Biomarker and carbon isotope constraints ($\delta^{13}C$, $\Delta^{14}C$) on sources and cycling of particulate organic matter discharged by large Siberian rivers draining permafrost areas

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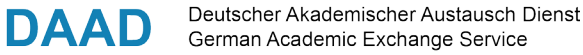

Meinen Eltern

"I may not have gone where I intended to go, but I think I have ended up where I intended to be."

Douglas Adams
(1952 – 2001)

Erklärung

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Hiermit versichere ich, das ich

1. die Arbeit ohne unerlaubte fremde Hilfe angefertigt habe,

2. keine anderen als die mir von mir angegebenen Quellen
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Bremen, den 8. August 2014

Maria Winterfeld

SUMMARY

Circumpolar permafrost soils store about half of the global soil organic carbon pool. These huge amounts of organic matter (OM) could accumulate due to low temperatures and water saturated soil conditions over the course of millennia. Currently most of this OM remains frozen and therefore does not take part in the active carbon cycle, making permafrost soils a globally important carbon sink. Over the last decades mean annual air temperatures in the Arctic increased stronger than the global mean and this trend is projected to continue. As a result the permafrost carbon pool is under climate pressure possibly creating a positive climate feedback due to the thaw-induced release of greenhouse gases to the atmosphere. Arctic warming will lead to increased annual permafrost thaw depths and Arctic river runoff likely resulting in enhanced mobilization and export of old, previously frozen soil-derived OM. 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.

The first part of this thesis deals with particulate organic matter (POM) from the Lena Delta and adjacent Buor Khaya Bay. The Lena River in central Siberia is one of the major pathways translocating terrestrial OM from its southernmost reaches near Lake Baikal to the coastal zone of the Laptev Sea. The permafrost soils from the Lena catchment area store huge amounts of pre-aged OM, which is expected to be remobilized due to climate warming. To characterize the composition and vegetation sources of OM discharged by the Lena River, the lignin phenol and carbon isotopic composition ($\delta^{13}C$ and $\Delta^{14}C$) in total suspended matter (TSM) from surface waters, surface sediments from the Buor Khaya Bay along with soils from the Lena Delta's first (Holocene) and third terraces (Pleistocene ice complex) were analyzed. The lignin compositions of these samples are consistent with inputs of OM from non-woody angiosperm sources mixed with organic matter derived from woody gymnosperm sources. A simple linear mixing model based on the lignin phenol distributions indicates organic matter in TSM samples from the delta and Buor Khaya Bay surface sediments contain comparable contributions from gymnosperm sources, which are primarily from the taiga forests south of the delta, and angiosperm material typical for tundra vegetation. Considering the small area covered by tundra (~12% of total catchment), the input of tundra-derived OM input is substantial and likely to increase in a warming Arctic. Radiocarbon compositions ($\Delta^{14}C$) of bulk OM in Lena River TSM samples varied from –55 to –391‰, translating into ^{14}C ages of 395 to 3920 years BP. Using $\delta^{13}C$ compositions to estimate the fraction of phytoplankton-derived OM and assuming that this

material has a modern ^{14}C signature, we inferred the $\Delta^{14}C$ compositions of terrigenous OM in TSM exported by the Lena River to range between –190 and –700‰. Such variability in the ages of terrigenous OM (i.e. 1640 to 9720 ^{14}C years BP) reflects the heterogeneous composition and residence time of OM in the Lena River catchment soils (Holocene to Pleistocene ages). Lignin phenol and $\Delta^{14}C$ compositions of surface sediments from the adjacent Buor Khaya Bay suggest that terrestrial OM deposited there is older and more degraded than materials present in river particles and catchment soils. Stronger diagenetic alteration in Lena Delta TSM and marine sediments relative to soils may reflect degradation of more labile components during permafrost thawing and transport. Despite the high natural heterogeneity in catchment soils, the lignin biomarker compositions and radiocarbon ages of terrestrial OM exported by the Lena River reflect catchment characteristics such as vegetation and soil type. Climate warming related changes in the Lena River catchment may be detectable in changing lignin biomarker composition, diagenetic alteration, and radiocarbon age.

The second part of this thesis investigates past permafrost dynamics and the possible permafrost/wetland climate feedback during the last deglaciation and Early Holocene. The Amur hinterland in East Siberia was most likely characterized by extensive permafrost during the last glacial maximum and is today permafrost-free with the exception of small areas in the northern reaches of the catchment. The organic matter flux of the Amur River into its receiving basin, the Okhotsk Sea, was reconstructed for the last 16,000 years in a high-resolution AMS ^{14}C-dated sediment core from the Sakhalin continental margin, based on organic geochemical multi-proxy data and compound-specific radiocarbon dating of *n*-alkanoic acids. Within the deglacial discharge maximum of organic matter to the Okhotsk Sea, two peaks of organic matter release episodes; the first occurring during the Bølling-Allerød warm phase, and the second, larger one after Termination Ib in the earliest Preboreal could be identified. The results highlight the sensitivity of the Amur drainage basin's carbon reservoir to rapid deglacial temperature and precipitation changes. It is hypothesized that large amounts of carbon were activated upon deglacial permafrost thawing within this southernmost Siberian large catchment and quickly transferred to the oceanic carbon reservoir via riverine freshwater transport into the Okhotsk Sea and the North Pacific.

ZUSAMMENFASSUNG

In den Permafrostböden der hohen nördlichen Breiten ist ungefähr die Hälfte des globalen organischen Bodenkohlenstoffs gespeichert. Diese riesigen Mengen organischen Materials (OM) haben sich über Jahrtausende aufgrund der niedrigen Temperaturen und der wassergesättigten Böden angereichert. Gegenwärtig ist ein Großteil des OM gefroren und nimmt daher nicht am aktiven Kohlenstoffkreislauf teil, was wiederum bedeutet, dass die Permafrostböden eine global bedeutende Kohlenstoffsenke darstellen. In den letzten Jahrzehnten ist die jährliche Lufttemperatur in der Arktis stärker gestiegen als im globalen Mittel und dieser Trend wird weiter anhalten. Dadurch gerät der Kohlenstoffpool im Permafrost unter starken Einfluss des sich erwärmenden Klimas, was wiederum zu einer positiven Rückkopplung auf das Klima führen könnte, da der tauende Permafrostboden Treibhausgase in die Atmosphäre frei setzt. Eine Erwärmung der Arktis wird außerdem zum tieferen Auftauen der sommerlichen Bodenschichten und zu einem verstärkten Abfluss der arktischen Flüsse führen, was die verstärkte Mobilisierung und den Export von altem, vorher gefrorenem Boden-OM zur Folge hat. Aus diesem Grund spielen die arktischen Flüsse eine wichtige Rolle im globalen biogeochemischen Kreislauf, d.h. sie verknüpfen somit den riesigen Permafrostkohlenstoffpool ihrer Einzugsgebiete mit den arktischen Schelfmeeren und dem Arktischen Ozean.

Im ersten Teil dieser Arbeit wird partikuläres organisches Material (POM) aus dem Lena Delta und der angrenzenden Buor Khaya Bucht untersucht. Die Lena ist in Zentralsibirien eine der Haupttransportadern, entlang derer terrestrisches OM vom südlichen Einzugsgebiet nahe des Baikalsees bis zur Küste der Laptewsee transportiert wird. Die Permafrostböden ihres Hinterlandes enthalten große Mengen alten organischen Materials, das mit großer Wahrscheinlichkeit im Zuge der Klimaerwärmung remobilisiert wird. Die Zusammensetzung und Vegetationsquellen des OM in suspendiertem Material aus dem Oberflächenwasser, in Oberflächensedimenten der Buor Khaya Bucht sowie in holozänen (erste Terrasse) und pleistozänen (dritte Terrasse) Böden des Lena Delta wurden durch Bestimmung der Ligninzusammensetzung sowie der Kohlenstoffisotope ($\delta^{13}C$, $\Delta^{14}C$) analysiert. Die Ligninzusammensetzung dieser Proben spiegelt den Eintrag sowohl von nicht hölzernen Angiospermen als auch verholzten Gymnospermen wider. Die Anwendung eines linearen Mischungsmodells deutet auf ungefähr gleichgroße Mengen organischen Materials von gymnospermen Pflanzen, die ausschließlich im südlichen Einzugsgebiet vorkommen, und

angiospermen Pflanzen, die typisch für die Tundra sind, hin. Wenn man die geringe Größe des Tundragebiets bedenkt (circa 12% des gesamten Einzugsgebietes) ist dieser Anteil an angiospermem OM erheblich und könnte im Zuge der Erwärmung der Arktis sogar noch größer werden. Die $\Delta^{14}C$ Konzentrationen des bulk OM in Lena TSM reicht von –55 bis –391‰, was ungefähr einem Altersbereich von 395 bis 3920 Jahre vor heute (v.h.) entspricht. Mit Hilfe der stabilen Kohlenstoffisotopenzusammensetzung wurde der Anteil des OM von Phytoplankton abgeschätzt. Unter der Annahme, dass dieses Material eine moderne ^{14}C-Signatur hat, wurde die $\Delta^{14}C$-Konzentration der terrestrischen OM-Fraktion in Lena TSM abgeleitet, welche sich zwischen –190 und –700‰ bewegte, was einer Altersspanne von ungefähr 1640 bis 9720 Jahren v.h. entspricht. Diese Variabilität in der Altersstruktur des terrestrischen OM spiegelt die Heterogenität der holozänen bis pleistozänen Böden im Lena Einzugsgebiet sehr gut wider. Die Ligninzusammensetzung und Kohlenstoffisotopie der Oberflächensedimente in der Buor Khaya Bay deutet darauf hin, dass dieses OM stärker zersetzt und älter ist als TSM aus dem Oberflächenwasser und aus Lena Delta Böden. Die stärkere Zersetzung des OM im TSM relativ zu den Deltaböden weist wahrscheinlich darauf hin, dass labile OM-Komponenten bereits nach dem Tauen der Böden oder während des Transports abgebaut wurden. Trotz der starken natürlichen Heterogenität innerhalb der Böden spiegeln sowohl die Ligninzusammensetzung als auch die Kohlenstoffisotopie, die für das Lena-Einzugsgebiet typischen Vegetations- und Bodentypen (bezogen auf die Altersstruktur) wider.
Durch die Klimaerwärmung verursachte Veränderungen im Lena Einzugsgebiet können mit hoher Wahrscheinlichkeit anhand der Ligninzusammensetzung, des Zersetzungszustandes und der Altersstruktur des transportierten OM detektiert werden.

Der zweite Teil dieser Arbeit beschäftigt sich mit der Permafrostdynamik während des Übergangs von der letzten Eiszeit zur holozänen Warmphase und einer daraus resultierenden möglichen Klimarückkopplung aus Permafrostböden und/oder Feuchtgebieten. Das Amur Einzugsgebiet in Ostsibirien war mit hoher Wahrscheinlichkeit während des letzten glazialen Maximums (LGM) vollständig Teil der Permafrostzone, während es heute bis auf einen kleinen Teil im Norden keinen Permafrost mehr enthält. Der Export von Amur OM in das Okhotskische Meer wurde hier für die letzten 16,000 Jahre in einem hoch aufgelösten AMS ^{14}C-datierten Sedimentkern vom Sakhalin Kontinentalrand mit Hilfe organisch-geochemischer Methoden und komponentenspezifischer Radiokarbonanalysen rekonstruiert. Kennzeichnend für die Zeit des maximalen Exports von OM in das Okhotskische Meer im Deglazial sind zwei Höchstwerte, der erste tritt während der Bølling-Allerød Warmphase auf und der zweite nach der

Termination Ib im frühen Präboreal. Diese Ergebnisse unterstreichen die Sensibilität des Kohlenstoffreservoirs im Amur Einzugsgebiet gegenüber den raschen deglazialen Temperatur- und Niederschlagsveränderungen. Es wird deshalb vermutet, dass große Mengen von Kohlenstoff in diesem südlichsten der großen sibirischen Flusssysteme durch das Tauen des Permafrostes während des Deglazials aktiviert und anschließend mit dem Flussaustrag schnell ins Okhotskische Meer und den Nord Pazifik umgelagert wurden.

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1 INTRODUCTION

1.1 Scientific background and rationale

Arctic and boreal terrestrial ecosystems are essential components in the global carbon cycle. One characteristic feature of these cold ecosystems are permafrost soils, which are perennially frozen and as of today cover about one quarter of the circumpolar land area north of 50°N (Jones et al. 2010; Fig. 1-1A). These permafrost soils have accumulated huge amounts of organic matter (OM) during the Quaternary (Fig. 1-1B; e.g. Gorham et al., 2007; Smith et al., 2004; Zimov et al., 2006b) due to reduced organic matter decomposition under the low temperatures and high moisture conditions and the very limited accessibility to biogeochemical cycling of the freeze-locked OM in deeper soil layers. A recent estimate including OM from deeper soil layers (down to 3 m depth) suggests circumarctic permafrost soils store 1466 Pg C (Pg = 10^{15}g = Gt) (Tarnocai et al., 2009), which is roughly twice as much carbon as held in the atmosphere (Houghton, 2007). Against the backdrop of both, observed and predicted increased Arctic warming (ACIA, 2005; AMAP, 2012; IPCC 2013; Serreze et al., 2000) the destabilization of this huge carbon pool has the potential for a positive climate feedback further accelerating global warming trends. As a consequence, carbon cycling and the fate of organic carbon (OC) released from permafrost soils have received growing attention (e.g. Elberling et al., 2013; Koven et al., 2011; McGuire et al., 2009; Oechel et al., 1993; Schuur et al., 2013; 2008; 2009; Zimov et al., 2006b; 2006a).

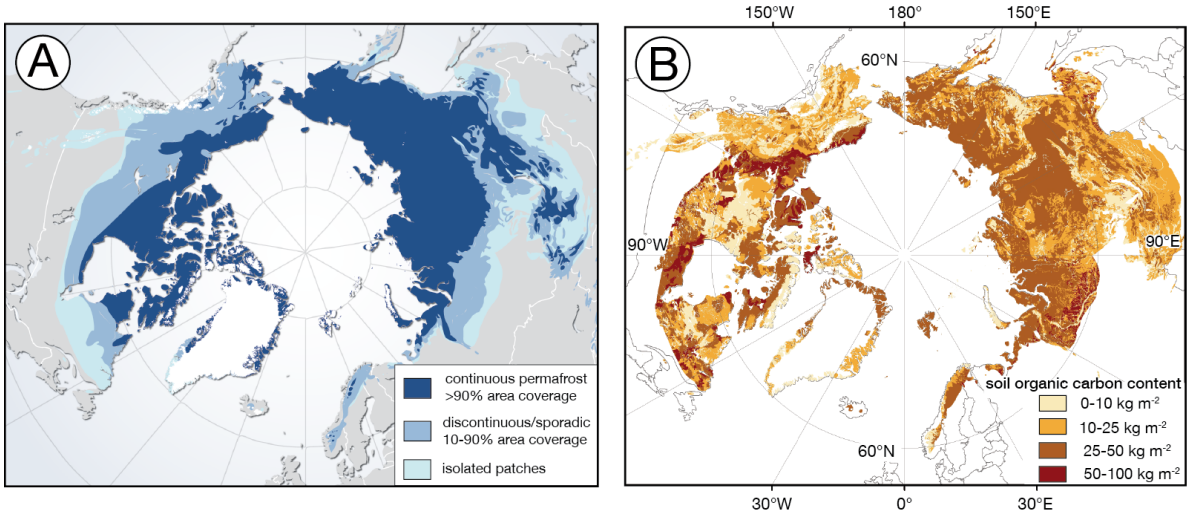

Figure 1-1. A) Northern Hemisphere permafrost distribution (map by Hugo Ahlenius, UNEP/GRID-Arendal, see www.grida.no/graphicslib/detail/permafrost-extent-in-the-northern-hemisphere_1266; source data from Brown et al. 1998). B) Permafrost soil organic carbon content of surface soils (1m depth) estimated using the Northern circumpolar Soil Carbon Database (Hugelius et al., 2013).

Since the 1980s average air temperatures have increased twice as much over the Arctic than in lower latitudes (Dicks and Almond, 2012) and models predict further amplifications of the Arctic warming trend until the end of the 21st century (IPCC, 2013). This currently has large-scale impacts on high latitude ecosystems, which will likely amplify in the future, such as a reduction of sea-ice cover, increasing precipitation (snow and rain), changes in snow cover duration, shifts of vegetation zones (northward migration of the boreal forests), higher forest fire frequencies, and widespread permafrost thawing (ACIA, 2004; AMAP, 2012; IPCC, 2013). The latter will most likely result in the release of large amounts of OM currently excluded from active biogeochemical cycling and, thus, creating further positive carbon-climate feedbacks.

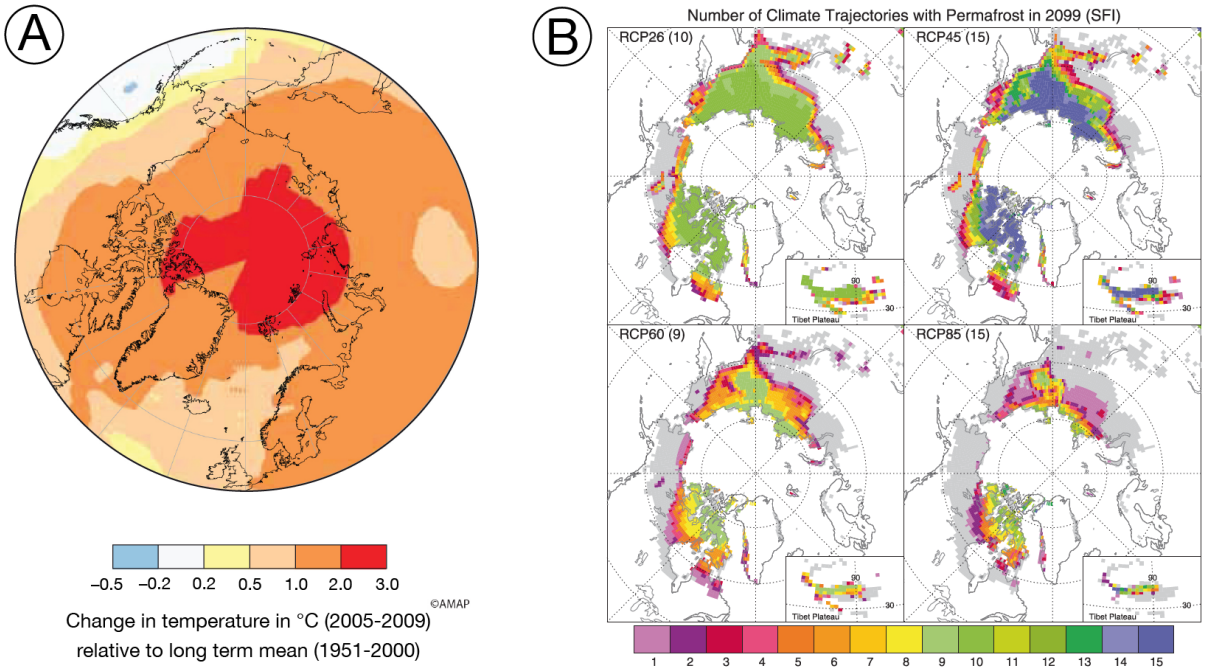

Figure 1-2. A) Mean annual air temperature changes for the time period from 2005 to 2009 relative to the long term average of 1951-2000 (AMAP, 2011). B) Modeled permafrost distribution for the year 2099 using different climate trajectories for the main Representative Concentration Pathway (RCP) scenarios according to IPCC (2013). Grey areas represent the modern permafrost distribution (Slater and Lawrence, 2013).

Thawing-induced degradation of permafrost involves several processes, which are connected via interactions and feedbacks (Jorgenson et al., 2010). These processes include increasing summer thaw depth (active layer depth), development of thermokarst lakes and basins (resulting from surface subsidence through ground ice melting), increasing river runoff and riverbank erosion (AMAP, 2012; McClelland et al., 2012; Peterson et al., 2002) and enhanced coastal erosion of permafrost deposits (caused by extended sea-ice free periods of coastal waters (Markus et al.,

2009). Consequently, these processes will make previously frozen, pre-aged OM available for microbial (re-)mineralization as well as for remobilization and export to the Arctic shelf seas (e.g. Grosse et al., 2011; Guo et al., 2006; 2004; McGuire et al., 2009; Schuur et al., 2008; Vonk et al., 2010).

The magnitude and dynamics of the permafrost carbon feedback are still partially unknown and/or associated with large uncertainties. Model projections of permafrost distribution (Zhang et al. 2008a, b; Saito et al. 2007; Lawrence and Slater, 2005; Slater and Lawrence, 2013) and changes of active layer depth until the end of the 21st century vary largely (Saito et al., 2007; Zhang et al. 2008a, b; Schaefer et al. 2011), but the consensus is a decrease of the spatial permafrost extent with a concurrent increase of active layer depth.

Only recently are permafrost soils implemented into terrestrial carbon-climate projections, which indicate that thawing permafrost soils are likely sources of large greenhouse gas emissions (Koven et al., 2011; MacDougall et al., 2012; Schaefer et al., 2011; Schneider von Deimling et al., 2012). However, these models rarely account for processes that could slow down or counterbalance the effects of carbon released from permafrost such as increased uptake of CO_2 through photosynthesis due to spatial extension of vegetated areas and prolonged growing seasons, development of wetlands with reducing redox conditions, which slow down OM decay (Fig. 1-3).

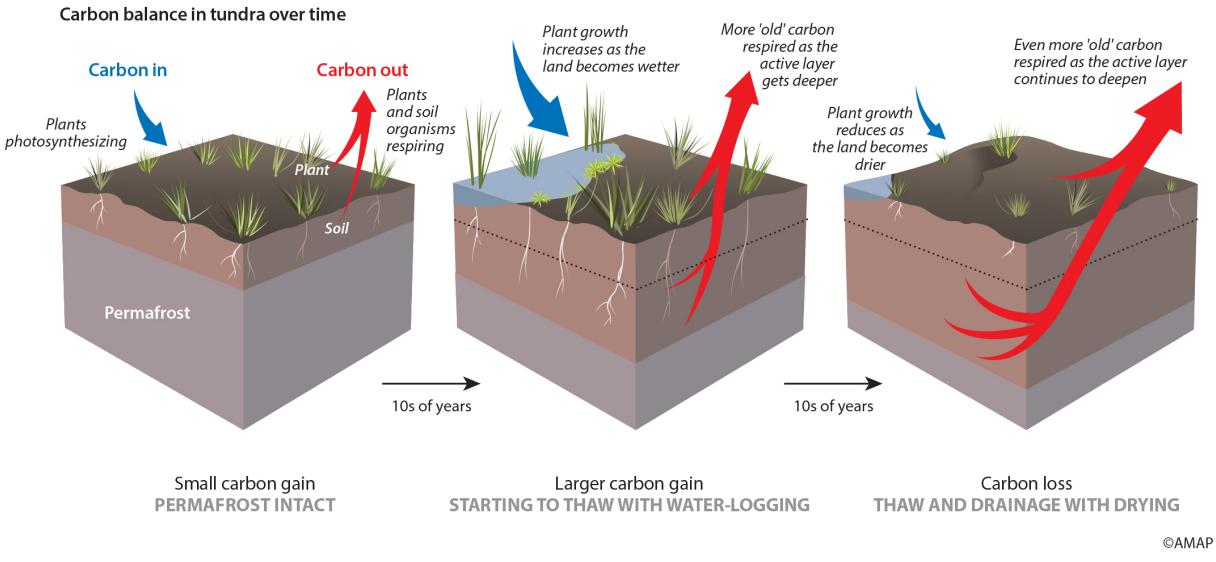

Figure 1-3. Tundra carbon cycle in response to permafrost thawing (AMAP, 2012).

