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Characterization of particulate organic matter in the Lena River Delta and adjacent nearshore zone, NE Siberia – Part 1: 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

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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

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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

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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 vs. 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, character-

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izing 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 (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 (~ 2 m) 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)

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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^{-1} (Holmes et al., 2002), 5.7 Tg yr^{-1} (Holmes et al., 2012), and 1.2 Tg yr^{-1} 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^{-1} and 1.8 Tg yr^{-1}, respectively (Stein and Fahl, 2004).

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 %

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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

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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 (4.5 h at 450 °C) and pre-weighed glass fiber filters (GF / F Whatman, 0.7 µm membrane, Ø142 mm) 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 5 cm) connected to a rope. Penetration depths into sediment were between 3 and 6 cm.

The peat and sediment samples were stored in pre-combusted glass jars (4.5 h 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

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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 24 h. 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).

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 1.5 h using a microwave digestion system. After

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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). The yields of individual lignin and non-lignin oxidation products were quantified by GC-MS using selective ion monitoring. Compounds were separated chromatographically in a 30 m × 250 µm DB1 (0.25 µm film thickness) capillary GC column, using an initial temperature of 100 °C, a temperature ramp 4 °C min^{-1} and a final temperature of 300 °C. Lignin phenol yields were determined using the response factors of commercially available standards. Yields of non-lignin products were quantified using the detector response of *t*-cinnamic acid. The MS was run in electron impact mode, monitoring positive ions from a range of 50–650 amu. 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 para-hydroxybenzenes (P = *p*-hydroxybenzaldehyde, *p*-hydroxybenzophenone, *p*-hydroxy benzoic 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:

$$\mathbf{X} = \mathbf{AS} + \mathbf{R}$$

X represents a *n*-by-*m* matrix of *n* samples and *m* of lignin compounds. **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 **S** (*l*-by-*m*). **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 ($\mathbf{A} \geq 0$) and sum-to-one constraint for the rows in **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 **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.

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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^{-1} to 174.9 mg L^{-1} in 2009 and from 3.5 mg L^{-1} to 32.2 mg L^{-1} in 2010. The maximum value of 174.9 mg L^{-1} 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 and Mollenhauer, 2014) 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^{-1} the highest TSM loads determined during this study.

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

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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 Supplement (Tables 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^{-1} dws^{-1}. 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^{-1} dws^{-1} (mean Σ8 1.93 mg g^{-1} dws^{-1}). Contents from the third terrace on Kurungnakh Island are generally lower (< 2.0 mg g^{-1} dws^{-1}) except for the two Pleistocene samples from unit III (Σ8 is 1.81 mg g^{-1} dws^{-1} 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^{-1} dws^{-1} 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 Fig. 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

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8.81 mg/100 mg OC over all phenol groups (Table 5). The Λ8 were lower in TSM from the summers 2009 and 2010 (< 1.5 mg/100 mg 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, Tables 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. 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 and the moss sample (*Aulacomnium turgidum*), which have ratios > 0.4 most likely a result of high acid concentrations already contained in their fresh tissues (see Benner et al., 1990).

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. Figure 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).

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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

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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/August 2009 and 2010 (mean values are 28.5 and 19.85 mg L^{-1}, 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^{-1}) (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^{-1}) 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 (Arctic GRO, 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^{-1}. 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. 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 ($\Lambda 8$) yields instead of sediment-normalized ($\Sigma 8$) results of our TSM samples, because during sample preparation some glass fiber filter material was included in the analyzed sample, thus biasing the

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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/100 mg 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. The particulate organic carbon to nitrogen ratios from 2009 to 2011 (Table 2) suggest a considerable amount of nitrogen-rich plankton-derived OM is present in our TSM samples 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. 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 contribution of non-woody angiosperm sources, most likely tundra vegetation to Lena Delta TSM increased since 1994 due to active layer deepening and

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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 higher 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, the 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*-hydroxy phenols (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*-hydroxy phenols and the P/V and *p*-hydroxyacetophenone to P phenol 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) indicate a higher contribution of mosses to Lena Delta TSM in the summer season, presumably derived from local tundra vegetation. However, 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

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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 P/V ratios in TSM samples thus indicate that moss contribution is minor compared to a dominant non-woody angiosperm source.

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 de-

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graded 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.

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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, Tables 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 (sample ID 21), but the lignin phenol fraction of sedimentary OM (Λ8) at this location was smaller than at the river outlets.

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.

