.49	0.05	0.98	0.69	0.19	0.39	0.64	0.11
26	0.77	0.30	0.13	1.20	0.67	0.06	1.76	0.99	0.17	0.39	0.87	0.08
27	0.72	0.30	0.14	1.17	0.45	0.05	0.96	0.80	0.20	0.42	0.62	0.11
28	0.65	0.24	0.11	1.00	0.52	0.05	1.28	0.93	0.17	0.37	0.80	0.09
29	0.69	0.22	0.10	1.02	0.57	0.05	1.59	0.93	0.15	0.32	0.83	0.08
30	0.93	0.37	0.15	1.44	0.81	0.06	1.62	1.11	0.16	0.40	0.88	0.07
31	0.76	0.35	0.16	1.26	0.51	0.05	0.69	0.55	0.20	0.45	0.67	0.10
32	0.28	0.09	0.05	0.42	0.25	0.02	2.02	0.48	0.18	0.34	0.89	0.09

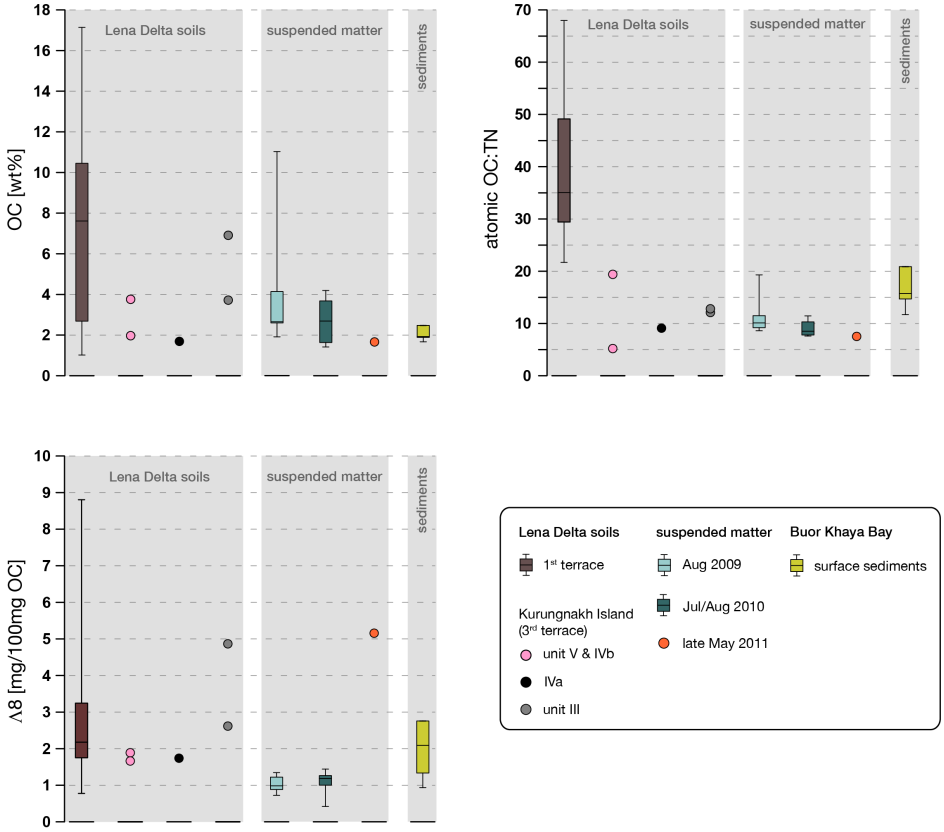

Figure S1. Bulk elemental parameters of Lena Delta soils, suspended matter from surface waters, and surface sediments from the Buor Khaya Bay. The OC content and OC:TN ratios of Kurungnakh Island samples are from (Wetterich et al., 2008).