Projections for future climate scenarios of atmospheric CO_2 increase might also benefit from improving our understanding of past increases in CO_2 and methane (CH_4). The parallel rise of atmospheric CO_2 and CH_4 concentration from the last glacial maximum (LGM) at ~21 thousand years before present (ka) to pre-industrial times, lead to speculations about a possible carbon-climate feedback from terrestrial high northern latitude environments including thawing permafrost as one additional source area of CO_2 next to the vast ocean reservoir (e.g. Ciais et al., 2012; Smith et al., 2004; Zech, 2012; Zimov et al., 2009; 2006b). Understanding past permafrost dynamics therefore might help to improve projections of future permafrost evolution in a warming Arctic.

While our knowledge of the Arctic carbon cycle and its warming-induced changes are constantly improving (AMAP, 2012; IPCC, 2013) the ultimate fate of the newly released OM remains less clear. Following permafrost thaw, on which timescales is OM remineralized and what are the magnitudes of the resulting CO_2 and/or CH_4 emissions? Or asked differently, how much of the OM gets eroded, transported, and reburied on the continental shelves? And how much of the OM transported fluvially is remineralized during transport to the ocean?
To answer these questions, this thesis investigates biomarkers and their radiocarbon concentrations as well as carbon isotopic signatures ($\delta^{13}C$, $\Delta^{14}C$) from particulate organic matter (POM) transported by large Siberian rivers in order to trace terrestrial OM in marine sediments and to characterize the carbon turnover timescales.

1.2 Objectives of this thesis

The dissolved and particulate loads of large river systems carry the characteristic OM signal of the respective river watershed. Climate-driven changes of the catchment properties (vegetation, soils, precipitation and erosion, etc.) will ultimately also impact the river OM signal exported to the ocean. Siberian rivers drain watersheds with large coverage of permafrost soils and will, thus, most likely experience significant increase of dissolved and particulate matter load during northward migration of the discontinuous permafrost areas and a general acceleration of permafrost degradation. As hypothesized by Guo et al. (2007) the signal of permafrost degradation might predominantly manifest itself in the enhanced erosion and export of previously frozen, old POM.

Lena River & Laptev Sea, NE Siberia (chapters 2 & 3)

The Lena River in central Siberia is one of the main pathways for terrestrial organic matter export from its southernmost reaches near Lake Baikal to the Laptev Sea and Arctic Ocean. Permafrost soils from its vast catchment area store huge amounts of pre-aged OM, which will likely remobilize due to climate warming. In order to track climate-induced changes of the carbon dynamics within the Lena River watershed, an assessment of today's riverine POM signature is crucial while most of the river basin is still part of the continuous permafrost zone. This includes the biogeochemical characterization of the POM exported by the Lena River to determine whether it reflects the vegetational composition and permafrost conditions of the hinterland. Furthermore, the Lena River POM is supplied to the Laptev Sea shelf where it impacts the biogeochemical cycling on the shelf. Besides the Lena River derived POM, terrestrial OM supplied to the Laptev Sea shelf also derives from coastal erosion of Pleistocene ice complex deposits. These two sources of terrestrial OM, which are estimated to contribute equal proportions, need to be distinguishable for C budgets. Chapter 2 and 3 investigate the sources, state of degradation, and age of POM in the Lena Delta and adjacent Buor Khaya Bay to provide the baseline needed to detect future changes within the watershed. The presented data furthermore improves the end-member definition of Lena River POM vs. coastal erosion-derived POM allowing for a better understanding and source-assignment of terrestrial POM cycling in the Arctic Ocean.

Amur River & Okhotsk Sea, E Siberia (chapter 4)

The Okhotsk Sea is the main recipient of dissolved and particulate organic matter delivered by the Amur River. Because the permafrost extent during the LGM reached much further south than today (Vaks et al., 2013; Vandenberghe et al., 2014), including the Amur catchment, the large pool of organic matter presumably stored in these permafrost soils was most likely predominantly released to the atmosphere in the course of the deglacial warming (e.g. Zech, 2012). This hypothesis contribute to the discussion about the convergent increases of atmospheric CO_2 and CH_4 during the last termination when Earth's climate transitioned from the LGM towards modern warm phase that have fueled speculations of possible contributions from high northern latitude environments (e.g. Zech, 2012; Zimov et al., 2009; 2006b). Despite the general assumption that less organic carbon was store on land during the LGM, Ciais et al. (2012) identified a terrestrial inert carbon pool that was larger (~700 Pg) during the LGM than today and they speculate that it could have been carbon stored in permafrost soils. Chapter 4 investigates especially the compound-specific radiocarbon concentration and ^{14}C age of terrestrial

biomarkers to relative to time of their deposition at the core location. The relative $\Delta^{14}C$ depletion of these biomarkers gives insights about the possible contribution of old previously freeze-locked OM released from permafrost. Climatic and environmental changes of this magnitude, particularly the degradation and disappearance of permafrost in the Amur basin should be detectable in the amount of POM exported to the Okhotsk Sea as well as in the radiocarbon concentration of terrestrial biomarkers.

1.3 Thesis outline

This thesis is composed of five main chapters including an introduction, three chapters representing manuscripts, and a summary. The manuscripts are either submitted to or prepared for publication in international peer-reviewed journals (Table 1-1).

Table 1-1. Overview of publications presented in this thesis.

Publication	Chapter
Winterfeld, M., Goñi, M. A., Just, J., Hefter, J., and Mollenhauer, M: Characterization of particulate organic matter in the Lena River Delta and adjacent nearshore zone, NE Siberia. Part I: Plant-derived phenol compositions, 2014. Submitted to Biogeosciences.	2
Winterfeld, M. and Mollenhauer, G.: Characterization of particulate organic matter in the Lena River Delta and adjacent nearshore zone, NE Siberia. Part II: Radiocarbon inventories, 2014. Submitted to Biogeosciences.	3
Winterfeld M., Lembke-Jene, L., Wacker, L., Tiedemann, R., Nürnberg, D. and Mollenhauer, G.: Rapid deglacial to early Holocene permafrost thawing and wetland dynamics in East Siberia revealed by Amur River discharge peaks into the Okhotsk Sea. In preparation for Geophysical Research Letters.	4

2 MANUSCRIPT I

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

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submitted to Biogeosciences Discussion

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 >0.4 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 >0.6 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. 2-1A). 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) 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).

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.

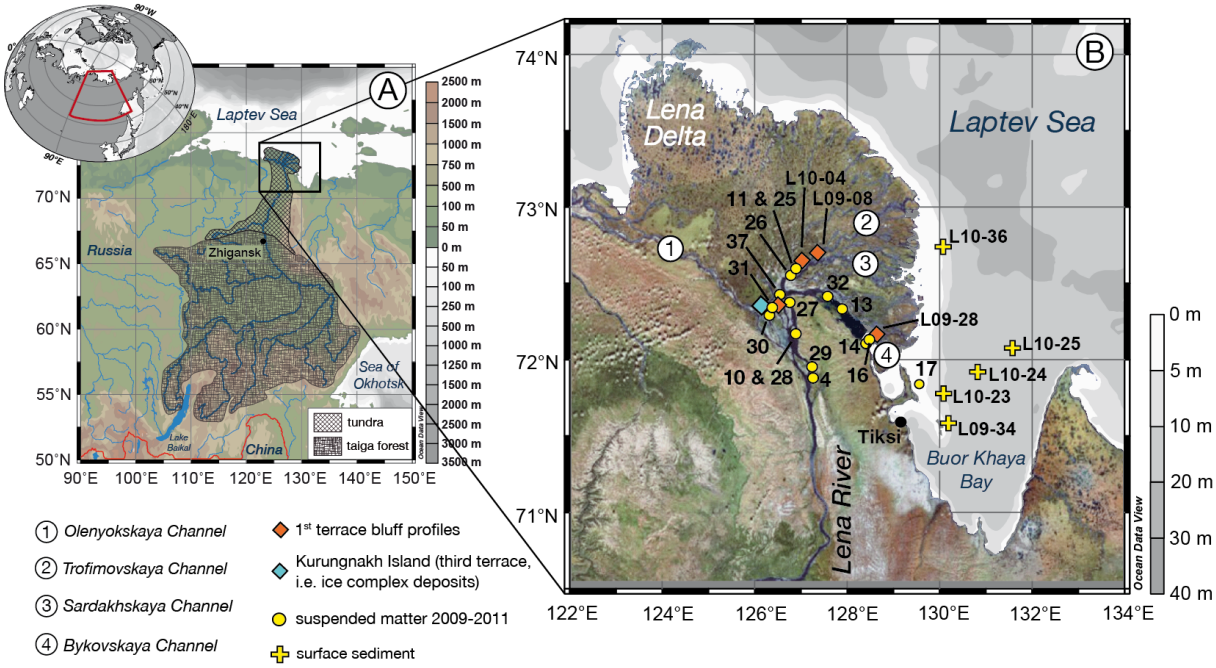

Figure 2-1. A) Lena River catchment area with approximate tundra and taiga forest distribution (modified after World Resources Institute, 2003), B) Lena Delta and Buor Khaya Bay sampling sites from 2009 to 2011 and associated sample codes.

Lena River water and sediment discharge is not equally distributed through the different delta channels (Fig. 2-1B). 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 16m) 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. 2-1B). 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 8m 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. 2-1B and Table 2-1). 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, 0.7 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 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).

Table 2-1. 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. 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	17-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

Table 2-1 continued.

Sample code	Sample & site description	Date of sampling	Latitude [dec]	Longitude [dec]	Bluff height [m a.r.l.]	Water depth [m]
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
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)	7-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]from Wetterich et al. (2008)
[b]see Herzschuh et al. (2009), Klemm and Zubrzycki (2009), and Zubrzycki et al. (2012)

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).

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). 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 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. 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).

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 2-7). The linear mixing system of lignin concentrations in the samples can be written in matrix notation as:

$$X = AS + R$$

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 ($A >= 0$) 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.

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 2-2). The concentrations varied from 3.1 mg/L to 174.9 mg/L in 2009 and from 8.9 mg/L to 29.3 mg/L in 2010. The maximum value of

174.9 mg/L in 2009 of sample 17 (Fig. 2-1B, Table 2-S2 supplement) 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; submitted as companion paper) and additionally given in Table 2-2. 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.

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 2-3, Fig. 2-S6 supplement). 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 2-3) 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 21 off Muostakh Island (see Fig. 2-1B). 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. 2-1B, Table 2-3), where the majority of the Lena River water and sediment discharge occurs.

Table 2-2. 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]	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	7.3	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=21*	*n=20*	*n=21*
mean	21.38	0.57	3.37	7.6

Table 2-2 continued.

	TSM [mg/L]	POC[a] [mg/L]	POC[a] [wt%]	atomic POC:PN[a]
median	22.56	0.47	3.25	7.8
min	3.52	0.15	1.34	3.7
max	32.23	1.30	5.68	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)

3.2 CuO oxidation products

Table 2-4 and 2-5 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 2-S4 and 2-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 16.66 mg/g dws. Only a few soil samples of the first terrace reach similar yields. Generally first terrace Σ8 contents vary from 0.78 to 8.81 mg/g dws (mean Σ8 2.64 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 2.62 and 4.87 mg/g dws). Suspended matter from 2009 to 2011 and surface sediment samples have CuO product yields in a similar range from 0.05 to 0.41 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 100mg OC (Λ8) for the different locations and sample types is presented in Figure 2-2. 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 0.14 and 3.62 mg/100mg OC over all phenol groups (Table 2-5). The Λ8 were lower in TSM from the summers 2009 and 2010 (<1.0 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. 2-2). 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. 2-2).

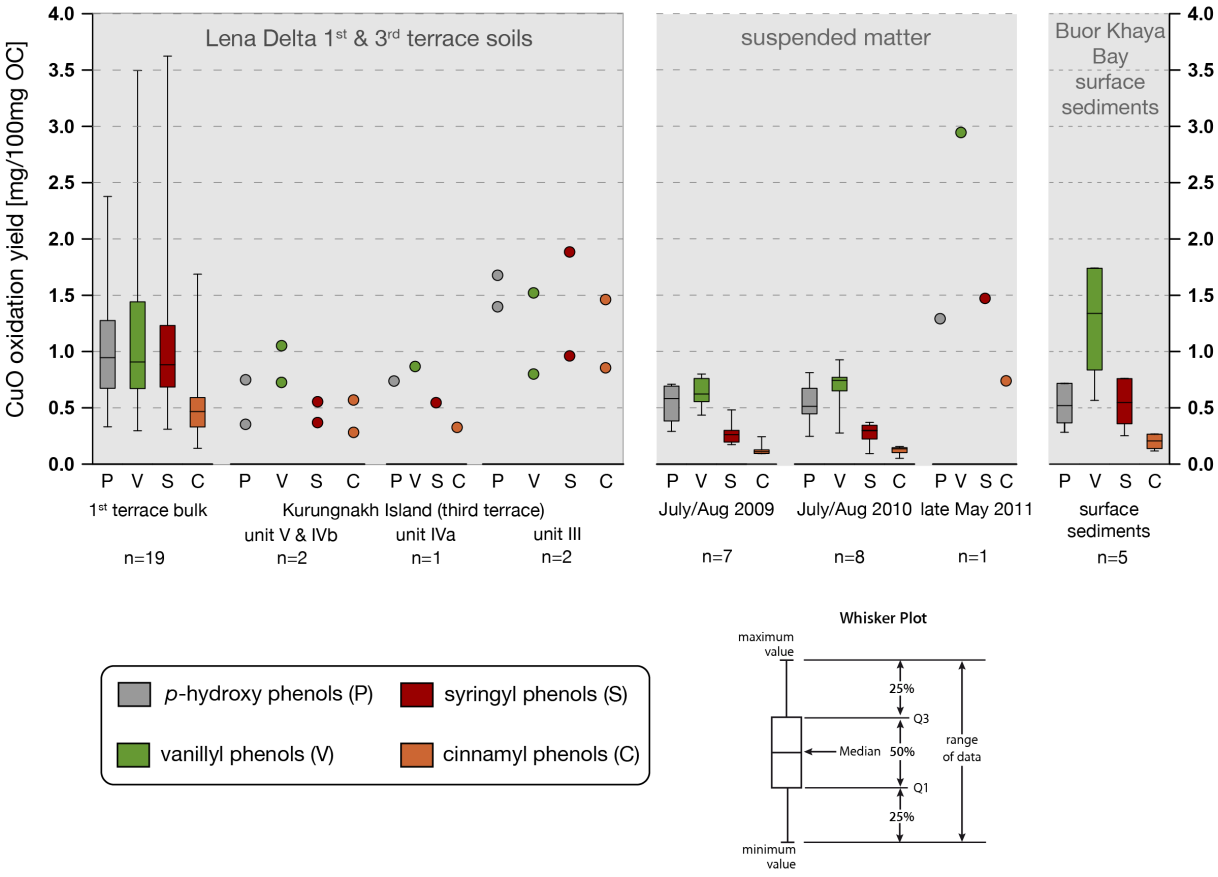

Figure 2-2. Carbon-normalized yields of phenols groups shown as Whisker plots when the number of samples was large enough and as individual samples for smaller numbers.

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 2-5 and 2-S5 and Fig. 2-S7 supplement). As shown in Fig. 2-4B 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. 2-4B and 2-5).

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) (Fig. 2-4A and 2-S7 supplement, Table 2-5). 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 2-5). $Ad/Al_{V,S}$ 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 21). 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 (EM) 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. 2-5 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 2-6) from Amon et al. (2012) and references therein, which covered the complete range measured in TSM and surface sediment samples (Fig. 2-4B).

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 2-7. 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. 2-1B). The contributions to the Buor Khaya Bay surface sediments vary to a lesser extent from 0.49 to 0.56 for gymnosperms.

Table 2-3. 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

Table 2-3 continued.

Sample code		OC [wt%]	TN [wt%]	atomic OC:TN
	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 2-4. 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*-hydroxy phenols (sum of *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone, *p*-hydroxybenzoic acid), Pn = *p*-hydroxyacetophenone.

	V	S	C	Σ8	P	Pn
	[mg/g dws]					
Lena Delta first terrace bulk, n=19						
mean	1.08	1.02	0.54	2.64	0.99	0.13
median	0.91	0.88	0.47	2.18	0.95	0.10
min	0.30	0.31	0.14	0.78	0.33	0.00
max	3.50	3.62	1.69	8.81	2.38	0.42
Lena Delta third terrace (Kurungnakh Island)						
S29 (unit V)	0.73	0.37	0.57	1.66	0.35	0.04
S17 (unit IVb)	1.05	0.55	0.28	1.89	0.75	0.02
S13 (unit IVa)	0.87	0.55	0.33	1.74	0.74	0.02
S22D (unit III)	0.80	0.96	0.86	2.62	1.40	0.13
S45 (unit III)	1.52	1.88	1.46	4.87	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

Table 2-4 continued.

	V	S	C	Σ8	P	Pn
	[mg/g dws]					
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

4 Discussion

4.1 Spatial and temporal patterns of Lena delta 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 20.2 mg/L, respectively) showed a high spatial and inter-annual variability (Fig. 2-3A-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 (Arctic GRO, www. www.arcticgreatrivers.org) and are taken at Zhigansk gauging station (66.77°N, 123.37°E) approximately 900km 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. 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 section 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 2-5) 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 2-2) suggest a considerable amount of nitrogen-rich plankton-derived OM is present in our TSM samples thus diluting L8 values relative to those from terrestrial source material.

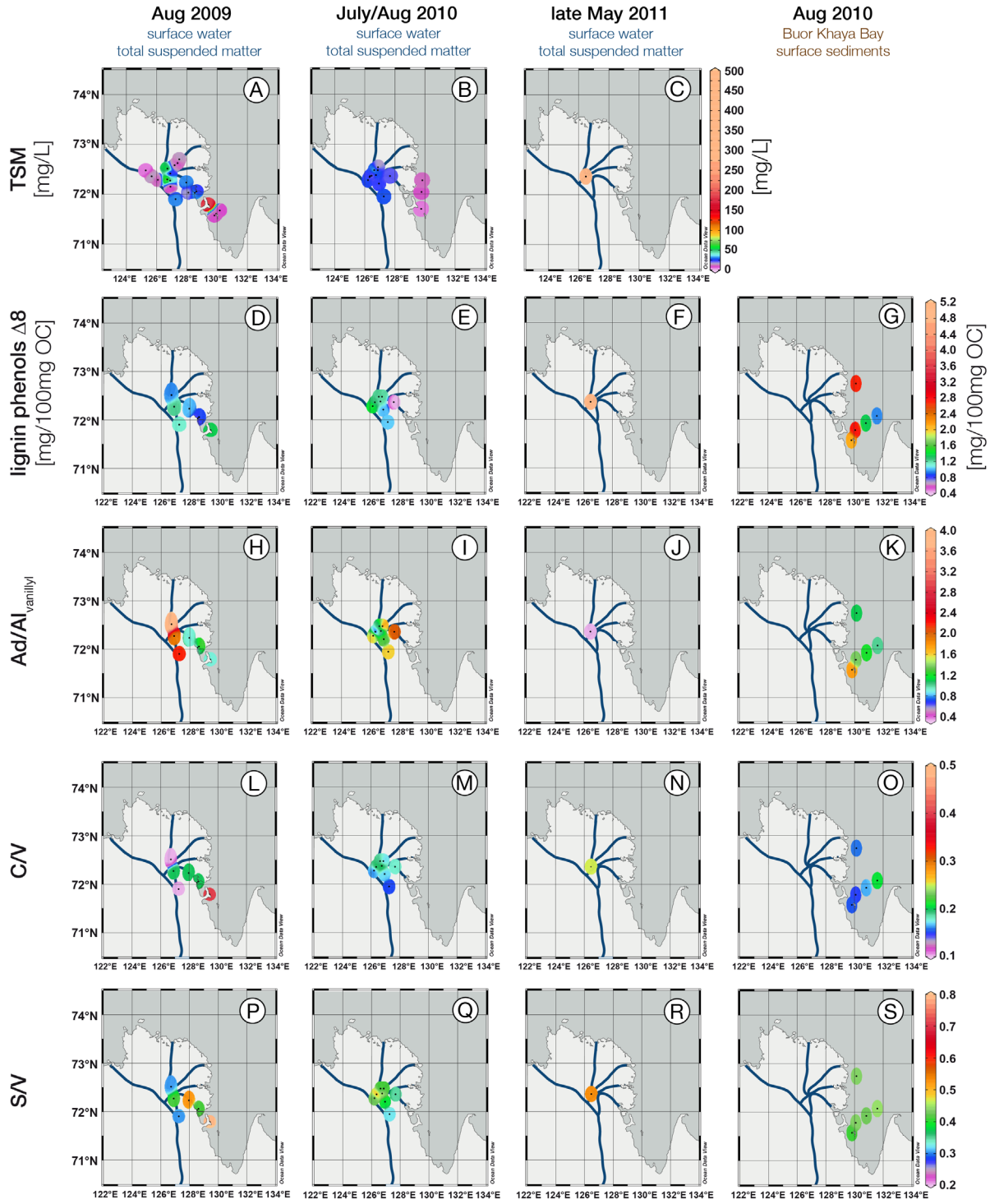

Figure 2-3. Spatial distribution of carbon-normalized lignin concentrations (Λ8) and lignin parameters of Lena Delta total suspended matter (TSM) and Buor Khaya Bay surface sediments. $Ad/Al_{vanillyl}$ = acid to aldehyde ratio of the vanillyl phenols, C/V = ratio of cinnamyl to vanillyl phenols, and S/V = ratio of syringyl to vanillyl phenols.

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. 2-4B, 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 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. 2-5, Table 2-5) 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 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. 2-5). The P/V ratios in TSM samples thus indicate that moss contribution is minor compared to a dominant non-woody angiosperm source.

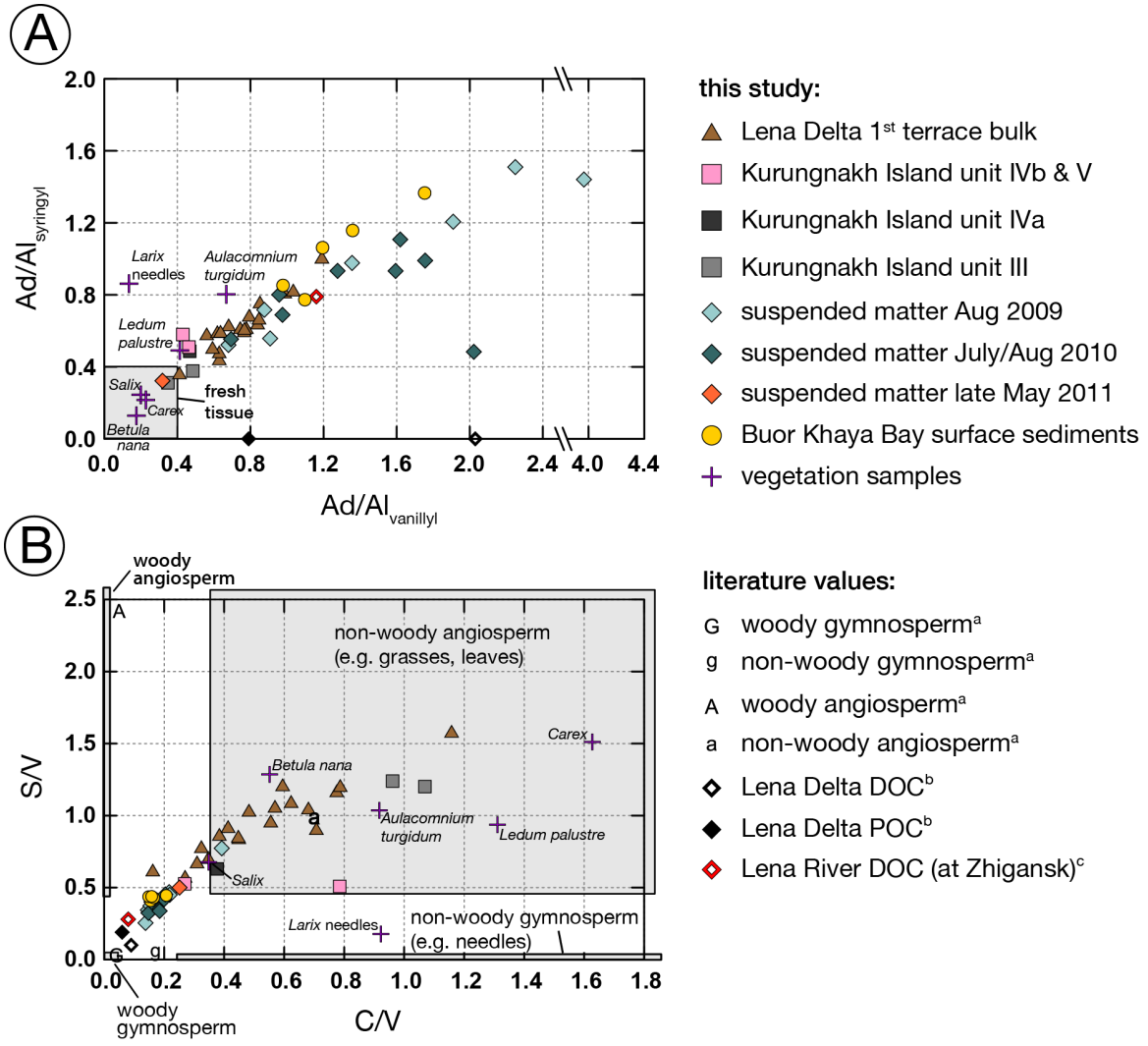

Figure 2-4. A) Lignin degradation indices (Ad/Al_V vs. Ad/Al_S) and B) vegetation source parameters (C/V vs. S/V). Note the different scales. Literature values: [a]table 4 in Amon et al. (2012) and references therein, [b]Lobbes et al. (2000), [c]Amon et al. (2012). Note in A) the two values on the Ad/Al_V axis where Ad/Al_S is zero, because there were no values given in Lobbes et al. (2000).