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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 within the range of the summer and spring TSM samples (Fig. 3l–s and 4b) indicating a considerable contribution of woody gymnosperm tissues from the Lena River to the Buor Khaya Bay sediments. 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). The relative contributions of the different vegetation zones in the Lena catchment will be discussed in the following section.

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 Sect. 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

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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. Assuming that the ice complex of Muostakh Island is similar to the ice complex deposits on Kurung-

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nakh Island analyzed in this study (mean Ad/Al_V ratios of 0.4 to 0.5), the lignin fraction of the OM must be 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 subaqeously in shallow Laptev Sea waters. 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

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of angiosperm vegetation, mainly present in the tundra is relatively big. Of course, 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.

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

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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 samples. Considering the relatively small area covered by tundra (~ 12 %; e.g. Amon et al., 2012) the relatively high angiosperm contribution emphasizes the importance of this small area as organic matter source to the Lena Delta and Laptev Sea coastal zone.

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 flood. 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

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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. 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 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 (I, 2007), 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.

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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 August 2009 and July/August 2010. 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 [dec]	Longitude [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.	0.5
10	Lena River main channel	19-Aug-2009	72.2760	126.9041	n.a.	0.5
11	Lena River main channel	19-Aug-2009	72.5159	126.7142	n.a.	0.5
13	Lena River Bykovskaya Channel	20-Aug-2009	72.2352	127.9619	n.a.	0.5
14	Lena River Bykovskaya Channel	20-Aug-2009	72.0341	128.5232	n.a.	0.5
16	Lena River Bykovskaya Channel	21-Aug-2009	72.0586	128.6309	n.a.	0.5
17	offshore Bykovsky Peninsula	22-Aug-2009	71.7889	129.4189	n.a.	0.5
25	Lena River Trofimoskaya Channel	31-Jul-2010	72.4764	126.6250	n.a.	0.5
26	Lena River Trofimoskaya Channel	31-Jul-2010	72.4764	126.8588	n.a.	0.5
27	Lena River main channel south of Samoylov	1-Aug-2010	72.3776	126.7478	n.a.	0.5
28	Lena River main channel north of Tit Ari Island	1-Aug-2010	72.2102	126.9423	n.a.	0.5
29	Lena River main channel south of Tit Ari Island	1-Aug-2010	71.9514	127.2582	n.a.	0.5
30	Lena River main channel off Kurungnakh	2-Aug-2010	72.2808	126.2091	n.a.	0.5
31	Lena River main channel	2-Aug-2010	72.3567	126.3521	n.a.	0.5
32	Lena River Bykovskaya Channel	3-Aug-2010	72.3604	127.6761	n.a.	0.5
37	Lena River main channel off Samoylov Island	29-May-2011	72.3651	126.4757	n.a.	0.5

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Table 1. Continued.

Sample code	Sample & site description	Date of sampling	Latitude [dec]	Longitude [dec]	Bluff height [m a.r.l.]	Water depth [m]
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
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).

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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.

	TSM [mg L^{-1}]	POC[a] [mg L^{-1}]	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 Jul/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 and Mollenhauer (2014, 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).

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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^{-1} dws^{-1}). 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*-hydroxy phenols (sum of *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, *p*-hydroxybenzoic acid), Pn = *p*-hydroxyacetophenone.

	V	S	C	Σ8	P	Pn
	[mg g^{-1} dws^{-1}]					
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	0.18
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	1.63	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	1.68	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 Jul/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/100 mg 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*-hydroxy to vanillyl phenols, Pn/P = *p*-hydroxyacetophenone to *p*-hydroxy phenols. Not determined denoted by n.d.

	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 Jul/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 Tables 4 and 5.

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

[a] Endmember ratios from Table 4 in Amon et al. (2011) including Hedges and Mann (1979), Hedges and Parker (1976), Prokushkin et al. (2014), Williams et al. (1998).

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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.

sample code	rel. V [%]	rel. S [%]	rel. C [%]	median (500 iterations) mixing coefficients: 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 Jul/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