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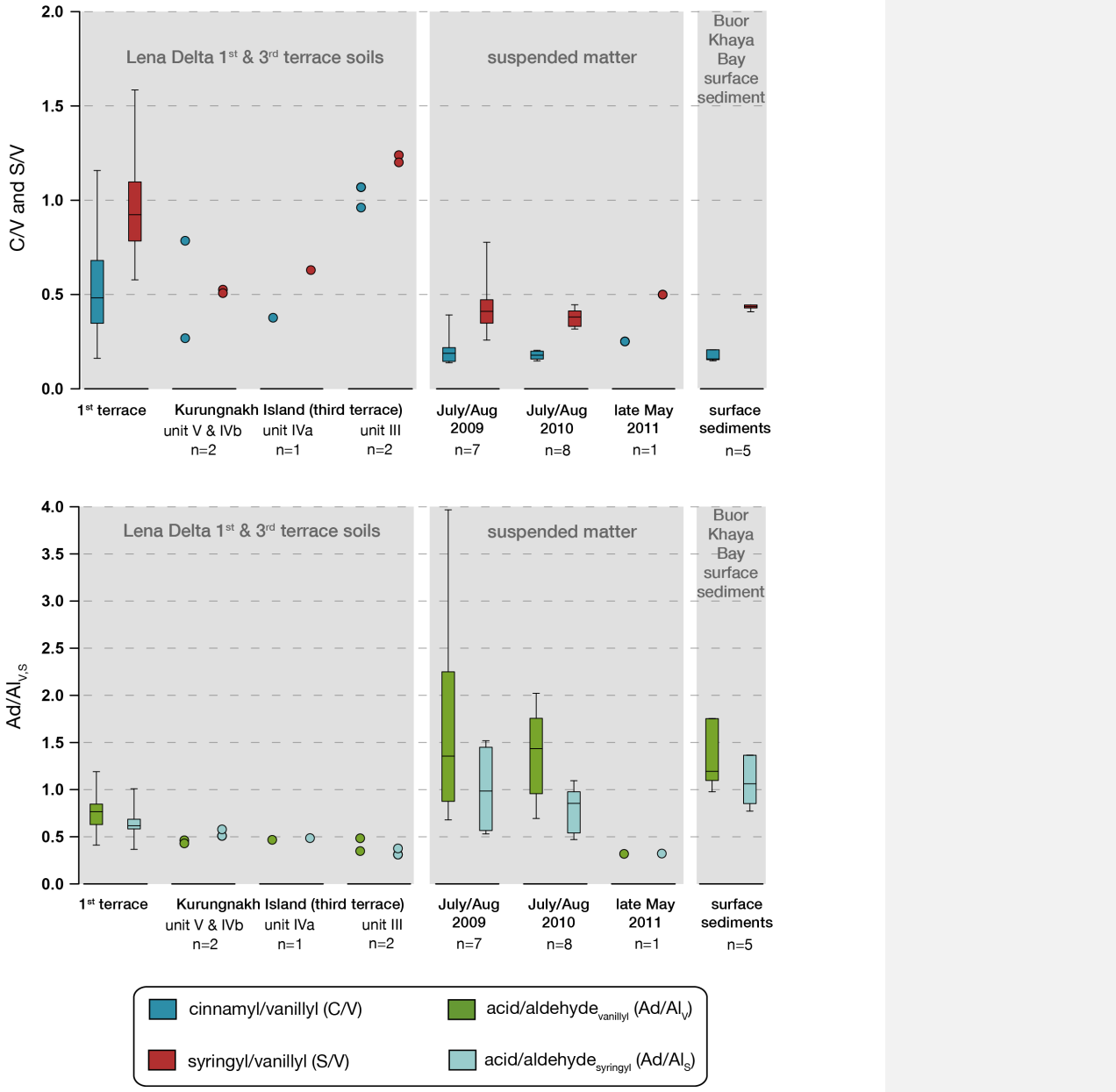

Figure S2. Parameters for different vegetation contributions (C/V and S/V) and degradation indicators (Ad/Al$_{V,S}$) for Lena Delta soils, suspended matter from surface water, and Buor Khaya Bay surface sediments.

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