Table 2-5. 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-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 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

Table 2-5 continued.

	V	S	C	Λ8	P	Pn	Ad/Al_V	Ad/Al_S	C/V	S/V	P/V	Pn/P
	[mg/100 mg OC]											
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

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. 2-4A) 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.

Table 2-6. 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 2-4 and 2-5.

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).

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. 2-3G, Table 2-4 and 2-5), 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 source contribution 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_{at} ratios (Table 2-3). An offshore trend of decreasing OC:TN_{at} ratios likely reflects the increasing marine contributions by plankton as well as decreasing amounts of terrigenous material reaching offshore locations.

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. 2-3L-S and 2-4B) 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. 2-5, Table 2-5). 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.

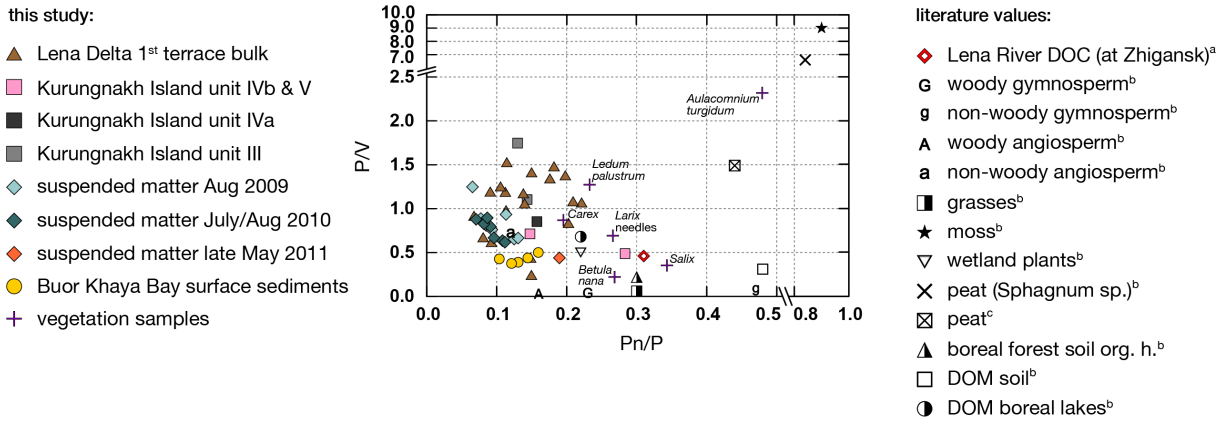

Figure 2-5. . Pn/P vs. P/V ratios of samples analyzed in this study and values from the literature. [a]Amon et al. (2012), [b]table 4 in Amon et al. (2012) and references therein, [c]Williams et al. (1998).

4.2.3 Degradation of terrigenous organic matter

The relatively high $Ad/Al_{V,S}$ ratios (0.77 to 1.75, Table 2-5, Fig. 2-3K) 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. 2-3K) 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. 2-3K, Table 2-5), which consists of Pleistocene ice complex deposits. 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), 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 2-7), 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 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 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.

Table 2-7. Results of unmixing model including relative abundances of V, S, and C phenols, median mixing coefficients and gymnosperm to angiosperm ratio. See tables 2-4 and 2-5 for abbreviations.

				median (500 iterations) mixing coefficients						
sample code	rel. V [%]	rel. S [%]	rel. C [%]	woody gymno-sperm	non-woody gymno-sperm	woody angio-sperm	non-woody angio-sperm	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
19	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

Table 2-7 continued.

sample code	rel. V [%]	rel. S [%]	rel. C [%]	median (500 iterations) mixing coefficients: woody gymno-sperm	non-woody gymno-sperm	woody angio-sperm	non-woody angio-sperm	median total gymno-sperm	median total angio-sperm	proportion of median gymnosperm/ angiosperm
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

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 contain more highly altered lignin and may have been affected by absorptive 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 (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.

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Supplement

Table 2-S1. Additional total suspended matter (TSM) samples, which were included into the mean TSM calculation, but not analyzed for CuO oxidation products.

Sample code	Sample & site description	Date of sampling	Latitude [dec]	Longitude [dec]	Water depth [m]
Lena River total suspended matter					
1	Olenyokskaya Channel	14-Aug-2009	72.4771	125.2856	0.5
2	Olenyokskaya Channel	14-Aug-2009	72.3598	125.6728	0.5
3	Lena River main channel	16-Aug-2009	72.1526	126.9159	0.5
5	Sardakhskaya/Trofimovskaya Channel	17-Aug-2009	72.5825	127.1891	0.5
6	Sardakhskaya Channel	17-Aug-2009	72.7002	127.4929	0.5
7	Sardakhskaya/Trofimovskaya Channel	17-Aug-2009	72.6268	127.3860	0.5
8	near Kurungnakh Island	18-Aug-2009	72.2904	126.0909	0.5
9	Lena River mai channel	19-Aug-2009	72.2987	126.7080	0.5
12	Bykovskaya Channel	20-Aug-2009	72.4140	126.9124	0.5
18	NE of Muostakh Island	22-Aug-2009	71.6761	130.1728	0.5
20	W of Muostakh Island	23-Aug-2009	71.6088	129.9393	0.5
21	close to Muostakh Island shoreline	23-Aug-2009	71.5750	129.8200	0.5
22	off Samoylov Island	30-July-2010	72.3650	126.4628	0.5
23	off Kurungnakh Island	30-July-2010	72.3392	126.3115	0.5
24	Trofimovskaya Channel	31-July-2010	72.5343	126.8794	0.5
33	Bykovskaya Channel	4-Aug-2010	72.3604	127.6765	0.5

Table 2-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

Table 2-S2 continued.

Sample code	TSM [mg/L]
11	52.51
12	20.20
13	29.26
14	33.32
15	15.72
16	19.56
17	174.92
18	6.72
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

Table 2-S3. Organic carbon (OC), total nitrogen (TN), and atomic OC to TN ratio ($OC:TN_{at}$) 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	$OC:TN_{at}$
	[m b.s.]	[wt%]		
Lena Delta first terrace bulk				
Gorgolevsky Island (L09-08)				
	0.02	5.39	0.18	35.06
	1.70	8.95	0.28	36.99
	3.40	7.91	0.28	33.55
Samoylov Island (L09-12)				
	0.45	9.24	0.45	23.73
	1.35	15.49	0.32	56.25
	2.50	17.14	0.39	51.51
	4.70	13.58	0.23	67.98
	5.80	11.69	0.24	56.47
Bykovsky Channel (L09-28)				
	0.30	6.14	0.19	33.13
	1.70	2.69	0.12	21.68
Baron Belkey Island (L10-04)				
	0.05	1.82	0.06	34.63
	0.28	1.13	0.03	38.11
	0.93	1.68	0.08	24.59
	1.25	5.48	0.26	24.45
	1.43	1.02	0.04	29.42
	2.15	4.59	0.16	32.81
	3.58	10.45	0.25	49.13
	4.70	7.61	0.24	37.68
	6.00	10.05	0.26	44.82

Table 2-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/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
	1.70	0.95	0.80	0.43	2.18	1.28	0.22
	3.40	1.13	0.70	0.18	2.01	1.04	0.07
Samoylov Island (L09-12)							
	0.45	1.02	0.80	0.33	2.14	1.09	0.24
	1.35	1.55	1.82	1.21	4.58	2.38	0.27
	2.50	0.91	1.44	1.05	3.39	1.25	0.25
	4.70	0.54	0.31	0.14	0.99	0.33	0.03
	5.80	0.67	0.61	0.47	1.75	0.56	0.11
Bykovsky Channel (L09-28)							
	0.30	1.44	1.25	0.55	3.24	1.41	0.16
	1.70	1.74	1.23	0.60	3.57	0.76	0.11
Baron Belkey Island (L10-04)							
	0.05	3.50	3.62	1.69	8.81	0.85	0.13
	0.28	0.34	0.31	0.14	0.79	0.41	0.04
	0.93	0.30	0.31	0.17	0.78	0.35	0.05
	1.25	0.57	0.68	0.45	1.70	0.67	0.08
	1.43	0.73	0.88	0.43	2.04	0.91	0.10
	2.15	1.51	1.02	0.47	3.00	1.02	0.08
	3.58	0.76	0.73	0.42	1.90	0.82	0.17
	4.70	0.89	0.98	0.56	2.43	0.95	0.13
	6.00	1.07	0.92	0.48	2.47	1.52	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

Table 2-S4 continued.

	Depth	V	S	C	Σ8	P	Pn
	[m b.s.]	[mg/100 mg OC]					
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

Table 2-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 2-4 and 2-5 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	2.14	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	3.39	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

Table 2-S5 continued.

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]											
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	2.04	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	1.90	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	0.09	0.99	0.52	0.05	0.91	0.56	0.22	0.47	0.65	0.12
14	0.43	0.20	0.09	0.73	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	1.35	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

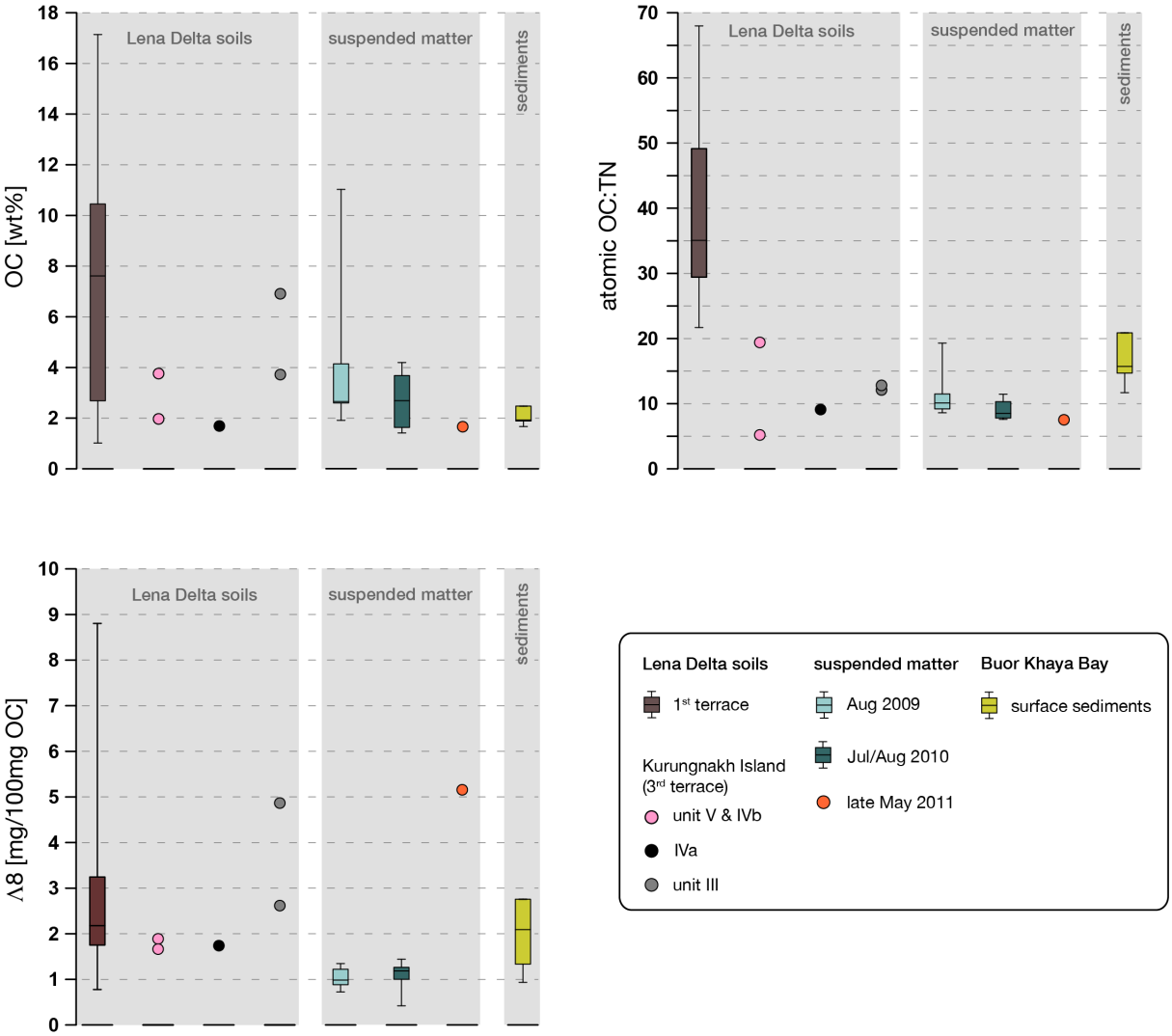

Figure 2-S6. Bulk elemental parameters of Lena Delta soils, suspended matter from surface waters, and surface sediments from the Buor Khaya Bay. The OC content and OC:TN ratios of Kurungnakh Island samples are from (Wetterich et al., 2008).

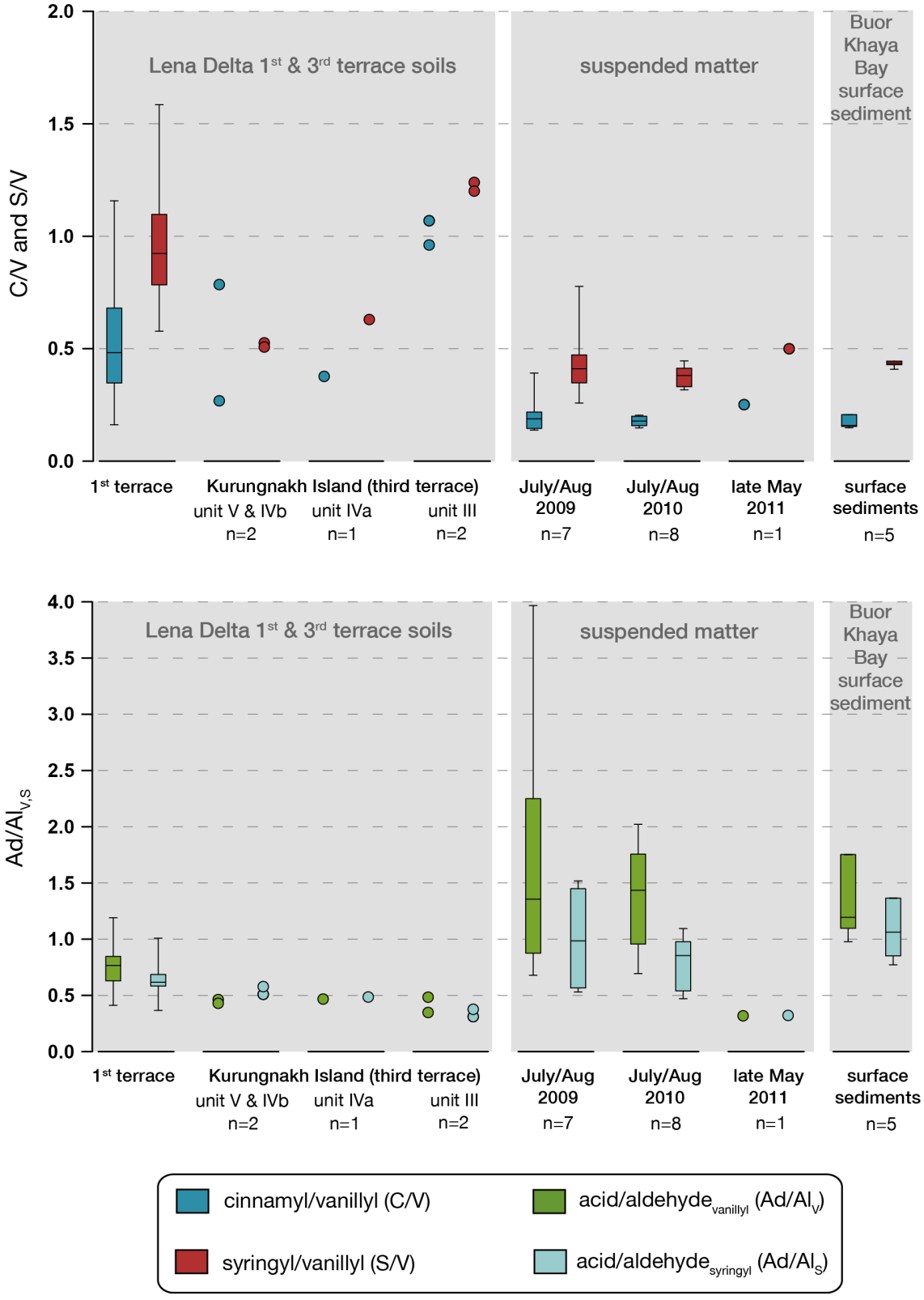

Figure 2-S7. Parameters for different vegetation contributions (C/V and S/V) and degradation indicators (Ad/Al$_{V,S}$) for Lena Delta soils, suspended matter from surface water, and Buor Khaya Bay surface sediments.

3 MANUSCRIPT II

Characterization of particulate organic carbon in the Lena River Delta and adjacent nearshore zone, NE Siberia. Part II: Radiocarbon inventories

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submitted to Biogeosciences Discussion

Abstract

Particulate organic matter (POM) derived from permafrost soils and transported by the Lena River represents a quantitatively important terrestrial carbon pool exported to Laptev Sea sediments (next to POM derived from coastal erosion). Its fate in a future warming Arctic, i.e. its remobilization and remineralization after permafrost thawing as well as its transport pathways to and sequestration in marine sediments is currently under debate. We present the first radiocarbon (^{14}C) data set of surface water POM within the Lena Delta sampled in summers 2009-2010 and spring 2011 (n=27 samples). The bulk $\Delta^{14}C$ concentrations varied from –55 to –391‰ translating into ^{14}C ages of 395 to 3920 years BP. We further estimated the fraction of phytoplankton-derived POM to our samples based on 1) particulate organic carbon to particulate nitrogen ratios (POC:PN) and 2) on the stable carbon isotope ($\delta^{13}C$) composition of our samples. Assuming that this phytoplankton POM has a modern ^{14}C signature we inferred the $\Delta^{14}C$ concentrations of the soil-derived POM fractions. The results ranged from –306 to –768‰ (i.e. 2870 to 11680 ^{14}C years BP) for the POC:PN-based scenario and from –191 to –704‰ (i.e. 1640 to 9720 ^{14}C years BP). Despite the limitations of our approach, the estimated $\Delta^{14}C$ concentrations of the soil-derived POM fractions seem to reflect the heterogeneous ^{14}C signal of the Lena River catchment soils covering a range from Holocene to Pleistocene ages. We therefore propose a typical isotopic signature of riverine soil-derived POM with a $\delta^{13}C$ of –26.6 ± 1.1‰ deduced from our data of Lena Delta soils and published values, and a $\Delta^{14}C$ concentration of –362 ±

123‰ deduced from our $\delta^{13}C$-based estimates. These data can help to improve the dual-carbon-isotope simulations used to quantify contributions from riverine soil POM, Pleistocene ice complex POM from coastal erosion, and marine POM in Siberian shelf sediments.

1 Introduction

Huge amounts of soil organic carbon are currently stored frozen in permafrost soils of the high northern latitudes (e.g. Tarnocai et al., 2009; Zimov et al., 2009) and excluded from biogeochemical cycling. Due to recent observed and projected amplified warming of the Arctic (ACIA, 2005; Serreze et al., 2000) carbon cycling and the fate of organic carbon released from permafrost soils have received growing attention (e.g. Guo et al., 2007; McGuire et al., 2009; Schuur et al., 2008; 2009; Zimov et al., 2006).

Increasing permafrost temperatures, thaw depth in summer (active layer depth), increasing river runoff (Boike et al., 2013; McClelland et al., 2012; Peterson et al., 2002), and increasing length of open water season (Markus et al., 2009) affecting coastal erosion of permafrost deposits will likely lead to enhanced mobilization and export of old, previously frozen organic matter (OM) to the Arctic shelf seas. The understanding of the different terrestrial OM sources (e.g. fresh vegetation, surface soils, Pleistocene ice complex), their age and quality has significantly improved over the last decade (e.g. Guo et al., 2007; Vonk et al., 2010). The use of carbon isotopes ($\delta^{13}C$, $\Delta^{14}C$) of dissolved and particulate organic matter as well as individual biomarkers has helped characterizing and distinguishing these different carbon pools, e.g. the old, yet little degraded Pleistocene ice complex-derived OM and comparatively younger and more degraded fluvial OM reaching the Siberian shelf seas (Feng et al., 2013; Guo et al., 2004; Gustafsson et al., 2011; Karlsson et al., 2011; Vonk et al., 2012; 2010).

However, particularly in Siberia ^{14}C data on riverine suspended particulate organic matter (POM) is only very sparsely available. To our knowledge there are no POM ^{14}C concentrations published which were sampled directly in Siberian rivers besides a few samples from the Kolyma River (supplementary data of Vonk et al., 2012). Available POM ^{14}C concentrations for Siberia are from offshore the deltas of the Lena (Karlsson et al., 2011) and Kolyma Rivers (Vonk et al., 2010) and inferred from a sediment core taken in a floodplain lake of the Ob' River (Dickens et al., 2011). Due to settling of POM and marine primary production fueled by the riverine nutrients, the ^{14}C concentrations of samples taken off the river mouths are already altered from the "original" river signal. In contrast to Siberia, there are detailed studies on riverine POM ^{14}C concentrations in the Yukon and Mackenzie Rivers in the North American Arctic (Goñi et al., 2005; Guo et al., 2007; 2006). Here, the POM was found to be significantly older than the dissolved organic matter

(DOM) of these rivers and interpreted to be derived from riverbank erosion and thawing permafrost soils compared to a modern vegetation source of DOM (Guo et al., 2006; 2007). Against the backdrop of a warming Arctic (ACIA, 2005; IPCC 2007) and the projected release of old OM in the future presumably as POM rather than DOM (Guo et al., 2007), it is important to assess the age heterogeneity carried by riverine POM and sequestered in the nearshore zone today. This will be an important benchmark to distinguish catchment related changes caused by increasing temperatures from the natural variability of the river system.

In contrast to sedimentary OM, POM provides limited spatial and temporal snapshots of its OM properties. However, it has been shown that riverine POM in arctic rivers carries an integrated signal from their permafrost watersheds and represents the environmental characteristics (e.g. Goñi et al., 2000; Lobbes et al., 2000; Vonk and Gustafsson, 2009). See also Winterfeld et al. 2014 submitted as companion paper dealing with lignin phenol compositions of POM. Despite the fact that Lena River POM flux is an order of magnitude smaller than its DOM flux it is more likely to transports the climate change signal from permafrost soils of the river catchment (Guo et al., 2007). Also, it has been proposed that the POM pool could be as important as the DOM pool for arctic carbon cycling, because of its possibly high degradation rates in the water column compared to DOM (Sanchéz-García et al., 2011; van Dongen et al., 2008).