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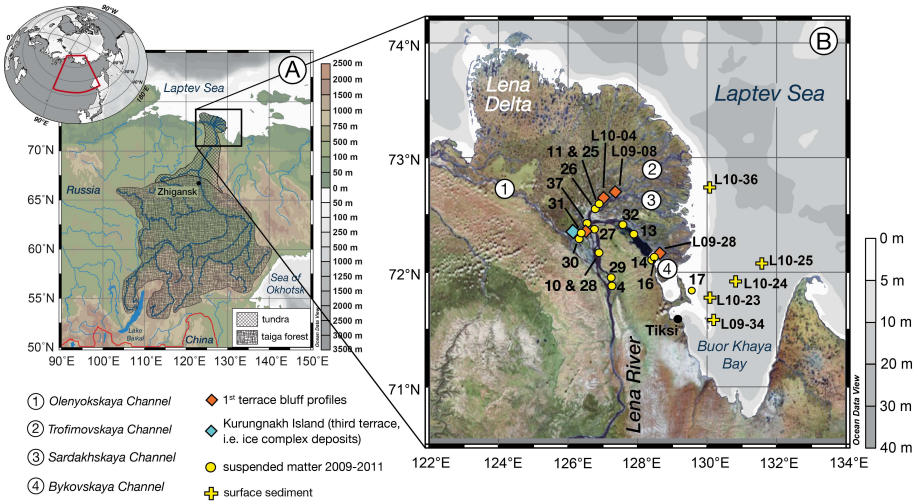

Figure 1. (A) Lena River catchment area with approximate tundra and taiga forest distribution, **(B)** Lena Delta and Buor Khaya Bay sampling sites from 2009 to 2011 and associated sample codes.

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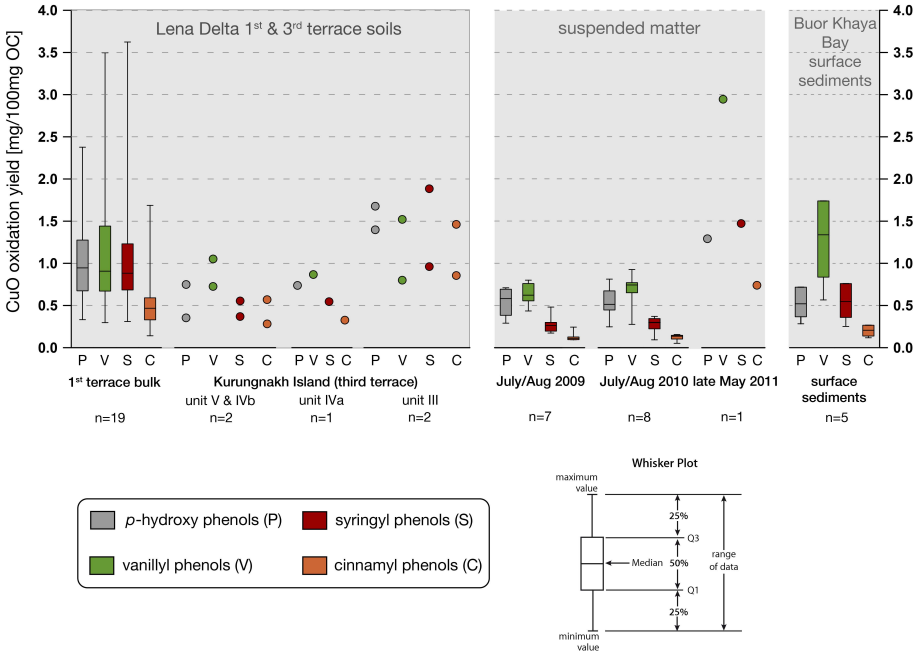

Figure 2. Carbon-normalized yields of phenols groups shown as Whisker plots when the number of samples was large enough and as individual samples for smaller numbers.

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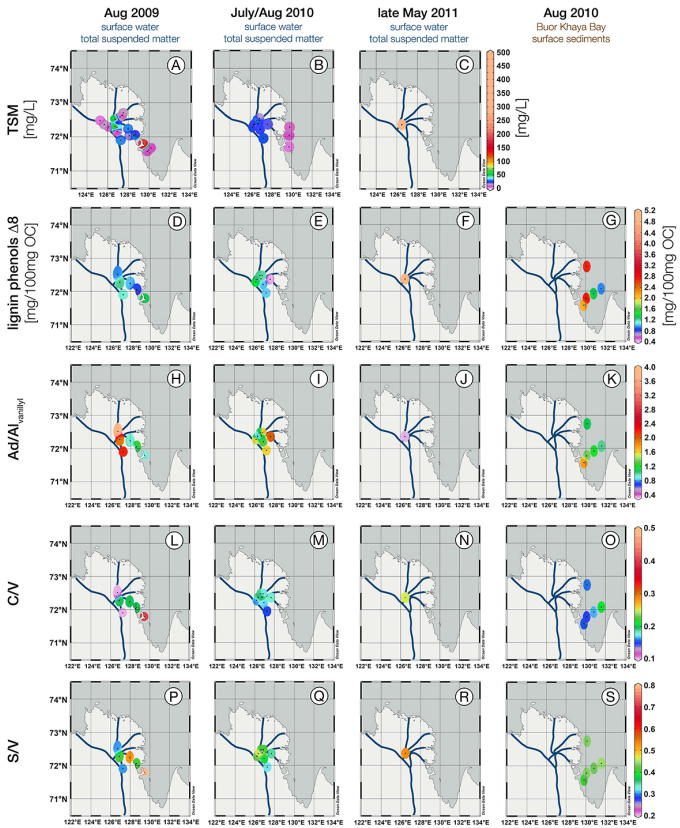