Here we present the second part of a study on particulate OM in the Lena Delta, Siberia (see Winterfeld et al. 2014; submitted as companion paper). Our POM samples taken in three consecutive years (2009-2011) in the spring and summer seasons add up to the existing data on elemental and stable carbon ($\delta^{13}C$) composition as well as provide a first POM ^{14}C data set for the Lena Delta. Because riverine and marine POM concentrations are usually too low for source specific biomarker ^{14}C analysis, the available ^{14}C data is from bulk OM. This could result in a considerable age bias depending on the contribution of phytoplankton OM with a rather enriched (modern) ^{14}C signature to the individual samples. We used different approaches to estimate the fraction of soil and plankton-derived OM in our POM samples and corrected the ^{14}C concentration for the soil-derived fraction of POM transported by the Lena River in summer and spring. The corrected ^{14}C composition of soil-derived POM will further help to define the typical isotopic signature of river POM more accurately for modeling riverine OM contributions to Laptev Sea shelf sediments

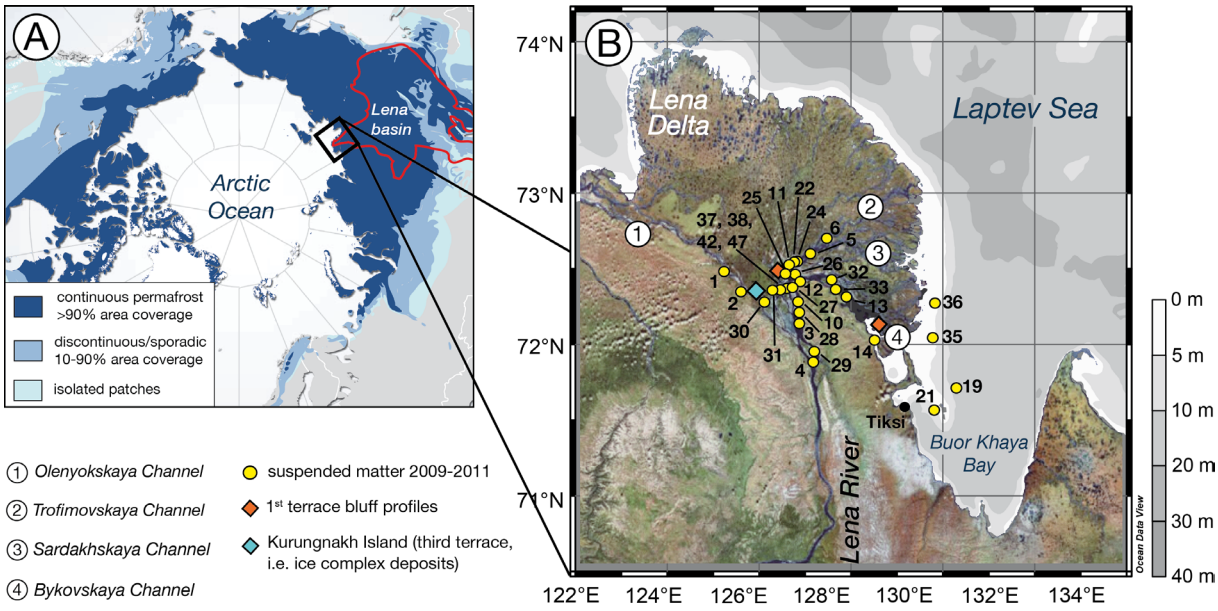

Figure 3-1. A) Lena River catchment area within the northern hemisphere permafrost zone (map by Hugo Ahlenius, UNEP/GRID-Arendal, see www.grida.no/graphicslib/detail/permafrost-extent-in-the-northern-hemisphere_1266; source data from Brown et al. 1998), B) Lena Delta and Buor Khaya Bay sampling sites from 2009 to 2011 analyzed for radiocarbon content (see also table 2-1).

2 Material and Methods

2.1 Study Area

A detailed description of the Lena River watershed and Lena Delta can for example be found in the first paper of this study dealing with the lignin composition of OM in the Lena Delta (Winterfeld et al., 2014, submitted as companion paper).

In short, the Lena River is one of the largest Russian Arctic rivers draining a watershed of ~2.46 × 10^6 km^2 in central Siberia into the Laptev Sea. Continuous permafrost makes up about 72-80% of the drainage area (Amon et al., 2012; Zhang et al., 2005) storing huge amounts of old OM. The permafrost acts as a water impermeable layer and thus affects the regional hydrology and hydrochemistry. The Lena River water discharge and related dissolved and particulate load discharge are highest during spring ice-breakup and snow melt in late May to June while summer and winter discharges are lower (Rachold et al., 2004). The mean annual water discharge is ~588 km^3 for the years 1999 to 2008 (Holmes et al., 2012). 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 terrigenous OM delivered to the Laptev Sea is the

thermal erosion of ice- and OM-rich Pleistocene ice complex deposits along the coast (see Gustafsson et al., 2011; Mueller-Lupp et al., 2000; Rachold and Hubberten, 1999; Rachold et al., 2004). Recently, it has been shown that the annual supply of total organic carbon from ice complex deposits along the Laptev Sea coast by erosion is ~0.66 Tg/yr (Günther et al., 2013).

The Lena River Delta is the largest arctic delta (~32,000 km^2). It is characterized by a polygonal tundra landscape with active floodplains. Water and sediment discharge are not equally distributed through the several delta channels. 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 (fig. 1B), 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; Charkin et al., 2011 and references therein; Ivanov and Piskun, 1999).

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 (Table 3-1, Fig. 3-1B) in and along the channels of highest discharge. Permafrost soil samples from the first delta and surface water total suspended matter (TSM) were collected during three expeditions in August 2009, July/August 2010, and in late May and late June/early July 2011. 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. 3-1B, 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, 0.45 µm membrane) for particulate organic carbon (POC) and nitrogen (PN) analysis as well as carbon isotope analysis. Additionally, one water sample of 20 L from the spring freshet in 2011 was 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.

The soil samples were stored in pre-combusted glass jars (4.5h at 450°C) and GF/F filters were either stored in pre-combusted petri dishes (Ø 47 mm) or wrapped in pre-combusted aluminum foil. All samples were kept frozen at –20°C during storage and transport until analysis.

Table 3-1. Samples presented in this study analyzed for stable and radiocarbon isotope composition. Information on additional samples analyzed for organic carbon content can be found in Winterfeld et al. (2014), submitted as companion paper, in table 2-1 and 2-S1. Bluff height is given in meters above river level [m a.r.l.] measured in August 2009. 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]
Soil samples						
L09-12	Samoylov Island, 5 depths sampled	17-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.
Total suspended matter						
1	Olenyokskaya Channel	14-Aug-2009	72.4772	125.2856	n.a.	0.5
2	Olenyokskaya Channel	14-Aug-2009	72.3598	125.6728	n.a.	0.5
3	Lena River main channel	16-Aug-2009	72.1526	126.9160	n.a.	0.5
4	Lena River main channel south of Tit Ari Island	16-Aug-2009	71.9040	127.2544	n.a.	0.5
5	Sardakhskaya/Trofimovskaya Channel	17-Aug-2009	72.5825	127.1891	n.a.	0.5
6	Sardakhskaya Channel	17-Aug-2009	72.7002	127.4930	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
12	Bykovskaya Channel	20-Aug-2009	72.4140	126.9124	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
19	NE of Muostakh Island	22-Aug-2010	71.7062	130.2900	n.a.	0.5
21	close to Muostakh Island shoreline	23-Aug-2010	71.5750	129.8200	n.a.	0.5
22	close to Samoylov Island	30-Jul-2010	72.3650	126.4628	n.a.	0.5
24	Sardakhskaya/Trofimovskaya Channel	31-Jul-2010	72.5343	126.8794	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

Table 3-1 continued.

Sample code	Sample & site description	Date of sampling	Latitude [dec]	Longitude [dec]	Bluff height [m a.r.l.]	Water depth [m]
32	Lena River Bykovskaya Channel	3-Aug-2010	72.3604	127.6761	n.a.	0.5
33	Bykovskaya Channel	3-Aug-2010	72.3604	127.6765	n.a.	0.5
35	offshore Lena Delta	6-Aug-2010	72.0379	129.7694	n.a.	0.5
36	offshore Lena Delta	6-Aug-2010	72.2753	129.8248	n.a.	0.5
37	Lena River main channel off Samoylov Island	29-May-2011	72.3651	126.4757	n.a.	0.5
38	Lena River main channel, south of Stolb	26-Jun-2011	72.3705	126.6538	n.a.	0.5
42	close to Samoylov Island	30-Jun-2011	72.3681	126.4738	n.a.	0.5
47	close to Samoylov Island	2-Jul-2011	72.3681	126.4738	n.a.	0.5

2.3 Laboratory analyses

Soil and sediment samples were freeze-dried, homogenized, and subsampled for elemental analysis. All filters were oven-dried at 40°C for 24h.

2.3.1 Elemental analyses

Weight percent organic carbon (OC) and total nitrogen (TN) content of soil samples were determined by high temperature combustion after removal of carbonates as described by Goñi et al. (2003). TSM samples were analyzed for OC and TN at the Alfred Wegener Institute in Bremerhaven, Germany, using the same protocol.

2.3.2 Carbon isotope analysis ($\delta^{13}C$, $\Delta^{14}C$)

Samples were radiocarbon-dated at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution, USA. Bulk sediment samples and filters with TSM were submitted unprocessed. The Radiocarbon analysis at NOSAMS were carried out using standard methods (McNichol et al., 1994). Results are reported as $\Delta^{14}C$, conventional radiocarbon ages (years BP), and fraction modern carbon (fMC) including the correction for isotope fractionation (Stuiver and Polach, 1977).

The stable carbon isotope composition ($\delta^{13}C$) was measured on splits of the CO_2 gas of the samples generated prior to graphite reduction at NOSAMS using a VG Optima IRMS. Results are reported in per mil (‰) relative to VPDB.

3 Results

3.1 Elemental composition

The organic carbon (OC) and total nitrogen (TN) concentrations of the first terrace soil samples can be found in tables 2-3 and 2-S3 in Winterfeld et al. (2014), submitted as companion paper.

The surface water POC concentrations within the delta showed a high spatial and interannual variability similar to the TSM concentrations of the respective samples (see table 2-2 and 2-S2 in Winterfeld et al., 2014; submitted as companion paper). The mean POC concentration for August 2009 was 1.24 mg/L (n=20, range 0.35-7.24 mg/L) and corresponding POC content was 7.3 wt% (range 1.9-37.7 wt%, table 3-2 and table 3-S1 supplement). The POC contents for July/August 2010 and June/July 2011 were lower than in 2009 with mean concentrations of 0.63 mg/L (n= 13, 0.17-1.30 mg/L) and 3.4 wt% (1.3-5.7 wt%) as well as 0.74 mg/L (n=9, 0.29-1.51 mg/L) and 4.3 wt% (3.2-5.0 wt%), respectively. The single sample from late May 2011 (sample ID 37) showed highest POC concentration per liter (8.2 mg/L) of all presented samples with a related POC content of 1.7 wt%. Our POC data are well within the range of values reported for the Lena Delta before (Cauwet and Sidorov, 1996; Rachold and Hubberten, 1999; Semiletov et al., 2011). The two samples from the Buor Khaya Bay surface waters showed the lowest POC concentrations per liter, i.e. 0.37 mg/L (sample 35) and 0.15 mg/L (sample 36) with corresponding 4.4 and 1.5 wt% POC, respectively (Table 2 and S1 supplement). The considerable drop of POC (and TSM) concentrations offshore the delta is due to flocculation and settling of TSM in the zone of fresh and salt water mixing (e.g. Lisitsyn, 1995) and was also observed during other years of sampling (e.g. Cauwet and Sidorov, 1996; Semiletov et al., 2011).

The atomic particulate organic carbon (POC) to particulate nitrogen (PN) ratios (POC:PN) of samples taken in summer 2009 were slightly higher than for summer 2010 samples with mean values of 9.6 (n=20, 6.8-19.3) and of 8.0 (n=13, 5.0-10.3, Table 3-2 and 3-S1 supplement), respectively. The POC:PN ratios of samples taken in June/July 2011 were rather similar to the July/August samples with a mean of 7.8 (n=9, 5.9-9.7). The sample from late May 2011 had a POC:PN ratio of 7.5.

Table 3-2. Particulate organic carbon (POC) contents in Lena Delta surface water (2009 to 2011) given in milligram per liter (mg/L) and percent based on sediment dry weight (wt%) as well as atomic particulate organic carbon (POC) to particulate total nitrogen (PN) ratios. Data on individual samples can be found in the supplement (table 3-S2).

		POC [mg/L]	POC [wt%]	atomic POC:PN
Lena Delta Aug 2009		*n=21*	*n=20*	*n=21*
	mean	1.21	7.3	9.6
	median	0.83	4.7	9.2
	min	0.35	1.9	6.8
	max	7.24	37.7	19.3
Lena Delta Jul/Aug 2010		*n=13*	*n=13*	*n=13*
	mean	0.57	3.37	7.6
	median	0.47	3.25	7.8
	min	0.15	1.34	3.7
	max	1.30	5.68	10.3
Lena Delta late May 2011				
sample code:	37	8.20	1.66	7.5
Lena Delta late Jun/early Jul 2011		*n=9*	*n=9*	*n=9*
	mean	0.74	4.32	7.8
	median	0.69	4.61	7.8
	min	0.29	3.20	5.9
	max	1.51	4.99	9.7

3.2 Carbon isotope inventories

The stable carbon ($\delta^{13}C$) and radiocarbon (^{14}C) results are shown in Table 3-3. The radiocarbon data presented here will predominantly be discussed in terms of $\Delta^{14}C$ in per mil (‰). Additionally, the fraction modern carbon (*fMC*) and ^{14}C ages in years before present (yrs BP) are given in table 3-3)

3.2.1 Stable carbon isotope composition ($\delta^{13}C$)

The two soil profiles from the first delta terrace showed $\delta^{13}C$ values between –27.0‰ and –25.1‰ with a mean of –26.1‰, (n = 7, table 3), which is within the range observed for Holocene soils in the delta (e.g. Schirrmeister et al., 2011 and references therein). The Lena Delta surface water POM $\delta^{13}C$ varied spatially and annually as described for the organic carbon contents above. POM from August 2009 showed more depleted $\delta^{13}C$ values compared to the other years, ranging from –34.2‰ to –28.8‰ (mean value = –30.6‰, n = 12). July/August 2010 and June/July 2011 POM isotopic compositions ranged from –30.2‰ to –28.3‰ (mean value = –29.2‰, n = 11) and from –29.3‰ to –28.3‰ (mean value = –28.7 ‰, n = 3), respectively. The isotopically most enriched POM $\delta^{13}C$ value of –26.5‰ was determined for the sample from late May 2011 (Table 3-3). The $\delta^{13}C$ of Buor Khaya Bay surface water POM in August 2010 could only be determined for one of the samples, i.e. sample 36 with –30.2‰.

3.2.2 Radiocarbon ($\Delta^{14}C$) composition

The $\Delta^{14}C$ concentrations of the two soil profiles decreased with depth from –197 to –377‰ for the riverbank profile L09-12 and from –204 to –466‰ for profile L09-28 (Table 3-3, Fig. 3-3A). The corresponding ^{14}C ages for both profiles together ranged from 1710 to 4900 years BP. Within profile L09-12 on Samoylov Island an age reversal was observed for the two oldest samples (Table 3-3), which most likely is due to allochthonous material that was transported to the delta from an upstream location. The same age reversal on Samoylov Island was also observed by Kuptsov and Lisitsin (1996). Overall, our $\Delta^{14}C$ concentrations reflect the late Holocene formation of these soils and fits within the range of ages determined for the Lena Delta first terrace (Bolshiyanov et al., 2014; Kuptsov and Lisitsin, 1996; Schwamborn et al., 2002).

As with other TSM parameters, the POM $\Delta^{14}C$ concentrations showed strong spatial and interannual variability. Lena Delta POM concentrations varied from –262‰ to –55‰ in August 2009 (mean of –158‰, n=12), from –391‰ to –167‰ in July/August 2010 (mean of –200‰, n=11), and from –154‰ to –144‰ in June/July 2011 (mean of –150‰, n=3). The sample from late May 2011 showed a $\Delta^{14}C$ concentration of –306 ‰ and the Buor Khaya Bay surface samples of –176‰ (sample 35) and –143‰ (sample 36, Table 3-3, Fig. 3-2R-S). Overall these ^{14}C compositions covered a range of ^{14}C ages from 395 to 3920 years BP. The samples with the most depleted $\Delta^{14}C$ values of –262‰ (sample 1) and –391‰ (sample 31) were taken close to the Pleistocene ice complex deposits of Kurungnakh Island (Fig. 3-1B), which likely contributed to the local POM in the Lena River surface water.

Table 3-3. Stable carbon isotope ($\delta^{13}C$) and radiocarbon composition (^{14}C) of Lena Delta first terrace bluff profiles and surface water particulate organic matter (2009-2011). Bluff profile samples are given in meters below bluff surface (m b.s.).

Sample code	$\delta^{13}C$ [‰ VPDB]	*fMC*[1]	1σ *fMC*	$\Delta^{14}C$ [‰]	conv. ^{14}C age[2] [yrs BP]	1σ ^{14}C age [yrs BP]	Lab ID
Lena Delta first terrace							
L09-12, 0.45m b.s.	-26.8	0.8084	0.0039	-197	1710	40	OS-84097
L09-12, 1.35m b.s.	-26.3	0.7311	0.0029	-274	2510	30	OS-84073
L09-12, 2.50m b.s.	-25.2	0.7023	0.0025	-303	2840	30	OS-84072
L09-12, 4.70m b.s.	-27.0	0.5708	0.0024	-433	4500	35	OS-84071
L09-12, 5.80m b.s.	- 25.1	0.6275	0.0027	-377	3740	35	OS-84070
L09-28, 030m b.s.	-26.1	0.8015	0.0026	-204	1780	25	OS-84074
L09-28, 070m b.s.	-26.6	0.5430	0.0028	-461	4900	40	OS-84087
Lena Delta Aug 2009							
1	-30.5	0.7436	0.0029	-262	2380	30	OS-84096
2	-32.6	0.8173	0.0034	-189	1620	35	OS-84090
3	-30.9	0.8735	0.0031	-133	1090	30	OS-84093
4	-29.6	0.8259	0.0029	-180	1540	25	OS-84091
5	-31.3	0.8717	0.0031	-134	1100	30	OS-84098
6	-30.5	0.8524	0.0032	-154	1280	30	OS-84127
10	-29.8	0.8419	0.0032	-164	1380	30	OS-84101
11	-28.9	0.8458	0.0031	-160	1340	30	OS-84100
12	-30.6	0.8913	0.0031	-115	925	25	OS-84102
13	-29.9	0.8672	0.0036	-139	1140	30	OS-84133
14	-28.8	0.7971	0.0031	-209	1820	30	OS-84099
19	-34.2	0.9522	0.0042	-55	395	35	OS-84086
21	-27.1	0.8210	0.0028	-185	1580	25	OS-84088
mean	-30.4	0.8462	0.0032	-160	1353	30	
standard deviation	1.7	0.0480	0.0003	48	457	3	
Lena Delta TSM Jul/Aug 2010							
22	-29.7	0.8344	0.0029	-172	1450	30	OS-95088
24	-29.4	0.8201	0.0034	-186	1590	35	OS-95100
25	-28.3	0.8288	0.0030	-177	1510	30	OS-95266
26	-28.9	0.8001	0.0028	-206	1790	30	OS-95382
27	-28.9	0.8386	0.0034	-167	1410	30	OS-95268
28	-28.8	0.8046	0.0035	-201	1750	35	OS-95380

Table 3-3 continued.

Sample code	$\delta^{13}C$ [‰ VPDB]	*fMC*[1]	1σ *fMC*	$\Delta^{14}C$ [‰]	conv. ^{14}C age[2] [yrs BP]	1σ ^{14}C age [yrs BP]	Lab ID
29	-28.9	0.8353	0.0117	-171	1440	110	OS-94853
30	-30.2	0.8389	0.0033	-167	1410	30	OS-95238
31	-28.6	0.6139	0.0021	-391	3920	25	OS-95239
32	-29.6	0.8390	0.0033	-167	1410	30	OS-95267
33	-29.8	0.8125	0.0144	-193	1670	140	OS-94857
35	n.d.	0.8299	0.0035	-176	1500	35	OS-95377
36	-30.4	0.8628	0.0150	-143	1180	140	OS-94858
mean	-29.3	0.8122	0.0056	-194	1695	54	
standard deviation	0.6	0.0594	0.0045	59	661	42	
Lena Delta TSM late May 2011							
37	-26.5	0.6988	0.0028	-306	2880	30	OS-94760
Lena Delta TSM late June/early July 2011							
38	-28.3	0.8623	0.0030	-144	1190	30	OS-95378
42	-29.3	0.8558	0.0033	-151	1250	30	OS-95384
47	-28.5	0.8519	0.0117	-154	1290	110	OS-94854
mean	-28.7	0.8567	0.0060	-150	1243	57	
standard deviation	0.4	0.0043	0.0040	4	41	38	

4 Discussion

4.1 Origin of organic matter in the Lena Delta

4.1.1 Particulate carbon to nitrogen ratios (POC:PN)

Riverine particulate organic matter consists of a heterogeneous mixture derived from two major sources, i.e. terrestrial (e.g. fresh vegetation and litter, surface and deep soils horizons) and aquatic (phytoplankton/bacterial primary production). The terrestrial OM in the Lena River catchment can further be differentiated into two pools of different age: the late Pleistocene

organic-rich ice complex or Yedoma deposits, particularly in the lowlands (0-400 m; e.g. Grosse et al., 2013) and the Holocene permafrost soils. POC:PN ratios as well as $\delta^{13}C$ and ^{14}C signatures of bulk OM can be used to estimate terrestrial and aquatic contributions (e.g. Hedges and Oades, 1997). However, due to overlaps in soil/plant and algal/bacterial signatures it might be difficult to unambiguously differentiate between terrestrial and aquatic sources.

Our POC:PN ratios from the summers 2009 and 2010 as well as spring 2011 vary largely throughout the delta (Table 3-2, Fig. 3-S2) similar to the TSM and lignin phenol concentrations sampled during the same field trips (Winterfeld et al. 2014, submitted as companion paper). The ratios range from 3.7 to 19.3 for all samples and seasons with mean atomic POC:PN ratios of 9.6 (2009), 7.6 (2010), and 7.8 (2011). Low POC:PN ratios, i.e. ~6 generally indicate high contributions from phytoplankton and/or bacterial primary production while ratios >20 are indicative of soil and plant contributions (e.g. Hedges et al., 1997; Meyers and Lallier-Vergés, 1999). Based on these end-members, our data from the summer and spring seasons suggest a considerable fraction of primary production OM to be present in our samples. Using a simple two end-member mixing model with POC:PN = 6 for primary production OM and 20.2 for soil-derived OM (mean of OC:TN ratios from the first delta terrace of this study and delta soils as well as tundra and taiga soils south of the delta from Zubrzycki, 2013), our soil fractions vary from 0.06 to 0.94 (mean 0.26) in 2009, from 0.10 to 0.30 (mean 0.16) in 2010, and from 0.08 to 0.26 (mean 0.14) in 2011.

The total flux of primary production OM in the Lena River is thought to be negligible due to low light penetration in the turbid waters (Cauwet and Sidorov, 1996; Sorokin and Sorokin, 1996). Yet, the surface water layer from which we took our TSM samples is characterized by an abundance of riverine plankton (Kraberg et al., 2013; Sorokin and Sorokin, 1996), which could explain the small soil-derived OM fraction.

However, due to possible sorption of inorganic nitrogen to clay minerals (Schubert and Calvert, 2001) our calculated POC:PN ratios might be too low, underestimating the soil-derived OM fraction. This will be discussed in more detail in section 4.3.1. Another possibility for lower, but mainly soil derived POC:PN ratios could be the selective degradation of labile OM compared to total nitrogen (Kuhry and Vitt, 1996).

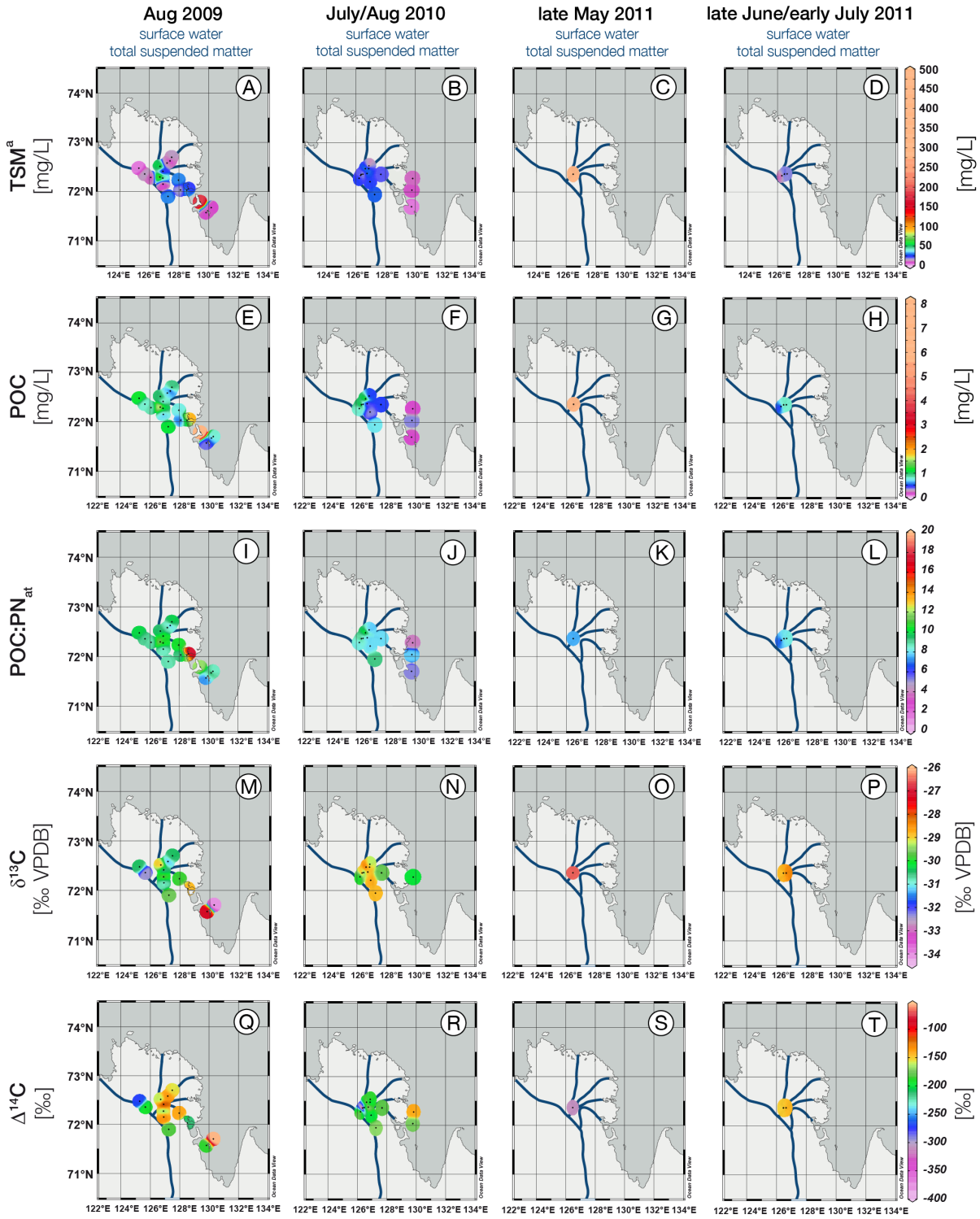

Figure 3-2. Spatial distribution of organic carbon concentrations, POC:PN ratios and stable and radiocarbon isotopic composition in surface water from 2009-2011. TSM concentrations of the years 2009 to late May 2011 (panels A-C) taken from Winterfeld et al. (2014), submitted as companion paper.

4.1.2 Stable carbon isotopes ($\delta^{13}C$)

The $\delta^{13}C_{POM}$ composition of our samples taken in 2009-2011 varies over a broad range (–31.3 to –26.5‰, Table 3-3), which is similar to $\delta^{13}C_{POM}$ values previously published by Rachold and Hubberten (1999) for the Lena Delta and Lena River upstream the delta (–31.3 to –25.7‰, July/August 1994/95), by ArcticGRO (www.arcticgreatrivers.org) ~900km upstream the Lena Delta at Zhigansk (–30.3 to –25.2‰, May-August 2004-2010), and by Semiletov et al. (2011) for the Lena Delta and Lena River (–30.0 to –25.0‰, August-September 1995-2008).

In general, the more enriched $\delta^{13}C_{POM}$ values (around –27‰) reflect the dominant contribution from C3 plants and soils (e.g. Hedges et al., 1997) from the river catchment. The more depleted $\delta^{13}C_{POM}$ values (<–29‰) point to mixing with riverine plankton utilizing dissolved inorganic carbon (DIC) with depleted $\delta^{13}C$ signatures as suggested for the Lena River (Alling et al., 2012; Rachold and Hubberten, 1999). Analogous to the POC:PN ratios, the $\delta^{13}C_{POM}$ compositions point to a considerable contribution of primary production OM to our samples from 2009-2011. Possible end-member calculation and implications for the ^{14}C concentration of the POM samples will be further discussed below in section 4.3.2.

4.2 Radiocarbon composition of POM ($^{14}C_{POM}$) in the Lena Delta

Terrestrial POM enters a river predominantly by physical weathering of adjacent soils (Raymond and Bauer, 2001 and references therein). Compared to vegetation utilizing modern atmospheric $^{14}CO_2$, the bulk POM of soil is pre-aged. The specific residence time of POM in the soil before entering the river depends on various environmental factors like humidity, temperature, topography, soil type, size and topography of the catchment area (e.g. Kusch et al., 2010; Oades, 1988; Raymond and Bauer, 2001; Trumbore, 2009; 1993). Furthermore, the fluvial transport of POM (and TSM) is governed by hydrological characteristics like runoff, discharge and flow velocity, sedimentation along riverbanks and floodplains as well as re-suspension of deposited material. Therefore, the age of terrestrial POM is a combination of its residence time within the soil plus its residence time within the river basin, which can differ substantially for different terrestrial POM fractions (lipids versus lignin) from arctic watersheds (e.g. Feng et al., 2013; Gustafsson et al., 2011). In permafrost affected watersheds with soils storing up to Pleistocene aged OM, the residence time within the watershed after entering the river might have only a minor effect.

The Lena Delta and Buor Khaya Bay surface water $^{14}C_{POM}$ concentrations presented here are depleted with respect to the current atmospheric $^{14}CO_2$ (Table 3-3). The $\Delta^{14}C$ concentrations

ranged from –391‰ to –115‰ for 2009 to 2011 translating into ^{14}C ages >1200 years and up to 3920 yrs BP for samples taken close to the Pleistocene ice complex deposits of Kurungnakh Island (Figs. 3-1B and 3-2Q-T, Table 3-3). These results are within the range of reported $\Delta^{14}C$ concentrations for surface water POM offshore the Lena Delta and influenced by Lena River outflow (Karlsson et al., 2011). Based on these results it seems reasonable to assume that a large fraction of Lena Delta POM originates from physical weathering of relatively young Holocene soils (active layer) of the first delta terrace and south of the delta.

However, soils outcropping along the Lena River south of the delta can be substantially older than late Holocene ages (Kuptsov and Lisitsin, 1996) including some areas of Pleistocene ice complex deposits (Grosse et al., 2013). Also, OM within the active layer and shallow permafrost table can be as old as 3,000 years BP in the Lena Delta (30cm below surface; Höfle et al., 2013) or more than >10,000 years BP south of the delta (Kuptsov and Lisitsin, 1996). As shown by the lignin phenol composition of Lena Delta POM (Winterfeld et al., 2014, submitted as companion paper) approximately half of the surface water particulate organic matter is derived from the catchment south of the delta with considerable contributions from delta soils, particularly in the summer season when riverbank erosion is strongest. Considering that, we would expect generally older POM ^{14}C ages. Additionally, riverbank erosion contributes POM covering the ^{14}C age range of the whole bluff profile, not only from the active layer.

One possible explanation for our relatively young POM ^{14}C ages could be the contribution of algal-derived OM with a rather modern ^{14}C signature concealing the "true" age of soil-derived OM. Algal-derived OM contribution was also suggested to be the reason for relatively young POM from the Ob' River inferred from a core of a floodplain lake (Dickens et al., 2011). Although the overall contribution and flux of autochthonous phytoplankton OM in the Lena River is rather small or even negligible due to the high turbidity and low light penetration (Cauwet and Sidorov, 1996; Sorokin and Sorokin, 1996), phytoplankton can be quite abundant in the surface water (Kraberg et al., 2013; Sorokin and Sorokin, 1996), which we sampled for our POM analyses. However, without directly determining the phytoplankton OM by microscopic counts or determining the chlorophyll-*a* content for each radiocarbon-dated sample, indirect evaluations have to be considered estimates. In the following chapter we describe three different scenarios for possible ^{14}C corrections of POM in the Lena Delta to assess the potential range of $\Delta^{14}C$ concentrations and ^{14}C ages of soil-derived particles. In these scenarios we assume that the algal-derived OM is of modern ^{14}C age ($\Delta^{14}C$ ~49‰) although this might not be true. DIC $\Delta^{14}C$ concentrations are not available for the Lena River. The DIC utilized by the phytoplankton is predominantly derived from the carbonate weathering within the Lena watershed and from soils,

both, providing a depleted ^{14}C carbon signature and only slowly exchanging with the atmosphere. Therefore, the following calculated $\Delta^{14}C$ concentrations of surface water POM from the Lena River have to be considered minimum, i.e. maximum ^{14}C ages.

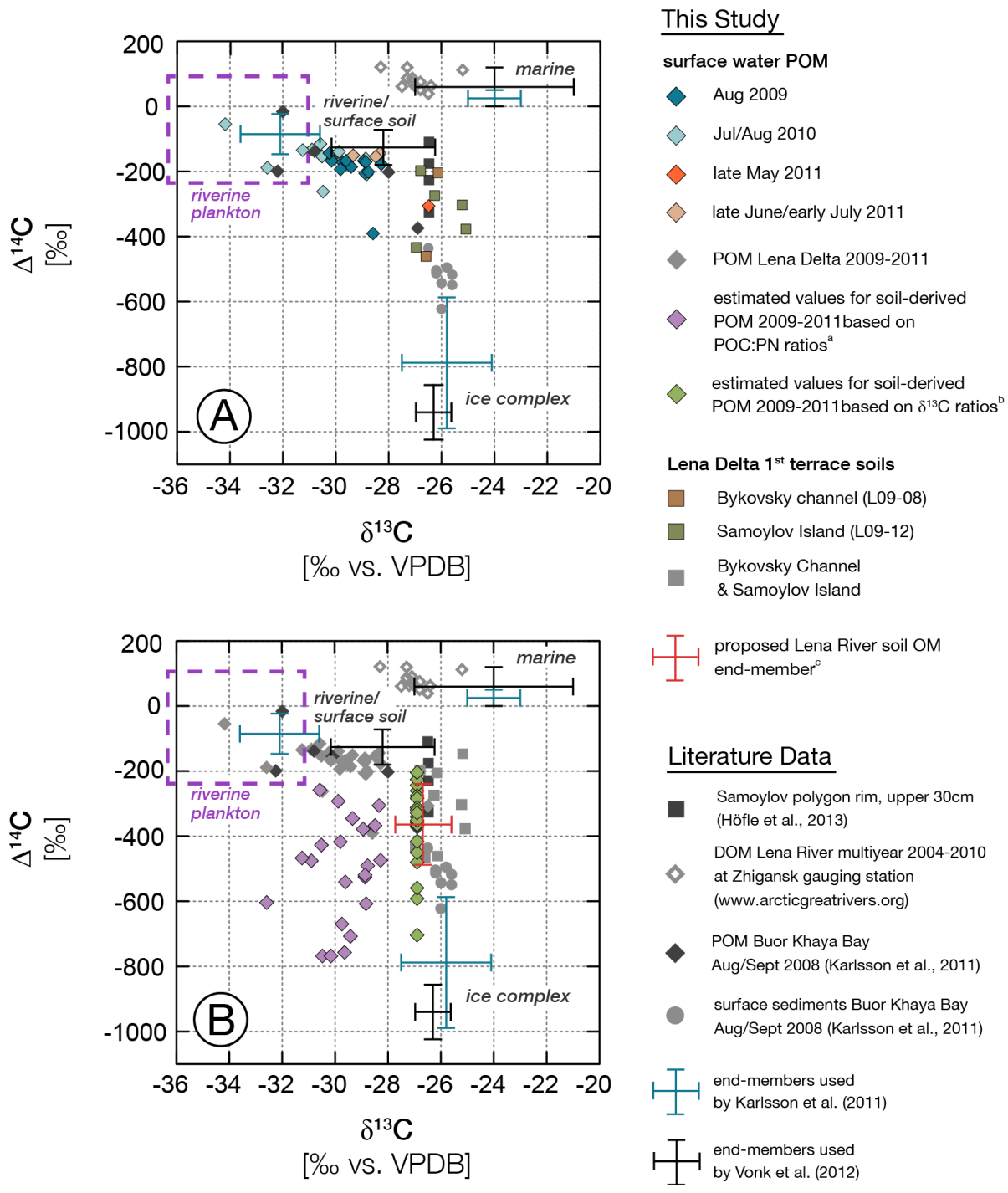

Figure 3-3. Stable and radiocarbon isotopic values of Lena Delta surface water POM of A) this study and literature data as well as B) estimated isotopic data of soil-derived POM based on POC:PN and $\delta^{13}C$ ratios. Ranges for different end-members for topsoil, ice complex, and marine are taken from the literature.

4.3 ^{14}C estimates of soil-derived POM for algal OM contribution

4.3.1 Scenario 1: Soil-derived OM ^{14}C estimates based on POC:PN ratios

POC:PN ratios around 6 are usually associated with OM derived from algal/bacterial primary production and higher ratios of >20 with OM derived from soils (Hedges et al., 1997; Meyers and Lallier-vergés, 1999 and references therein). However, adsorption of inorganic nitrogen derived from OM decomposition (e.g. ammonium) to clay minerals (Schubert and Calvert, 2001), which is not accounted for when determining the total PN content, may additionally affect the POC:PN ratio in TSM leading to lower values than would be expected from mixing of the two end-members alone. Likewise, selective degradation of labile organic carbon (Kuhry and Vitt, 1996) would have the same effect. Both processes would lead to low estimates of the soil-derived OM contribution and suggest a higher contribution from plankton. Both explanations were also suggested by Sanchéz-García et al. (2011) for POM in the Laptev Sea offshore the Lena Delta with unusually low POC:PN ratios.

In order to estimate the inorganic nitrogen content for our sample sets from each year, we used the intercept of the POC versus PN content regression line at zero POC (Fig. 3-S2 supplement). By subtracting these amounts from the analyzed total PN content of the respective samples, we could calculate soil POC:PN ratios (POC:PN) for our samples (table 3-S2 supplement). Based on these $POC:PN_{corr}$ ratios, we calculated the soil-derived fraction within our POM samples using a simple two end-member mixing model as following:

$$POC:PN_{POM} = f_{soil} \times POC:PN_{soil} + f_{plankton} \times POC:PN_{plankton} \quad (1)$$

$$\text{and } 1 = f_{soil} + f_{plankton} \quad (2)$$

where $POC:PN_{POM}$ is the measured value in the POM sample (Table 3-S1). As the end-member for $POC:PN_{soil}$ we assumed a value of 20.2, which is an average calculated from Lena Delta first terrace soils presented in Winterfeld et al. (2014), submitted as companion paper, and delta soils as well as soil from the Lena River watershed covering the taiga to tundra transition from Zubrzycki (2013). The $POC:PN_{plankton}$ endmember value is 6 (e.g. Meyers, 1994 and references therein).

The calculated soil-derived OM fractions of Lena Delta POM varied from 0.28 to 0.55 (mean of 0.41, n=11) for summer 2009, from 0.26 to 0.51 (mean of 0.43, n=10) in summer 2010, and from 0.48 to 0.69 (mean of 0.54, n=3) for late June/early July 2011 (Table 3-3). We used the POC versus PN (wt%) regression line from the summer 2010 samples within the delta to correct the two samples taken outside of the delta in the Buor Khaya Bay. They had calculated soil fractions

of 0.43 (sample 35) and 0.03 (sample 36). The same was done for the single sample from late May 2011. We used the regression line from the samples taken 4 weeks later in June/July and the soil fraction of sample 37 was 0.25 (Table 3-3). Note that these soil- and plankton-derived OM fractions can only serve as rough estimates. Without determining the particulate organic nitrogen directly for every sample our $POC:PN_{corr}$ ratios might be highly over- and underestimating OM fractions in individual samples.

The so calculated soil and plankton OM fractions (f_{soil} and $f_{plankton}$, Table 3-3 supplement) were further used in an isotopic mass balance to determine the $\Delta^{14}C$ concentration of the soil fraction assuming the plankton-derived OM is modern ($\Delta^{14}C_{plankton}$ = 49‰):

$$f_{POM} \times \Delta^{14}C_{POM} = f_{soil} \times \Delta^{14}C_{soil} + f_{plankton} \times \Delta^{14}C_{plankton} \quad (3)$$

$$\text{and } f_{POM} = f_{soil} + f_{plankton} \quad (4)$$

where f_{POM}, f_{soil}, and $f_{plankton}$ are the fractions of POM, soil- and plankton-derived OM and $\Delta^{14}C_{POM}$, $\Delta^{14}C_{soil}$, and $\Delta^{14}C_{plankton}$ are the $\Delta^{14}C$ concentrations of theses sources. As mentioned above, 49‰ is assumed as a maximum estimate for $\Delta^{14}C_{plankton}$.

The results of the newly calculated $\Delta^{14}C_{soil}$ concentrations using $POC:PN_{corr}$ ratios to partition between soil- and plankton-derived OM are shown in Table 3-4. The soil $\Delta^{14}C_{POC:PN}$ concentrations range from –786‰ to –258‰ for the sampling period of 2009-2011 translating into $^{14}C_{soil}$ ages >2300 yrs BP with an average of 6200 years BP (Table 3-4). Analogous to the two comparatively old $^{14}C_{POM}$ ages off Kurungnakh Island taken in 2009 and 2010 (Table 3-3), the calculated $^{14}C_{POC:PN}$ ages for these samples were with ~11,600 years BP the oldest. Considering that the riverbank outcrops of Kurungnakh Island cover an age range of approximately 100 kyears with organic-rich ice complex deposits of about 50 kyears (Wetterich et al., 2008) these ^{14}C ages seem to be realistic.

Again, the uncertainties associated with the contribution of inorganic nitrogen to our total PN contents are rather high resulting in a relatively rough estimation soil and plankton OM fractions. These uncertainties are further affecting the calculation of the soil $\Delta^{14}C_{POC:PN}$ concentrations. That means the calculated ^{14}C ages are estimates. Yet, they demonstrate that a possible underestimation of soil-derived OM ages can be considerable.

4.3.2 Scenario 2: Soil-derived OM ^{14}C estimates based on $\delta^{13}C$

Similar to the correction approach discussed above, we used a second scenario based on $\delta^{13}C$ compositions to distinguish between soil- and plankton-derived OM in our Lena Delta POM samples. The vegetation in the Lena River catchment (taiga and tundra) is dominated by C3 plants with a $\delta^{13}C$ of around –25‰ to –27‰ (Rachold and Hubberten, 1999) also reflected in our $\delta^{13}C$ data from the first delta terrace soils with an average of –26.2‰ (n=7, Table 3-3). Bird et al. (2002) determined the $\delta^{13}C$ composition of taiga and tundra soils (excluding peatlands) along Yenisey River on a latitudinal transect. Their data suggests an average $\delta^{13}C$ concentration of –26.9‰ for tundra and taiga soils combined, which we use as the soil OM end-member in our two end-member model.

The $\delta^{13}C$ composition of riverine plankton POM depends on the fractionation between phytoplankton and dissolved inorganic carbon (DIC). The distribution of the different DIC fractions (dissolved CO_2, bicarbonate (HCO_3^-), and carbonate ion (CO_3^{2-}) varies depending on temperature and pH. In the lower reaches of the Lena River and the Lena Delta >90% of the DIC are made up of bicarbonate (Alling et al., 2012), i.e. the $\delta^{13}C$ of bicarbonate represents the $\delta^{13}C$ of DIC. Sources for DIC are generally the CO_2 derived from soil OM degradation and CO_2 released during the dissolution of carbonates. The Lena River geochemistry is mainly influenced by carbonate weathering and groundwater in the summer season (Gordeev and Sidorov, 1993). Assuming a fractionation of -25‰ between phytoplankton and DIC these high latitude waters and a $\delta^{13}C_{DIC}$ of –8‰ for the Lena Delta (Alling et al., 2012) a plankton $\delta^{13}C$ end-member of –33‰ would be expected. Similar or more depleted $\delta^{13}C$ values of bicarbonate and phytoplankton POM were also determined in the Yenisey and Ob' Rivers (Galimov et al., 2006) and in temperate estuaries (e.g. Ahad et al., 2008; Chanton and Lewis, 2002). Our most depleted $\delta^{13}C_{POM}$ of –34.2‰ for a sample from the summer 2009 (Table 3-3) is even lower than the plankton end-member used here ($\delta^{13}C_{plankton}$ = –33‰). The sample location is offshore Muostakh Island (Fig. 3-1B) and influenced by mixing with marine waters, which complicates the DIC composition and processes affecting $\delta^{13}C$ of DIC (Alling et al., 2012).

We used the following two end-member model to estimate the soil- and plankton-derived OM fractions (f_{soil}, $f_{plankton}$) to our POM samples:

$$\delta^{13}C_{POM} = f_{soil} \times \delta^{13}C_{soil} + f_{plankton} \times \delta^{13}C_{plankton} \quad (5)$$

and

$$1 = f_{soil} + f_{plankton} \quad (6)$$

where $\delta^{13}C_{POM}$ is the analyzed $\delta^{13}C$ composition of our POM samples (Table 3-3), $\delta^{13}C_{soil}$ is the soil end-member value of –26.9‰, and $\delta^{13}C_{plankton}$ is plankton end-member value of –33‰.

The calculated soil OM fractions varied from 0.07 to 0.68 in summer 2009 (mean of 0.44, n=11), from 0.47 to 0.77 in summer 2010 (mean of 0.62, n=10), and from 0.60 to 0.76 in spring 2011 (mean of 0.70, n=3). The Buor Khaya Bay POM sample 21 showed a soil fraction of 0.45. Two samples are not considered in this end-member model, because their $\delta^{13}C$ values are outside the range of the end-member values chosen here (sample 37 and 19, see Table 3-3). This illustrates the limitations of our approach. Constraining a model with appropriate end-members strongly influences the quality of the model output and here we were not able to account for the whole range of natural variability observed in the Lena River. As discussed above in section 4.3.1, these soil OM fractions are rough estimates in the absence of direct plankton determination.