Figure 3. Spatial distribution of carbon-normalized lignin concentrations (Λ8) and lignin parameters of Lena Delta total suspended matter (TSM) and Buor Khaya Bay surface sediments. $Ad/Al_{vanillyl}$ = acid to aldehyde ratio of the vanillyl phenols, C/V = ratio of cinnamyl to vanillyl phenols, and S/V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

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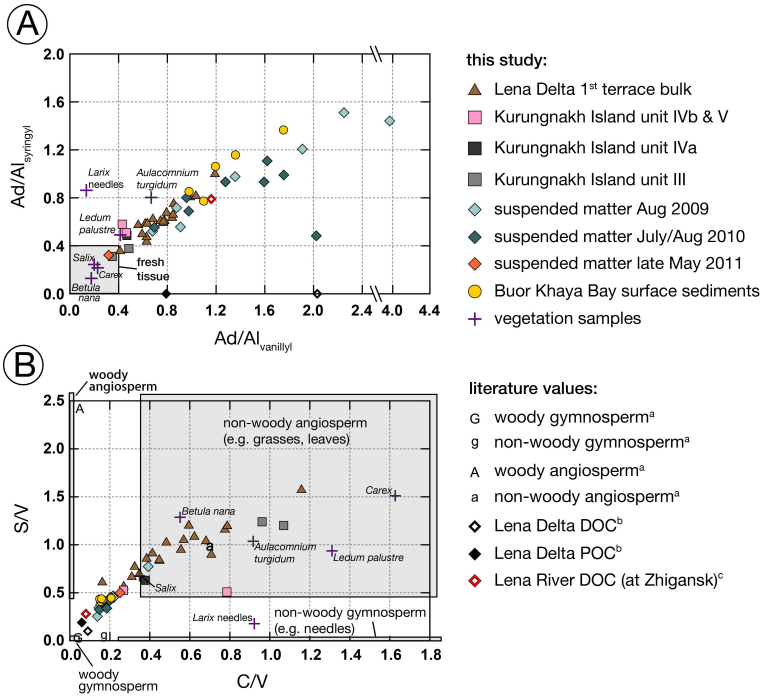

Figure 4. (A) Lignin degradation indices (Ad/Al_V vs. Ad/Al_S) and **(B)** vegetation source parameters (C/V vs. S/V). For abbreviations see Fig. 3. Note the different scales. Literature values: [a] Table 4 in Amon et al. (2012) and references therein, [b] Lobbes et al. (2000), [c] Amon et al. (2012). 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).

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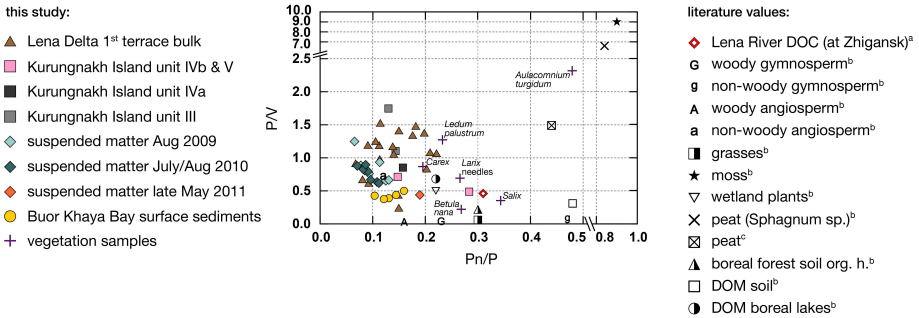

Figure 5. The ratios of *p*-hydroxyacetophenone to *p*-hydroxy phenols (Pn/P) vs. *p*-hydroxy phenols to vanillyl phenols (P/V) of samples analyzed in this study and values from the literature used as indicator for moss contributions. [a] Amon et al. (2012), [b] Table 4 in Amon et al. (2012) and references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

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