The $\Delta^{14}C$ concentrations are further corrected for the contribution of modern plankton OM as described in section 4.3.1 using the eq. (3) and (4). Because the soil contributions calculated in this scenario are slightly higher than in the POC:PN-based scenario, the $\Delta^{14}C$ calculations resulted in less radiocarbon depleted estimates compared to the POC:PN scenario (Table 3-4). Nonetheless, the $\Delta^{14}C$ concentrations based on the $\delta^{13}C$ end-member model are considerably depleted compared to bulk POM $\Delta^{14}C$ concentrations. The calculated $\Delta^{14}C$ concentrations range from –704‰ to –204‰ for all samples 2009-2011 representing ^{14}C ages from 9720 to 1770 years BP (Table 3-4). The oldest samples are, again, the ones taken close to Kurungnakh Island with its Pleistocene ice complex deposits (samples 1 and 31). In contrast to scenario 1, it is more obvious in this scenario that the POM samples taken in late June/early July 2011 are more enriched in ^{14}C (younger) than the POM samples taken later in the summer (Aug 2009 and July/Aug 2010). Similar observation were made for DOM $\Delta^{14}C$ concentrations of the Lena River at Zhigansk ~900 km south of the delta (Raymond et al., 2007) and the Kolyma River in East Siberia (Neff et al., 2006). Their explanation was that due to the deepening of the active layer in summer older soil layers are accessible for melt water and groundwater contributing an older DOM signature to the river than in spring when most soil is still frozen. A comparable scenario could explain estimated $\Delta^{14}C$ concentration decreasing from spring freshet to summer. Additional to active layer deepening riverbank erosion is strongest during the summer and might contribute a considerable amount of soil-derived OM to the Lena Delta surface water.

Table 3-4. Estimated ^{14}C concentrations of soil-derived POM fraction using POC:PN ratios and $\delta^{13}C$ ratios to estimate amount of soil-derived fraction. Not determined denoted by n.d.

	POC:PN based estimates			plankton $\delta^{13}C$-based estimates		
sample code	**fraction soil $POM_{POC:PN}$**	**$\Delta^{14}C_{POC:PN}$ [‰]**	**conv. $^{14}C_{POC:PN}$ age [yrs BP]**	**fraction soil $POM_{\delta13C}$**	**$\Delta^{14}C_{\delta13C}$ [‰]**	**conv. $^{14}C_{\delta13C}$ age [yrs BP]**
Lena Delta Aug 2009						
1	0.38	–768	11683	0.41	–704	9715
2	0.36	–604	7378	0.07	n.d.	n.d.
3	0.35	–475	5123	0.34	–480	5192
4	0.28	–757	11303	0.55	–367	3617
5	0.36	–467	4996	0.29	–592	7141
6	0.43	–427	4415	0.41	–450	4748
10	0.46	–417	4274	0.52	–358	3498
11	0.36	–526	5931	0.68	–260	2364
12	0.53	–258	2342	0.40	–365	3593
13	0.55	–292	2721	0.51	–319	3028
14	0.39	–607	7451	0.68	–328	3136
19	0.29	–306	2871	n.d.	n.d.	n.d.
21	0.34	–634	8019	0.98	–191	1643
Lena Delta Jul/Aug 2010						
22	0.31	–670	8843	0.53	–364	3579
24	0.31	–707	9812	0.59	–351	3419
25	0.43	–474	5100	0.77	–243	2183
27	0.51	–378	3755	0.67	–276	2541
28	0.46	–491	5360	0.69	–312	2946
29	0.38	–523	5890	0.68	–276	2533
30	0.26	–768	11672	0.47	–416	4258
31	0.33	n.d.	n.d.	0.72	–559	6521
32	0.37	–541	6191	0.56	–340	3280
33	0.34	–672	8893	0.52	–416	4266
35	0.43	–480	5190	n.d.	n.d.	n.d.
36	0.03	n.d.	n.d.	0.45	–377	3740
late May 2011						
37	0.25	n.d.	n.d.	n.d.	n.d.	n.d.

Table 3-4 continued.

	POC:PN based estimates			plankton $\delta^{13}C$-based estimates		
sample code	fraction soil $POM_{POC:PN}$	$\Delta^{14}C_{POC:PN}$ [‰]	conv. $^{14}C_{POC:PN}$ age [yrs BP]	fraction soil $POM_{\delta13C}$	$\Delta^{14}C_{\delta13C}$ [‰]	conv. $^{14}C_{\delta13C}$ age [yrs BP]
late Jun/early Jul 2011						
38	0.54	–306	2870	0.76	–204	1771
42	0.51	–345	3344	0.60	–284	2620
47	0.49	–367	3617	0.74	–226	2000

4.4 Implications of estimated soil-derived POM $\Delta^{14}C$

The two scenarios discussed above allow an estimate of the contribution of plankton-derived OM to our bulk POM samples and of the soil $\Delta^{14}C$ concentration estimates based on this modern phytoplankton contribution. Both scenarios show considerably depleted soil-derived OM compared to the bulk $\Delta^{14}C_{POM}$ concentrations. This implies that the bulk POM ^{14}C age of samples taken in surface water during the summer, when the riverine primary production is high, have likely underestimated the age of the soil-derived OM transported by the Lena River. The estimated soil $\Delta^{14}C$ concentrations and ^{14}C ages in both scenarios give a more plausible picture for soil-derived POM in the Lena River watershed. In contrast to DOM that is restricted in its flow path to the unfrozen soil layers, POM is not exclusively derived from surface soils. It also originates from re-suspension of accumulated pre-aged material along the river channels and from riverbank erosion. The latter contributes POM with $\Delta^{14}C$ concentrations representing the whole range covered by the respective riverbank bluffs. In the Lena Delta this is predominantly OM of late Holocene age with local inputs from ice complex deposits of Pleistocene age (e.g. Bolshiyanov et al., 2014; Schirrmeister et al., 2011; Schwamborn et al., 2002). About half of the POM in the Lena Delta originates from the boreal forest hinterland south of the delta (Winterfeld et al. 2014, submitted as companion paper). Here the soils along the Lena River and its tributaries can be older than the delta soils, i.e. covering the whole age range from Holocene soils to Pleistocene ice complex deposits (e.g. Grosse et al., 2013; Kuptsov and Lisitsin, 1996). Our estimated soil ^{14}C ages of about 2300 to 11,600 years (Table 3-4) for both scenarios therefore better reflect these hinterland deposits contributing a heterogeneous ^{14}C age mix to riverine POM than the bulk POM ^{14}C ages.

The POM ^{14}C estimates as well as Lena Delta first terrace soil data ($\delta^{13}C$ and $\Delta^{14}C$) presented here improve our knowledge of the stable and radiocarbon isotopic range characteristic for soil-

derived OM exported by the Lena River to the Laptev Sea. This information is critical for modeling the OM contribution from different terrestrial (fluvial vs. coastal erosion) and marine sources to Laptev Sea sediments and thus help characterizing and quantifying the OM pools released from permafrost thawing. Recent studies suggest that OM exported by arctic rivers and OM derived from erosion of ice complex coasts differ in their mineral and OM composition and thus show different potential for remineralization by microorganisms after thawing as well as different modes of transport and burial (e.g. Feng et al., 2013; Gustafsson et al., 2011; Knoblauch et al., 2013; Vonk et al., 2012). This has a direct impact on how to assess the possibility of a positive carbon-climate feedback from permafrost degradation, which has the potential to enhance global greenhouse warming by releasing huge amounts of previously frozen OM to the atmosphere.

A promising approach to distinguish OM sequestered in arctic sediments is the dual-carbon-isotope end-member simulation applied by Karlsson et al. (2011) and Vonk et al. (2012; 2010) to Laptev and East Siberian Sea sediments. The authors use the $\delta^{13}C$ and $\Delta^{14}C$ concentrations of surface water suspended matter and surface sediments to quantify OM derived from Pleistocene ice complex deposits, soil/top-soil OM exported by Siberian rivers, and marine phytoplankton OM. Their end-member definitions for ice complex deposits and marine primary production are rather well constrained. In contrast, the soil/topsoil end-member is more difficult to define, particularly when using indirect parameters such as riverine DOM and POM. Here our first terrace soil data and estimates for soil-derived POM (Table 3-4) provide new $\delta^{13}C$ and $\Delta^{14}C$ concentration ranges (Fig. 3-3B) for fluvially exported soil POM. Together with published $\delta^{13}C$ concentrations from tundra and taiga soils in Siberia and Alaska (Bird et al., 2002; Pitkänen et al., 2002; Xu et al., 2009) we can define a Lena River soil OM end-member with a $\delta^{13}C$ value of –26.6 ± 1.1‰. The corresponding $\Delta^{14}C$ concentration is –362 ± 123‰ is taken from the second scenario discussed above (Table 3-4). The $\delta^{13}C$-based scenario is favored here over the POC:PN-based scenario, because it allows to calculate the soil fraction of each POM sample based on its bulk $\delta^{13}C$ composition, which is a mixture of soil and phytoplankton OM. In contrast, in the POC:PN-based scenario a constant value for particulate inorganic nitrogen is subtracted, which does not necessarily represent the actual inorganic nitrogen content of the particular sample. Moreover, it does not account for selective degradation of labile carbon, which could result in overestimating the phytoplankton contribution. The uncertainties associated with the $\delta^{13}C$-based estimates are smaller, as the $\delta^{13}C$ end-member for soil-derived and phytoplankton-derived OM are fairly well constrained (see also section 4.3.2).

However, our soil OM end-member for the Lena River catchment makes it more complicated to distinguish between soil/top-soil derived OM from the river and ice complex deposits from coastal erosion (see Fig. 3-3B). The $\delta^{13}C$ signatures of both end-members are almost indistinguishable. The $\Delta^{14}C$ range of our soil-derived POM estimates is more depleted than the end-member used by Karlsson et al. (2011) and Vonk et al. (2012; 2010). Furthermore, Höfle et al. (2013) have shown that OM within the first 30 cm of a polygon rim of the Lena Delta first terrace can be 3000 ^{14}C yrs old, which make the end-members chosen for fluvial exported soil/top-soil OM by Karlsson et al. (2011) and Vonk et al. (2012; 2010) appear too young. Using the bulk surface water POM and DOM $\delta^{13}C$ and $\Delta^{14}C$ compositions as end-member could therefore highly over- or underestimate the soil OM contribution from permafrost watersheds and in turn highly over- or underestimate OM contribution from ice complex to marine sediments.

However, we are aware of the limitations and uncertainties associated with the soil $\Delta^{14}C$ estimates discussed above. Without determining the phytoplankton biomass of each sample by microscopic counting or from chlorophyll-*a* analysis, the plankton OM fraction calculated based on POC:PN ratios (section 4.3.1) and based $\delta^{13}C$ composition (4.3.2) can only be regarded as estimates. These estimates give orders of magnitude of OM contribution from the individual sources rather than exact values, which in turn provide a possible range of $\Delta^{14}C$ concentrations for soil-derived POM. An additional source of uncertainty is our assumption of a modern $\Delta^{14}C$ concentration of plankton OM. Without determining the $\Delta^{14}C$ concentration of the Lena River DIC, which is utilized by phytoplankton, we cannot be sure of a modern ^{14}C signature. Lena River geochemistry and DIC are dominated by dissolution of carbonates in the watershed contributing fossil ^{14}C to the DIC pool, leading likely to ^{14}C-depletion in river phytoplankton. The true contribution of modern phytoplankton OM is thus likely smaller than estimated above. Consequently, the soil-derived POM would be less ^{14}C depleted than calculated here. Therefore, our estimated ^{14}C soil ages have to be considered maximum ages.

The best way to determine the $\Delta^{14}C$ concentration of riverine soil-derived OM would be a biomarker-specific radiocarbon analysis using source-specific compounds, e.g., short- and long-chain fatty acids for plankton- and terrestrial-derived OM, respectively. However, for these analyses large samples of POM are needed. The samples analyzed during our study were too small to allow for compound-specific dating.

5 Conclusions

There is only scarce data available on ^{14}C contents of POM from Lena River surface water, but within the likely positive carbon-climate feedback to greenhouse warming the quality and fate of this permafrost OM pool in the coastal waters of the Laptev Sea is currently under debate (e.g. Feng et al., 2013; Gustafsson et al., 2011; Karlsson et al., 2011; Vonk et al., 2012). With this study we provide the first data set on surface water POM $\Delta^{14}C$ concentrations from the Lena Delta sampled during the summers 2009 and 2010 and during spring 2011 (n=27 samples). The contribution of modern phytoplankton POM to these samples was estimated based on POC:PN ratios and $\delta^{13}C$ values to allow for calculation of the $\Delta^{14}C$ concentrations of the soil-derived POM fraction. These soil $\Delta^{14}C$ estimates are depleted compared to the bulk POM $\Delta^{14}C$ concentrations and therefore seem to represent the heterogeneous ^{14}C mix of soil OM ranging from Holocene to Pleistocene age (e.g. ice complex deposits) in the Lena River watershed more accurately. Because of the limitations of our approach, particularly the assumption of modern phytoplankton OM without determining the $\Delta^{14}C$ concentration of the Lena River DIC utilized by phytoplankton, our ^{14}C estimates for the soil-derived fraction have to be considered minimum $\Delta^{14}C$ concentrations and maximum ^{14}C ages, respectively. Nonetheless, we propose average values for soil POM isotopic composition based on our data and published values ($\delta^{13}C$ = –26.6 ± 1.1‰; $\Delta^{14}C$ = –362 ± 123‰), which will be useful for dual-carbon-isotope simulations focusing on unraveling the OM contributed by different terrigenous (fluvial vs. coastal erosion) and marine sources to arctic sediments.

The complete data set presented here can also be found in PANGAEA.

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Supplement

Table 3-S1. Additional total suspended matter (TSM) samples from June/July 2011 shown in figure 3-2D and analyzed for POC and PN content as well as carbon isotopes.

Sample code	Sample & site description	Date of sampling	Latitude [dec]	Longitude [dec]	Water depth [m]
Lena River total suspended matter					
38	close to Stolb	26-Jun-2011	72.3705	126.6538	0.5
39	off Kurungnakh	28-Jun-2011	72.3334	126.2914	0.5
40	off Samoylov Island	29-Jun-2011	72.3681	126.4738	0.5
41	off Samoylov Island	29-Jun-2011	72.3681	126.4738	0.5
42	off Samoylov Island	30-Jun-2011	72.3681	126.4738	0.5
43	off Samoylov Island	30-Jun-2011	72.3681	126.4738	0.5
44	off Samoylov Island	1-Jul-2011	72.3681	126.4738	0.5
45	off Samoylov Island	1-Jul-2011	72.3681	126.4738	0.5
46	off Samoylov Island	2-Jul-2011	72.3681	126.4738	0.5
47	off Samoylov Island	2-Jul-2011	72.3681	126.4738	0.5

Table 3-S2. Particulate organic carbon contents in milligram per liter (mg/L), per cent based on dry weight sediment (wt%), and atomic particulate organic carbon to total particulate nitrogen ratios of individual Lena Delta surface water samples from 2009-2011. Additionally, total suspended matter concentrations (TSM) are given for samples from late June/early July 2011.

Sample code	POC [mg/L]	POC [wt%]	atomic POC:PN	$POC:PN_{new}$ [a]	TSM [mg/L]
Lena Delta Aug 2009					
1	1.17	37.7	9.6	11.4	
2	0.80	5.7	8.8	11.2	
3	0.72	11.3	8.4	10.9	
4	1.13	3.9	8.6	10.0	
5	0.74	6.4	8.6	11.1	
6	0.97	6.9	9.7	12.1	
7	0.54	7.3	7.5	10.3	
8	0.87	9.8	8.6	10.7	
9	1.69	2.5	11.0	12.6	
10	1.03	2.6	10.1	12.5	
11	1.00	1.9	9.2	11.2	

Table 3-S2 continued.

Sample code	POC [mg/L]	POC [wt%]	atomic POC:PN	POC:PN_{new} [a]	TSM [mg/L]
12	0.80	3.9	10.2	13.6	
13	0.76	2.6	10.2	13.8	
14	0.87	2.6	9.2	11.6	
15	0.59	3.8	8.9	12.7	
16	2.16	11.0	19.3	23.4	
17	7.24	4.1	11.5	11.8	
18	0.69	10.3	9.3	12.6	
19	0.83	n.d.	8.2	10.2	
20	0.48	4.5	8.5	12.9	
21	0.35	4.8	6.8	10.9	
Lena Delta Jul/Aug 2010					
22	0.54	4.0	7.7	10.4	
24	0.47	5.3	7.5	10.4	
25	1.19	4.2	10.3	12.1	
26	n.d.	n.d.	n.d.	n.d.	
27	0.36	1.3	7.6	13.2	
28	0.37	1.6	7.8	12.6	
29	0.75	2.9	9.0	11.5	
30	0.79	3.3	8.0	9.8	
31	1.30	5.7	9.4	10.7	
32	0.46	2.4	7.8	11.2	
33	0.51	2.6	7.8	10.8	
34	0.17	4.7	5.0	10.7	
35	0.37	4.4	7.6	12.1	
36	0.15	1.5	3.7	6.4	
late May 2011					
37	8.20	1.7	7.5	9.6	
late Jun/early Jul 2011					
38	0.78	4.7	8.3	13.7	16.60
39	0.29	4.6	5.9	15.8	6.25
40	n.d.	n.d.	n.d.	n.d.	15.70
41	0.65	5.0	7.5	12.8	13.10
42	0.54	4.7	7.2	13.2	11.50

Table 3-S2 continued.

Sample code	POC [mg/L]	POC [wt%]	atomic POC:PN	POC:PN$_{new}$ [a]	TSM [mg/L]
43	1.51	4.7	9.7	13.7	31.70
44	0.69	4.2	7.8	13.2	16.35
45	0.85	3.9	8.5	13.6	21.55
46	0.64	3.8	8.0	14.1	16.95
47	0.73	3.2	7.8	12.9	22.90

[a] calculated after subtracting intercept at zero POC from total particulate nitrogen content, Intercept is 0.023 for samples from 2009, 0.021 for 2010, and 0.028 for 2011 (for more details see figure S2 supplement and description in text section 4.3.1)

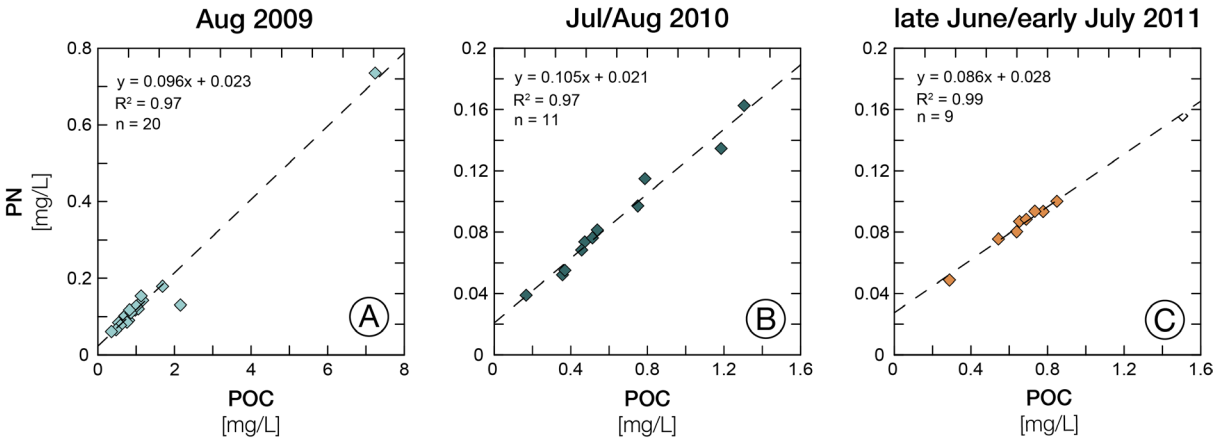

Figure 3-S3. Organic carbon (OC), total nitrogen (TN), and atomic OC to TN ratio (OC:TN$_{at}$) for individual soil samples of the Lena Delta first terrace bulk samples. Bulk samples include the >2mm fraction. Sample depth is given in meter below surface [m b.s.].

4 MANUSCRIPT III

Rapid deglacial to early Holocene permafrost thawing and wetland dynamics in East Siberia revealed by Amur River discharge peaks into the Okhotsk Sea

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Abstract

Global atmospheric methane (CH_4) and carbon dioxide (pCO_2) concentrations underwent dramatic and rapid variations during the last glacial termination and the Early Holocene, with major exchanges between the main terrestrial, oceanic and atmospheric carbon reservoirs. However, assigning transfer mechanisms to different forcing and processes remains difficult. While the ocean is a main capacitor for overall global carbon budget changes, the role of terrestrial carbon storage during the last glacial remains largely unconstrained. Permafrost thawing and wetland initiation with the subsequent activation of a large soil organic carbon pool in the temperate to subpolar Northern Hemisphere is one prime candidate to explain existing discrepancies in land-ocean and land-atmosphere fluxes. Despite this importance, the long-term deglacial history of East Siberia, one of the major regions with past permafrost occurrence that was lost in the last deglaciation, remains poorly known. Here, we show that deglacial terrigenous organic matter transport from the Amur River, one of the largest modern Siberian river and boreal wetland areas, into the marine realm was significantly larger during the last glacial termination than under modern conditions. We reconstruct the organic matter flux of the Amur River into its receiving basin, the Okhotsk Sea, for the last 16,000 years in a high-resolution AMS

^{14}C-dated sediment core from the Sakhalin continental margin, based on organic geochemical multi-proxy data and compound-specific radiocarbon dating of *n*-alkanoic acids. Within the deglacial discharge maximum of OM to the Okhotsk Sea, we identify two peak OM release episodes, the first occurring during the Bølling-Allerød warm phase, and the second, larger one after Termination Ib in the earliest Preboreal. Our results highlight the sensitivity of the Amur drainage basin's carbon reservoir to rapid deglacial temperature and precipitation changes. We hypothesize that large amounts of carbon were activated upon deglacial permafrost thawing within this southernmost Siberian large catchment and quickly transferred to the oceanic carbon reservoir via riverine freshwater transport into the Okhotsk Sea and the North Pacific. Superimposed on the higher Early Holocene OM transfer, we record a short centennial-scale relapse into colder and drier conditions that corresponds to the 8.2 ka cooling event first detected in Greenland ice core records, with its concomitant short-term decrease in atmospheric CH_4 concentrations. Overall, a fast and widespread boreal wetland expansion in the Amur hinterland point to a potentially prominent role of this catchment as a methane source that contributed to the observed rapid, but still unassigned rises of atmospheric CH_4 during the Bølling and early Preboreal.

1 Introduction

Changes in atmospheric carbon dioxide (pCO_2) and methane (CH_4) during the last glacial–interglacial transition (Termination I) reflect the redistribution of carbon between the atmospheric, terrestrial, and ocean reservoirs and their respective responses to climate forcing. Determining the causes and magnitude of fluxes, as well as the sensitivities and sizes of the carbon reservoirs remains difficult and is associated with large uncertainties (e.g. Elsig et al., 2009; Peterson et al., 2014; Schmitt et al., 2012). The ocean is a dominant driver of pCO_2 changes, both as a carbon sink through biological and physical sequestration, and as source through the release of old carbon by upwelling of deep water (Fischer et al., 2010). However, models have so far been unable to sufficiently constrain the individual sources in explaining the increase in pCO_2 of ~100 ppmv from the Last Glacial Maximum to pre-industrial times (e.g. Archer et al., 2000; Brovkin et al., 2007; Köhler et al., 2005). These models usually work under the general assumption that the terrestrial carbon reservoir was much smaller during the Last Glacial Maximum (LGM) than in the late Holocene. Contrary to this assumption, Ciais et al. (2012) identified an inert terrestrial carbon reservoir that was larger by ~700 Pg during the LGM than the modern pool of inert carbon. They speculated that this carbon pool could have been stored in permafrost soils. A large fraction of this inert carbon may have been released to the

atmosphere by permafrost decay during the deglacial warming, adding to the global pCO_2 increase. Atmospheric CH_4 concentrations recorded in ice cores also show prominent rapid increases during the termination (e.g. Monnin et al., 2001). In contrast to the increased pCO_2, which is mainly an ocean signal, the CH_4 increases are thought to be driven by tropical and boreal wetland expansion (Fischer et al., 2010), although the actual source regions, particularly within the permafrost zone, are under debate (e.g. MacDonald et al., 2006; Reyes and Cooke, 2011; Smith et al., 2004). There is only scarce physical data available supporting the proposed thawing of LGM permafrost. Its role as an additional source of CO_2 and the development of boreal wetlands as source for CH_4 during the last glacial termination thus remains controversial.

A key region for studying deglacial permafrost dynamics is East Siberia, because it constitutes the most extensive boreal-arctic region not permanently covered by extensive glaciers during the last glacial (Brigham-Grette et al., 2007; Hubberten et al., 2004) This condition allowed for permafrost soil development, and storage of large organic carbon amounts. The extent of the continuous permafrost zone during the LGM reached as far south as 38-40°N in East Asia (Zhao et al., 2013) while the modern continuous permafrost boundary lies at circa 50-52°N (Brown et al., 1997; Saito et al., 2013). Furthermore, Vaks et al. (2013) reconstructed permafrost conditions near Lake Baikal from repeatedly terminated and re-started stalagmite growth under permafrost and permafrost-free conditions, and showed that the continuous permafrost zone shifted north of 52°N around 10 ka. The Amur River catchment is located between 41° and 57°N in East Siberia (Fig. 4-1). Due to its location directly between the modern and the last glacial permafrost boundaries, it represents the southernmost large Siberian river system that was affected by these shifts of the cryosphere during the last deglacial. The Amur River has been shown to deliver large amounts of organic matter (OM) from its catchment into the Okhotsk Sea, thereby recording the hinterland changes in marine sediments (e.g. Nürnberg and Tiedemann, 2004; Seki et al., 2012; 2014; Ternois et al., 2001). These continental margin sediment archives thus provide the unique possibility to study catchment-wide changes in a far-field site and complement the few available land-based proximal records of local changes.

We determined the long-chain *n*-alkane concentrations as proxy for OM input by higher terrestrial plants from a sediment core located on the Sakhalin continental margin for the last 16,000 calibrated years before present (ka). Additionally, we analyzed the compound-specific radiocarbon concentration of short- and long-chain *n*-alkanoic acids, representing marine primary production and higher terrestrial land plants, respectively, to obtain information about past hinterland permafrost dynamics and sensitivity to deglacial warming

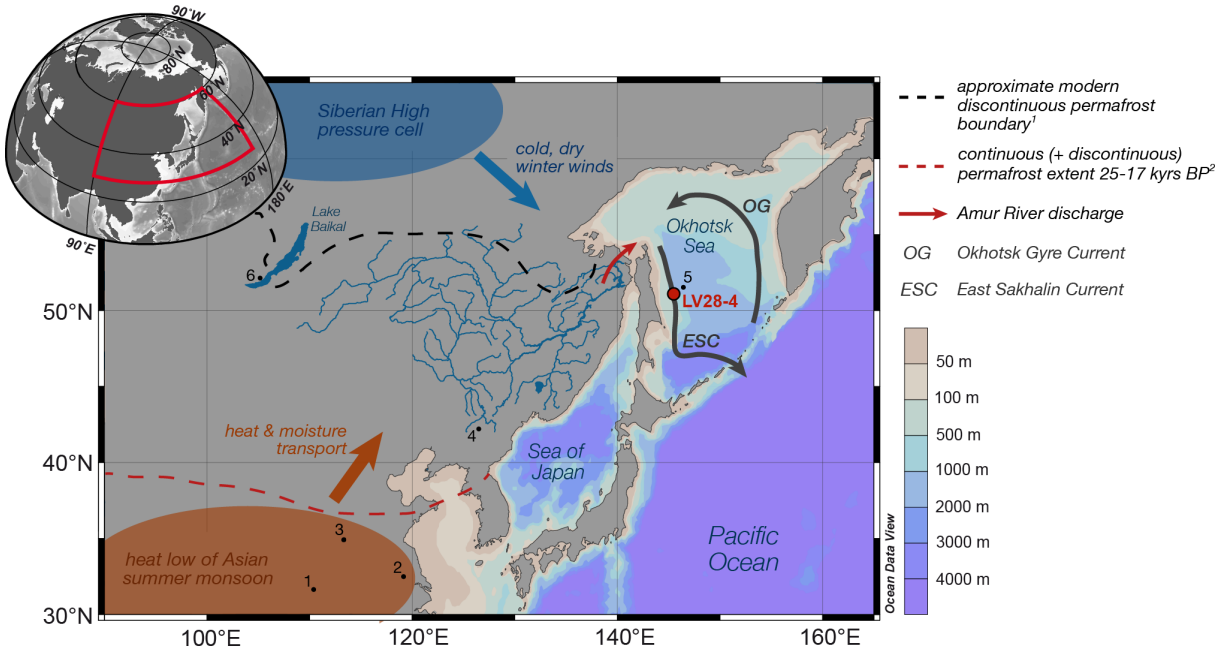

Figure 4-1. Amur River catchment. Approximate modern permafrost boundary (southern edge of discontinuous permafrost) modified after Brown et al. (1997). Permafrost extent 25-17 ka modified after (Vandenberghe et al., 2014). Numbers 1 to 6 refer to locations of paleoclimatic archives mentioned in the text: 1 – Sanbao Cave (31°30'N, 110°26'E; (Wang et al., 2008); 2 – Hulu Cave (32°30'N, 119°10'E; (Wang et al., 2001); 3 – Mangshan loess plateau (34°56.1'N, 113°22.4'E; (Peterse et al., 2011); 4 – Hani peat bog (42°13'N, 126°31'E; (Seki et al., 2009); 5 – sediment core XP07-C9 (52°24'N, 146°00'E; (Seki et al., 2012); 6 – Okhotnichya Cave (52°07'N, 105°29'E; (Vaks et al., 2013).

2 Study Area

The Amur river is one the largest rivers in East Siberia, discharging about 333 km^2 freshwater per year to the Okhotsk Sea (Ogi et al. 2001). Associated estimated exports of dissolved organic matter and particulate organic matter (OM) are 4.85 Tg and 0.8 Tg per year, respectively (Levshina, 2008). The Okhotsk Sea in turn is the second largest marginal sea of the North Pacific. Its circulation is dominated by the Okhotsk Gyre (Oshima et al. 2002, 2004) and includes the southward-flowing East Sakhalin Current (ESC, Fig. 4-1), which transports surface and deep waters from the northern shelves to the Kuril Basin. During the sea-ice season in fall and winter, Dense Shelf Water (DSW) is formed north of Sakhalin by brine rejection in large polynyas (Fukamachi et al. 2009; Shcherbina et al. 2004a). The DSW flows south along the Sakhalin margin, transporting high concentrations of organic matter, lithogenic particles and suspended matter that are entrained by vigorous tidal mixing on the northeastern shallow continental shelf into a highly turbid water layer. This water mass is subsequently transported to our core site (e.g. Nakatsuka et al., 2004; Seki et al., 2012; 2014; Ternois et al., 2001). Both the Amur River

catchment and the Okhotsk Sea are characterized by strong seasonal climatic changes. The winters are influenced by the strength and location of the Siberian High pressure cell bringing cold and dry winds (Honda et al., 1996). In contrast, the summers are influenced by the East Asian Summer Monsoon maximum reaching its northernmost position during July and August and bringing heat and precipitation to the Amur basin (Tachibana et al., 2008).

3 Material and methods

Gravity core LV28-4-4 that is used in this study (further referred to as LV28-4) was retrieved from the East Sakhalin margin (674 m water depth, 51°08.475 N, 145°18.582 E) during expedition LV28 with R/V Akademik Lavrentiev in the framework of the German – Russian KOMEX I project. The core consists of undisturbed, continuous hemipelagic sediment sequences (Biebow and Hütten, 1999). The carbonate-bearing sediment facies consists of silty clay with diatoms in the lower part of the core, while the upper part consists of diatomaceous ooze with clay and silt. The age model is based on AMS ^{14}C dating of planktic foraminifera, supplemented by benthic dates in core sections, where abundance of planktic foraminifera was too low to permit dating. The full age model is reported in Lembke-Jene (2014). Sedimentation rates vary between 15 cm/kyr in the lowermost section and up to 160 cm/kyr during the Holocene.

Total lipids were extracted from freeze-dried, homogenized sediment (2-5 g) using a three-step ultrasonic extraction with 1) dichloromethane, 2) dichloromethane:methanol (1:1 v:v), and 3) methanol (modified after Bligh and Dyer, 1959). Neutral lipids and *n*-alkanoic acids were separated by saponification in 0.5 M potassium hydroxide/methanol solution at 80°C for 2h. Neutral compounds were isolated with *n*-hexane and further split into three subfractions (hydrocarbons, ketones, alcohols) by silica gel chromatography. The *n*-alkane concentrations were determined using an HP5890 GC with flame ionization detector. Each compound was identified based on retention time and comparison with an *n*-alkane standard and quantification was achieved using an internal standard (squalane).

For compound-specific radiocarbon analysis of *n*-alkanoic acids we sampled four depth intervals of core LV28-4 (Table 4-1). The freeze-dried sediment samples were extracted, *n*-alkanoic acids separated and purified following established protocols (Mollenhauer and Eglinton, 2007). Single *n*-alkanoic acids were isolated with preparative capillary gas chromatography (Eglinton et al., 1996) using an Agilent HP6890N GC with Gerstel CIS injection system and Gerstel preparative fraction collector. The detailed method and GC settings are described in (Kusch et al., 2010). The

recovered purified individual *n*-alkanoic acids were transferred into pre-combusted quartz tubes filled with 150 µg of pre-combusted copper oxide for oxygen supply. The tubes were half immersed in dry ice and evacuated, flame sealed, and combusted at 900°C for 4h. The resulting CO_2 was stripped from water and quantified (Kusch et al., 2010). The CO_2 samples were analyzed for radiocarbon content at ETH Zürich using the MICADAS system equipped with a gas ion source (Ruff et al., 2010; Synal et al., 2007; Wacker et al., 2013). Results are reported as $\Delta^{14}C$ and conventional radiocarbon ages (^{14}C ages) in years BP (Stuiver and Polach, 1977). The radiocarbon concentration of the individual *n*-alkanoic acids was corrected of for the addition of one methyl group during derivatization using isotopic mass balance.

4 Results and discussion

4.1 Deglacial permafrost and wetland dynamics in East Siberia

Vascular plant wax lipids such as the long-chain odd carbon-numbered *n*-alkanes used in this study (C_{25-33}) have been widely used as proxy for terrestrial OM input into marine sediments (e.g. Prahl et al., 1994; Seki et al., 2012; 2003; Ternois et al., 2001). The C_{25-33} *n*-alkane concentrations in core LV28-4 vary from 38.8 to 486.2 µg/g organic carbon (OC), with the highest concentrations found in the lower part of the core between 16 and about 9 ka (Fig. 4-2D). The dominant compounds are the *n*-C_{27} and *n*-C_{29} alkanes. Although the sample resolution in this part of the core is relatively low the higher *n*-alkane concentrations during the Bølling-Allerød (B/A) warm phase, the Younger Dryas cold phase (YD), and the Preboreal (PB) period imply a much higher input of terrestrial OM to the core site than during the remainder of the Holocene. These observations are supported by peaks in organic carbon to total nitrogen (OC:TN) ratios in our core at the beginning of the B/A and PB and to a minor extent by increasing OC contents during these periods (Fig. 4-2E-F). A similar pattern in *n*-C_{25}-$_{35}$ alkane concentrations was found by Seki et al. (2012) in nearby core C9 (see also Fig. 4-1).

The higher input of terrestrial OM to our core location during the late deglacial and early Holocene can be supplied from two major sources: (1) flooding of the northern Okhotsk Sea shelves and resulting remobilization of sediment and OM in the course of the deglacial sea level rise and/or (2) increased discharge and export of terrigenous OM by the Amur River. (1) Input of terrigenous OM to our core site through sea level rise could occur, although this would have likely been only significant in the pre-Bølling deglacial period not covered by core LV28-4, when the majority of the northern Okhotsk Sea shelf was flooded. In line with this reasoning, maxima

in OM input as inferred from the *n*-alkane concentrations and OC:TN ratios do not coincide with established maxima in sea level rise (Lembke-Jene, 2014). (2) Instead, the terrestrial OM found in our core was predominantly delivered by the Amur River, which had a much higher discharge during the last termination based on the abundances of freshwater algae (Lembke-Jene, 2014). Two distinct peaks in freshwater algae counts (*Pediastrum spp.*) indicate substantial riverine influx to the study site, with a first, smaller maximum during the B/A and a second, larger one during the PB (Fig. 4-2). During the Holocene, including the present-day conditions, no substantial numbers of freshwater algae are found at the core site, although the Amur River discharge is quite large. The stronger discharge during the B/A and PB was most likely a result of high precipitation in the Amur hinterland and thawing of permafrost. Records from peat bogs in the Amur catchment indicate maxima in effective precipitation during the same time periods (Bazarova et al., 2008; Seki et al., 2009) and hence support this scenario.

Under the assumption that the Amur River catchment was part of the permafrost zone during the LGM and is predominantly free of permafrost today (e.g. Saito et al., 2013; Vaks et al., 2013; Vandenberghe et al., 2014) we would expect to detect the permafrost thawing and associated remobilization of pre-aged, previously frozen OM in the studied core. In general, the terrestrial residence time of OM is depending on several factors including the structure and recalcitrance of the organic compounds themselves, environmental controls like topography and climate, as well as size of the catchment area (Feng et al., 2013; Hedges and Oades, 1997; Kusch et al., 2010; Oades, 1988; Raymond and Bauer, 2001). The development of permafrost can be understood as a factor that results in "storage" of OM thus withdrawing carbon from biogeochemical cycles. To test whether indeed permafrost played a role in OM/carbon retention in the Amur River catchment we determined the compound-specific radiocarbon content in four key age intervals (Table 4-1, Fig. 4-3A). The youngest sample deposited at around 0.7 ka reflects the modern timescales of terrigenous OM transported to the core location. The *n*-C_{16} alkanoic acid (marine origin; Ohkouchi and Eglinton, 2008) yields a $\Delta^{14}C$ concentration of –187 ± 13‰, i.e. an age of 1600 ± 125 ^{14}C years. This is less depleted and thus younger than the *n*-C_{26} and *n*-C_{28} alkanoic acids (terrestrial origin) with $\Delta^{14}C$ of –398 ± 12‰ and –415 ± 14‰, respectively (i.e., ages of 4010 ± 160 and 4240 ± 200 ^{14}C years) from the same sample. The relatively strong depletion of the *n*-C_{16} alkanoic acid relative to the deposition age is most likely due to the marine reservoir age of the DIC utilized by the marine phytoplankton. When considering a marine reservoir age of 900 years in the Okhotsk Sea (Max et al., 2012) the corrected age of *n*-C_{16} alkanoic acid is with 780 ± 115 ^{14}C years within the range of the depositional age of 0.7 ka.

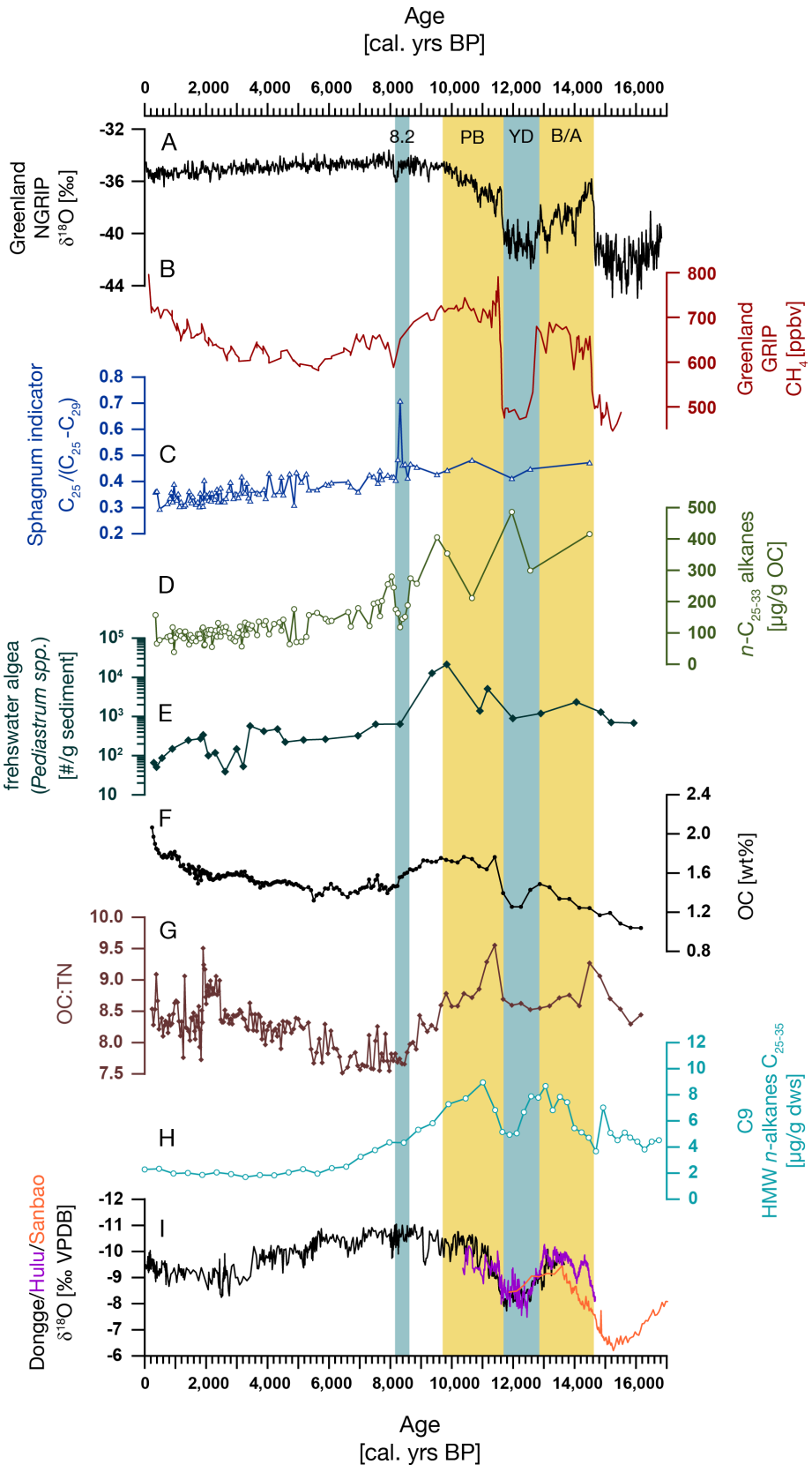

Figure 4-2. Comparison of proxies indicative of terrestrial organic matter transport in core LV28-4 and published data. A – Greenland NGRIP $\delta^{18}O$ on the timescale of Rasmussen et al. (2008). B – Greenland GRIP CH_4 from Brook et al. (2000). C – Sphagnum proxy based on *n*-alkanes of this study, after Vonk and Gustafsson (2009). D – *n*-$C_{25\text{-}33}$ alkane concentrations [µg/g OC] this study. E – freshwater algae (*Pediastrum spp.*) counts [#/g sediment] in core LV28-4 (Lembke-Jene,

2014). F – organic carbon content [wt%] of core LV28-4 (Lembke-Jene, 2014). G – atomic organic carbon to nitrogen ratio of core LV28-4 (Lembke-Jene, 2014). H – *n*-C_{25-35} alkane concentrations [µg/g sediment] of nearby core C9 (Seki et al., 2012). I - $\delta^{18}O$ speleothem record from Dongge (black; (Dykoski et al., 2005), Hulu (purple; (Wang et al., 2001), and Sanbao Caves (orange SB3; (Wang et al., 2008). For comparison Hulu and Dongge $\delta^{18}O$ records are plotted offset by 1.6‰ to the negative to account for the higher $\delta^{18}O$ values in the Hulu and Dongge records compared to the Sanbao record (cf. Wang et al., 2008).

We calculated the initial $\Delta^{14}C$ concentration ($\Delta^{14}C_{ini}$) of our *n*-alkanoic acids at the time of deposition (Ohkouchi et al., 2002), thereby correcting for the ^{14}C decay since the deposition. We further calculated the difference between the *n*-alkanoic acid $\Delta^{14}C_{ini}$ and the atmospheric $\Delta^{14}C$ concentration ($\Delta^{14}C_{atmo}$) at the time of deposition (derived from IntCAL13; Reimer et al., 2013) in order to assess the depletion and thus ^{14}C age at the time of deposition of the terrestrial biomarkers (Table 4-2, Fig. 4-3B). For the *n*-C_{26} and *n*-C_{28} alkanoic acids the values for $\Delta^{14}C_{ini}$-$\Delta^{14}C_{atmo}$ are similar in the youngest (~0.7 ka) and oldest sample interval (~16 ka), i.e. around –350‰ and –407‰, respectively. The two samples taken at around 8.3 ka and 11.75 ka show much higher $\Delta^{14}C_{ini}$-$\Delta^{14}C_{atmo}$ values such as –580‰ and –600‰, which means they are more depleted relative to $\Delta^{14}C_{atmo}$ at the time of deposition. It is striking that the $\Delta^{14}C_{ini}$–$\Delta^{14}C_{atmo}$ values of the 0.7 ka and 16 ka samples are in a similar range, although the climatic and Amur discharge conditions were different for these two time slices. The oldest sample represents the cold, early deglacial climatic conditions before the B/A warming, when Amur River discharge was still as low as during the LGM, while the 0.7 ka sample reflects the present climatic and discharge conditions.

Table 4-2. Radiocarbon isotopic data for individual *n*-alkanoic acids. Errors are given as 1σ analytical uncertainty.

n-alkanoic acid	sample depth [cm below surface]	deposition age [cal. years BP][a]	$\Delta^{14}C$ [‰]	^{14}C age [years BP]	size CO_2 [µg]	ID No.[b]
n-C_{16}	54-56	699	–187 ± 13.5	1,600 ± 125	31	49685.1.1
n-C_{26}	54-56	699	–398 ± 12.6	4010 ±160	42	49686.1.1
n-C_{28}	54-56	699	–415 ± 12.1	4240 ± 200	33	49687.1.1
n-C_{28}	751-753	8,282	–817 ± 14.4	13,600 ± 890	107	49688.1.1
n-C_{26}	860-862	11,758	–866 ± 22.7	16,100 ± 1,400	99	49690.1.1
n-C_{28}	860-862	11,758	–856 ± 27	15,500 ± 1,500	86	49691.1.1
n-C_{26}	926-928	15,999	–868 ± 23.2	16,200 ± 1,400	85	49695.1.1

[a] age model from Lembke-Jene (2014)

[b] ETH ID number

Apparently, the modern baseline for reservoir ^{14}C ages of *n*-alkanoic acids in the Amur River catchment is around 3450 years (Table 4-2). This calculated terrestrial reservoir age is comparable to published Danube River catchment values of 1840 to 4400 years (*n*-C_{28+30} alkanoic acids, cf. (Kusch et al., 2010), a river which is situated approximately at the same latitude in Europe and has a similar length as the Amur. In analogy, we presume that catchment size to a first order approximation determines the carbon turnover rate in the Amur River basin, bearing in mind that additional factors like topography, temperature, and precipitation can have a notable influence on turnover times as well. In contrast to the modern value, our two early Holocene samples with more depleted $\Delta^{14}C_{ini}$–$\Delta^{14}C_{atmo}$ values and their related ^{14}C ages (Table 4-2) are similar to terrigenous compound-specific $\Delta^{14}C$ concentrations and ^{14}C ages from modern sediments off the Siberian Arctic Rivers, particularly off the Yenisei River and to the east of its mouth. There, $\Delta^{14}C$ of C_{24}-C_{28} *n*-alkanoic acids were –530‰ to –660‰ and mean ^{14}C ages ranged between 6000 and 8600 years (Feng et al., 2013; Gustafsson et al., 2011).

Permafrost degradation and northern wetland initiation are widely thought to play a significant role in the global deglacial changes in CO_2 and CH_4, both powerful greenhouse gases (IPCC, 2013). However, the timing and importance of sources has been difficult to ascertain and regional reconstructions of wetland initiation based on basal peat age determinations so far have given controversial results for the B/A and PB. While West Siberian peatland onset only exhibits a very small temporal lag of c. 500 years (Smith et al., 2004) after the rapid rise of CH_4 during Termination Ib, a recent re-evaluation of Alaskan and circumarctic ^{14}C data sets essentially precluded a significant role of high latitude wetland regions to the PB rapid CH_4 rise (Reyes and Cooke, 2011). We assume that the large Amur catchment with its location at the southernmost East Siberian boundary of the deglacial permafrost zone represents a potential major source area for CH_4 through early PB and B/A wetland initiation after permafrost thawing.

Our detected mean age of river transported mobilized terrigenous OM of *n*-C_{26} and *n*-C_{28} alkanoic acids at 11.75 ka falls into the beginning of the Preboreal warm phase. In addition, our OC:N ratios and OC concentrations show relatively rapid increases during Termination Ib, within the errors of our age model. The freshwater algae counts from our core (Fig. 4-2), which indicate massive Amur River discharge events during the PB, evidence huge volumes of freshwater transport to our core location, with massive export of pre-aged OM from the Amur basin, most likely derived from thawing permafrost soils. This explanation is in line with previous interpretations that high concentrations of C_{25-33} *n*-alkanes at that time compared to the late Holocene reflect input maxima of terrigenous OM by the Amur River (Seki et al., 2012). Corroborating this marine evidence, independent results from peat bogs directly in the Amur

catchment have shown that the deglacial warm phases and the PB were characterized by high effective precipitation (Bazarova et al., 2008; Seki et al., 2009), thought to coincide with extensive thawing of permafrost (Bazarova et al., 2008) and potentially leading to the rapid, widespread establishment of wetland-based CH_4 sources during that time interval.

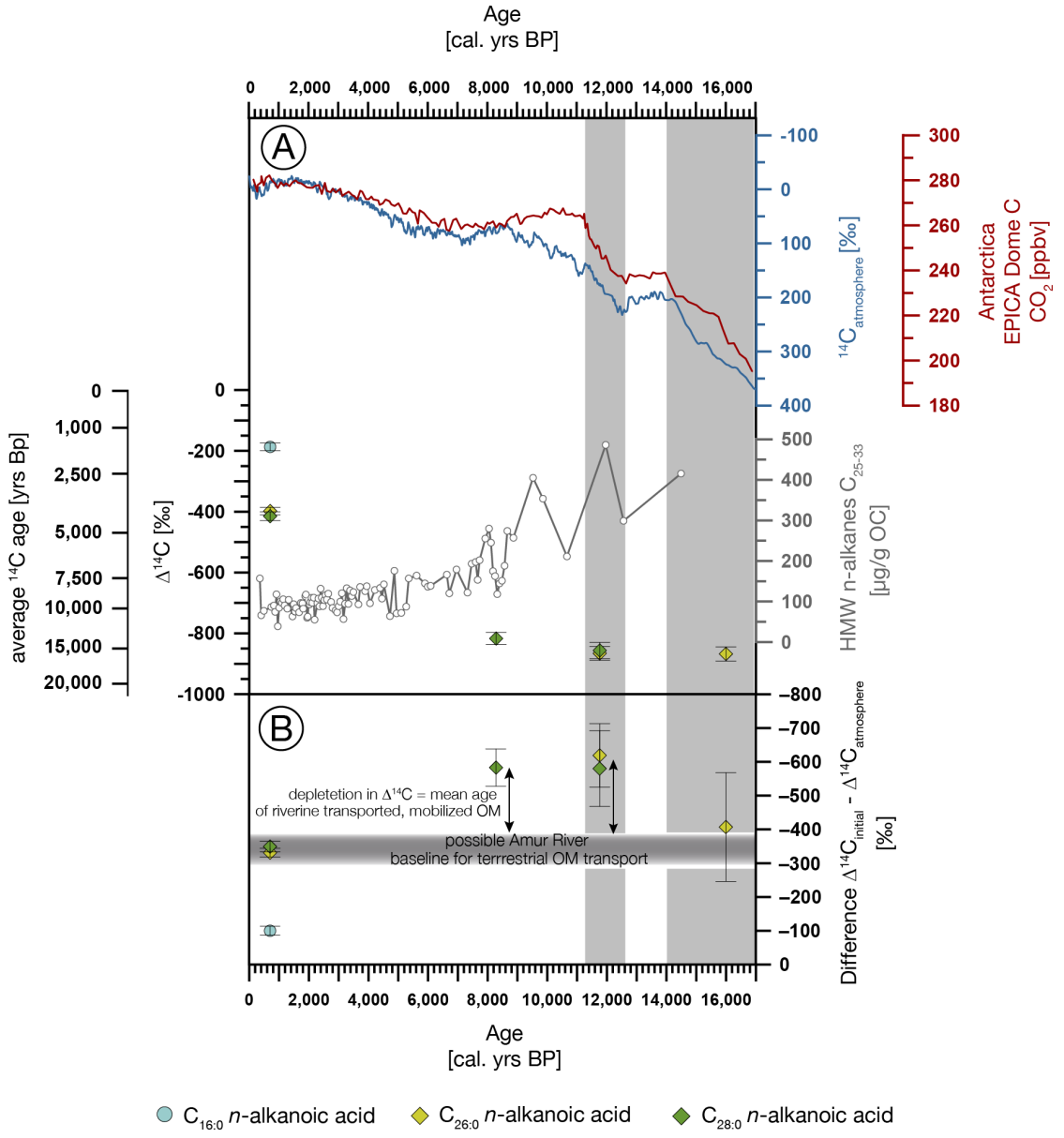

Figure 4-3. A – Radiocarbon concentrations of individual n-alkanoic acids of core LV28-4. *n*-C_{16} alkanoic acid is of marine origin while the *n*-C_{26} and *n*-C_{28} alkanoic acids are of terrestrial origin. For comparison the *n*-C_{25-33} alkane concentrations [µg/g OC] as proxy for terrestrial organic matter transport are shown from the same core. Antarctic EPICA Dome C record for atmospheric CO_2 (Monnin et al., 2001) and reconstructed atmospheric $\Delta^{14}C$ concentration based on IntCAL13 (Reimer et al., 2013) are shown in topmost panel. B – Values for $\Delta^{14}C_{atmo} - \Delta^{14}C_{ini}$ indicative of the depletion of terrestrial *n*-alkanoic acids relative to the atmospheric $\Delta^{14}C$ concentration at the time of their deposition at the core location and thus indicative of the terrestrial residence time of these compounds. $\Delta^{14}C_{ini}$ calculated according to (Ohkouchi et al., 2002). For detailed description see text.

Table 4-2. Initial radiocarbon concentrations ($\Delta^{14}C_{ini}$) of individual n-alkanoic acids and relative depletion to atmospheric $\Delta^{14}C$ concentration ($\Delta^{14}C_{atmo}$) at the time of deposition (see text for details).

n-alkanoic acid	sample depth [cm below surface]	deposition age[a] [cal. years BP]	$\Delta^{14}C_{ini}$ [‰]	$\Delta^{14}C_{ini} - {}^{14}C_{atmo}$ [‰]	mean ^{14}C age of riverine transported OM [years]
n-C_{16}	54-56	699	–115 ± 13.5	–100 ± 13.7	780 ± 125[c]
n-C_{26}	54-56	699	–345 ± 13.2	–330 ± 13.2	3,160 ± 160
n-C_{28}	54-56	699	–363 ± 15.7	–348 ± 15.7	3,360 ± 200
n-C_{28}	751-753	8,282	–501 ± 54.8	–583 ± 54.8	6,970 ± 890
n-C_{26}	860-862	11,758	–443 ± 94	–619 ± 94	7,690 ± 1,400
n-C_{28}	860-862	11,758	–404 ± 111.9	–580 ± 111.9	6,970 ± 1,500
n-C_{26}	926-928	15,999	–84 ± 160.6	–407 ± 160.6	4120 ± 1,400

[a]derived from age model (Lembke-Jene, 2014)

4.1 Deglacial permafrost and wetland dynamics in East Siberia

Apart from our observed deglacial sequence of terrestrial hinterland change, we observe a prominent short-term decrease in $C_{25\text{-}33}$ *n*-alkane concentrations between 8.4 and 8.1 ka (Fig. 4-2D), which is accompanied by a corresponding peak in the Sphagnum moss indicator $C_{25}/(C_{25}+C_{29})$ (Fig. 4-2C; cf. Vonk & Gustafsson, 2009). This conspicuous event likely depicts the short-term "8.2 ka Event" associated with a sudden meltwater outflow into the Labrador Sea (Alley et al., 1997) that led to a slow-down of the Atlantic Meridional Overturning Circulation and widespread continental cold and dry conditions in the Northern Hemisphere (e.g. Alley et al., 1997; Daley et al., 2009; Dominguez-Villar et al., 2009; Rohling and Palike, 2005; Young et al., 2012). According to Rohling and Pälike (2005) who reviewed numerous marine and terrestrial records with sufficient age resolution to determine the timing of the 8.2 ka event around the world, most records show a longer lasting climate deterioration between 8.6 and 8.1 ka, only in some records punctuated by a sharp "event" at 8.2 ka. Most parts of northern Europe were characterized by colder and dryer conditions, partly leading to substantial vegetation shifts within short time periods of about 20 years (Alley and Agustsdottir, 2005 and references therein). Particularly in the region influenced by the East Asian Summer Monsoon there is often little or no coherent evidence for an 8.2 ka event (Fig. 4-2), although speleothem records from Oman suggest a weakened Asian summer monsoon leading to drier conditions (Fleitmann et al. 2003; (Alley and Agustsdottir, 2005).

Based on our proxy records, we suggest that between 8.3 and 8.1 ka a cold and dry centennial-scale climatic deterioration occurred in the East Siberian Amur catchment. However, based on our relatively low sample resolution at the time of this cold event and the available proxy data to date we can only speculate about the processes that led to the pattern observed in core LV28-4. Most likely, anomalous cold and/or dry conditions were connected to (1) circum-(sub-)Arctic teleconnection patterns such as the expansion of the polar vortex in analogy to Arctic Oscillation/North Atlantic Oscillation dynamics and/or (2) a mid-latitude southward displacement and strengthening of the wintertime atmospheric action centers (Siberian High/Aleutian Low pressure system). A resulting weaker East Asian Summer Monsoon, with a summer rain belt confined to a more southerly location, would cover less of the Amur catchment area (Fig. 4-1), which at present already lies at the northernmost extension of significant seasonal precipitation. This would most likely have resulted in drier, colder summer conditions within the Amur River basin and lead to subsequent decreased river discharge, which would explain the decreased *n*-C_{25-33} alkane concentrations exported to the core location, Furthermore, the 8.2 ka event is thought to be especially pronounced in form of more severe winter conditions (Rohling and Palike, 2005). More severe winters in the Amur catchment would probably be characterized by longer, thicker snow cover, later ice-breakup of the river, and later thawing of seasonally frozen soil layers, which could also have resulted in decreased export of OM. Additionally, the distinct peak in the Sphagnum proxy (cf. Vonk and Gustafsson, 2009) suggests a vegetation shift towards typical tundra plants like mosses and sedges as the peak is a result of relatively higher *n*-C_{25} alkane concentrations compared to *n*-C_{29} alkane concentrations (see supplementary data in PANGAEA). Summarizing, the occurrence of the 8.2 ka event known from North Atlantic and European high-mid latitude records implies a hemisphere-wide propagation of early Holocene climate anomalies, which in turn had a discernible influence on global greenhouse gas records (e.g. CH_4), potentially through modulation of the emerging boreal wetlands in Eastern Siberia.

5 Summary and Conclusions

We employed organic biomarker analyses and compound-specific ^{14}C dating of n-alkanoic acids on a high-resolution, well-dated sediment core from the Sakhalin continental margin in the Okhotsk Sea to reconstruct deglacial and Early Holocene hinterland dynamics in the Amur River catchment. We showed that substantially higher concentrations of terrigenous organic carbon were delivered from the hinterland to the Okhotsk Sea during the deglacial Bølling-Allerød and early Holocene Preboreal warm phases. Radiocarbon dating results support our conclusion that

widespread degradation of permafrost in the Amur River drainage basin led to the deglacial activation of old terrigenous carbon previously "locked" in frozen soils and its subsequent delivery via freshwater transport into the Okhotsk Sea. By invoking analogy to modern OM transportation patterns, we speculate that large amounts of particulate and dissolved organic matter were exported from the Okhotsk Sea to the North Pacific. Such a pattern would provide a so far under-investigated, but potentially significant exchange pathway between terrestrial and mid-depth oceanic carbon reservoirs during the last glacial termination.

In combination with earlier studies directly from the hinterland (Bazarova et al., 2008; Vaks et al., 2013), our *n*-C_{25-33} alkane and other geochemical data give support to the notion that rapid establishment of boreal wetlands followed the permafrost retreat in our studied, southernmost East Siberian Amur River catchment, and may have contributed to the fast rise of atmospheric CH_4 concentration recorded in ice core records. Further studies are needed to elucidate the deglacial Amur River catchment and associated peatland development with its potential as additional CH_4 source, especially as recent synthesis studies of other polar-boreal peatland areas have often failed to provide a coherent picture of the temporal and spatial evolution of other probable CH_4 source regions during that period (e.g. Reyes and Cooke, 2011).

Lastly, our high-resolution Early Holocene data provide first evidence for the occurrence of a brief cold, dry spell within a major Siberian watershed that closely corresponds in timing to the Northern Hemisphere centennial-scale 8.2 ka cold event. The short-term decrease in fluvial OM discharge based on our *n*-C_{25-33} alkane concentrations, coupled with the inferred rapid changes in peat moss vegetation indicates widespread, highly responsive and susceptible wetland contraction or desiccation within the East Siberian hinterland during the Early Holocene. These dynamic changes point to a potentially more important capacity of our study region in the exchange between the different carbon reservoirs than previously thought and necessitate further studies to constrain its potential role in shaping the deglacial and Early Holocene CH_4 and CO_2 evolution.

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7 SYNTHESIS AND PERSPECTIVES

Permafrost soils store huge amounts of organic matter, which accumulated under cold temperatures and high soil water content over millennia. Large fractions of this OM are perennially frozen and, thus, escape microbial decomposition. However, current projections for future global warming predict the most pronounced warming in the Arctic (IPCC, 2013) causing destabilization of the large permafrost carbon pools. Thawing will expose previously frozen and presumably labile OM to microbial remineralization, which in turn leads to release of CO_2 and CH_4 into the atmosphere. Likewise, newly available OM will be susceptible to increased erosion due to ground subsidence, collapse of riverbanks, lake shores, and coastal deposits. The eroded material will be transported and transferred as dissolved and particulate matter by rivers until it is ultimately deposited in the coastal oceans. Accordingly, POM exported by rivers retains information about the hinterland vegetation and other permafrost conditions.

In this thesis POM sources and cycling by large Siberian rivers draining permafrost watersheds were studied in order to investigate the sources, state of degradation, and age of POM in the Lena Delta and adjacent Buor Khaya Bay. This can serve as baseline needed to detect future changes within the watershed.
The chapters 2 and 3 deal with soils and POM from the Lena Delta sampled during different seasons (spring and summer) as well as surface sediments from the adjacent Buor Khaya Bay.

In Chapter 2 lignin biomarkers (representing vascular land plants) were used to distinguish contributions of woody gymnosperm vegetation supplied from the southern taiga forests and non-woody angiosperm vegetation derived from the tundra areas in the northernmost part of the Lena catchment. A simple linear mixing model based on the lignin biomarker distribution indicates that POM within the Lena Delta and organic matter in Buor Khaya Bay surface sediments contains comparable amounts of gymnosperm and angiosperm sources. Considering the small area covered by tundra (~12 % of total watershed), the input of tundra-derived organic matter is substantial. On the other hand, it is known that POM transport efficiency from the most distal parts of a watershed to the ocean is relatively small since large fractions of organic matter get trapped on floodplains where it gets stored for extended periods of time. Nonetheless, the fact that gymnosperm-derived organic matter is present in Buor Khaya Bay sediments implies that substantial fractions of Lena River POM from the southern catchment are not simply trapped in the Lena Delta but also accumulate in the Buor Khaya Bay.

Moreover, the lignin biomarker composition can be used as an indicator for organic matter degradation. The investigated soils within the Lena Delta show a large variability of degradation state and notably, the oldest samples retrieved from an ice complex profile within the delta show lowest degradation impact. This supports the hypothesis that organic matter freeze-locked in these Pleistocene deposits is less degraded than organic matter in Holocene permafrost soils, most probably due to protection of organic matter in organo-mineral complexes. Based on the lignin biomarkers riverine POM and coastal surface sediments are more degraded than the soils in the Lena Delta. These findings imply that the coastal sediments either receive more degraded OM from an additional source south of the Lena Delta, or more degraded soil OM present in the fine fraction suspended matter, which was not sampled for this study. The fine grain-size fraction of soils and riverine suspended matter are generally associated with higher lignin degradation and is also most likely to be held in suspension during lower summer flows compared to coarser grain sizes.

In chapter 3, the bulk radiocarbon concentrations ($\Delta^{14}C$) of POM in the Lena Delta are discussed. In the context of a likely positive carbon-climate feedback to greenhouse warming the quality and fate of this permafrost OM pool in the coastal waters of the Laptev Sea is currently under debate. Although riverine POM can only provide temporal and spatial snapshots, the data set presented is the first POM ^{14}C data available for Lena Delta surface water and, thus, improves our knowledge of the carbon isotopic composition of riverine POM. Because of strong riverine primary production in the surface waters during spring and summer, bulk POM $\Delta^{14}C$ concentrations and related ^{14}C ages might be biased by the contribution of modern phytoplankton/bacterial organic matter to the POM. The $\delta^{13}C$ isotopic composition of the POM was used to estimate the fraction of phytoplankton-derived organic matter using isotope mass balance. Similarly, assuming riverine planktonic POM has a modern ^{14}C signature, the $\Delta^{14}C$ concentration of the terrigenous organic matter could be inferred via mass balance. The resulting more depleted $\Delta^{14}C$ concentrations reflect spatially heterogeneous compositions and variable residence times of organic matter in Lena River catchment soils (Holocene to Pleistocene ages). Due to the fact that $\Delta^{14}C$ concentrations of soil-derived organic matter exported by the Lena River and organic matter delivered by coastal erosion are closer together now, both sources are difficult to distinguish in sediments from the Buor Khaya Bay and Laptev Sea (according to the newly defined end-members). However, using only bulk riverine POM $\Delta^{14}C$ concentrations as soil end-member results in an underestimation of the true soil OM age and could therefore lead to over- or underestimations when calculating soil-derived organic matter contribution from the Lena River to coastal sediments.

The studies performed in the Lena Delta, NE Siberian could improve our knowledge of sources and cycling of particulate organic matter in the Lena Delta and adjacent coastal zone. However, many open questions are left for future research in this area. The vegetation and soil sample set analyzed to identify organic matter sources contributing to surface water POM is rather small. Particularly when considering the vast catchment area of the Lena River, soil samples from the southern catchment with taiga forest vegetation would add valuable information. Further, the lignin biomarker composition of different grain size fractions in soils and sediments from the catchment would improve our understanding of strongly degraded POM samples.

With the goal to characterize sources and cycling of terrigenous organic matter in the Laptev Sea and on other East Siberian shelves several studies have used similar approaches, i.e. determined biomarker composition, bulk carbon isotopic composition, and biomarker-specific radiocarbon concentrations. These studies improved our knowledge about carbon pools contributing to Arctic shelf sediments, have identified their different molecular recalcitrance (and, thus, ^{14}C age), and determined different C sources. To study organic matter sources and organic matter cycling in the water column and thereby track remineralization of settling POM, it would be necessary to determine the biomarker composition as well as biomarker-specific isotopic composition of POM at different water depths in order to trace compositional changes. Yet, the suggested analyses need large amounts of organic matter, which will be difficult to obtain since thousands of liters might have to be filtered. Furthermore, more integrated studies of organic matter sinking on the Siberian shelves are needed if valuable information of current and future changes of permafrost OM supply to the ocean and the quality of this OM are desired. The published compound-specific radiocarbon concentrations of sediments off the river mouths of the large Siberian rivers are derived from grab samplers, sometimes even combined along a transect. Since this sampling method does not provide an undisturbed surface uncertainty persists whether these sediments (and the biomarkers analyzed in these samples) actually represent the modern surface sediment or rather combine deeper and older sediment layers. Under these circumstances independent age controls, e.g., using ^{210}Pb chronologies, are needed to provide sedimentation and OM burial rates against which biomarker-specific radiocarbon concentrations may be calibrated. However, the shallow Siberian shelves are characterized by sediment re-distribution due to the action of waves, sea-ice, tidal currents, and nepheloid layer transport, which make it challenging but not impossible to establish ^{210}Pb age models

In the context of a positive and reinforcing permafrost-carbon feedback upon future permafrost thaw and organic matter decay, the possibility to study past permafrost dynamics will improve our understanding and prediction of potential future processes. In Chapter 4 the supply of OM from the Amur River into the Okhotsk Sea during the last termination was investigated using compound-specific radiocarbon analysis of terrigenous biomarkers from a sediment core. The Amur catchment is the southernmost large Siberian river system and was characterized by permafrost during the LGM while it is almost permafrost-free today. It, thus, represents an analog for future permafrost destabilization scenarios. Terrestrial biomarkers were ^{14}C depleted (pre-aged) relative to the reconstructed past atmospheric $^{14}CO_2$ concentrations in all investigated sampling depths. However, the degree of pre-aging was different over time. Both, the oldest (16 ka) and the youngest (0.7 ka) samples were significantly less ^{14}C-depleted relative to the atmosphere than the samples from ~11.75 ka and 8.2 ka to the respective atmospheric ^{14}C concentrations at the time. Since the Amur River discharge was very strong during these time periods the increased ^{14}C-depletion of the terrigenous organic matter in the termination I samples is interpreted to represent an increased contribution of more strongly pre-aged organic matter caused by the destabilization/thawing of permafrost soils and the resulting release of previously unavailable old C in the Amur hinterland. This study is a valuable contribution to the discussion about possible contributions of CO_2 and CH_4 to atmospheric concentrations from permafrost thawing and wetland development during the last deglacial.

An improved understanding of the global carbon cycle and carbon sources during the last deglacial will ultimately improve projections of future global carbon cycle including permafrost soils. So far, there are only a few models investigating future permafrost degradation, the resulting northward retreat of the permafrost zone, and deepening of the active layer. Although the proposed rates of permafrost degradation are estimated differently in these publications, they is general consensus that the spatial permafrost extent will decrease and summer thaw layer will deepen by the end of the 21st century. However, the magnitude and time scales of the permafrost-carbon feedback are largely unknown. Permafrost thawing and subsequent release of greenhouse gases is a rather slow process that would continue for decades or centuries even after global climate is stabilized at higher atmospheric CO_2 concentrations/higher temperatures.

There is an urgent need to improve the understanding of the permafrost-carbon feedback and implement this knowledge in current model projections for future atmospheric greenhouse gas concentrations. Carbon released from thawing permafrost adds to the anthropogenic CO_2 emissions and identifying the amount of permafrost carbon released

is crucial for climate change mitigation goals. Permafrost carbon will contribute to the climatic effects resulting from anthropogenic fossil fuel burning and presumably accelerate climate change. This may lead to even higher CO_2 levels and further temperature increases than currently assessed by the IPCC.

However, the sedimentations rates in the studied core are very low in the time intervals of interest and additional compound-specific radiocarbon data from higher resolution sedimentary records would be necessary to better constrain the timing of pre-aged organic matter deposition. More locations with the potential to detect old OM from thawed permafrost during the last termination are needed to support the here presented hypothesis and confine the timing of thawing in other part of the northern hemisphere. This in turn would help model simulations to account for a possible additional terrestrial source contributing to the increase in atmospheric CO_2 during the last termination, which could also be applied to model terminations further in the past.

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