1 Historical records of organic matter supply and degradation status in the East
2 Siberian Sea
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ABSTRACT

Destabilization and degradation of permafrost carbon in the Arctic regions could constitute a positive feedback to climate change. A better understanding of its fate upon discharge to the Arctic shelf is therefore needed. In this study, bulk carbon isotopes as well as terrigenous and marine biomarkers were used to construct two centennial records in the East Siberian Sea. Differences in topsoil and Pleistocene Ice Complex Deposit permafrost concentrations, modeled using $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$, were larger between inner and outer shelf than the changes over time. Similarly, lignin-derived phenol and cutin acid concentrations differed by a factor of ten between the two stations, but did not change significantly over time, consistent with the dual-carbon isotope model. High molecular weight (HMW) *n*-alkane and *n*-alkanoic acid concentrations displayed a smaller difference between the two stations (factor of 3–6). By contrast, the fraction for marine OC drastically decreased during burial with a half-life of 19–27 years. Vegetation and degradation proxies suggested supply of highly degraded gymnosperm wood tissues. Lipid carbon preference index (CPI) values indicated more extensively degraded HMW *n*-alkanes on the outer shelf with no change over time, whereas *n*-alkanoic acids appeared to be less degraded towards the core top with no large differences between the stations. Taken together, our results show larger across-shelf changes than down-core trends. Further investigation is required to establish whether the observed spatial differences are due to different sources for the two depositional settings or, alternatively, a consequence of hydrodynamic sorting combined with selective degradation during cross-shelf transport.

Keywords: Arctic; East Siberian Arctic Shelf; ^{210}Pb ; Monte Carlo; $\delta^{13}\text{C}$; $\Delta^{14}\text{C}$; lignin; HMW wax lipids

1. Introduction

Amplified global warming in the Arctic may affect regional and global carbon cycles. A putative carbon–climate coupling process in the Arctic is the accelerated destabilization and remobilization of carbon currently held in permafrost. Remobilization of this vulnerable carbon pool can occur as a result of several climate-driven mechanisms including deepening of the permafrost active layer, thermokarst processes, enhanced river discharge as well as thermal destabilization and erosion of coastal permafrost (Peterson et al., 2006; Wagner et al., 2011; Vonk and Gustafsson, 2013). Considering the vast amount of carbon stored in permafrost soil (1307 Pg; Hugelius et al., 2014), the translocation and ultimate fate of the terrigenous organic carbon (TerrOC) in the coastal ocean is insufficiently understood (Vonk and Gustafsson, 2013).

Furthermore, marine ecosystems are also undergoing rapid changes with rising temperatures (Walther et al., 2002; Hoegh-Guldberg and Bruno, 2010). Shrinking ice-cover and a warmer Arctic Ocean have the potential to highly increase marine primary production (Slagstad and Wassmann, 1996; Arrigo et al., 2008). Organic matter dynamics in the Arctic shelf seas, however, remain understudied, due to the complex nature of the system with heterogeneous pools and pathways from different sources, in addition to the logistical challenges for field campaigns.

The East Siberian Arctic Shelf (ESAS), the world's largest continental shelf, receives TerrOC that is delivered by the Great Russian Arctic Rivers that drain extensive areas of permafrost (e.g., Stein and Macdonald, 2004; van Dongen et al., 2008; Gustafsson et al., 2011; Holmes et al., 2012; Semiletov et al., 2012). An additional important source of particulate organic carbon (POC) derives from the continuous erosion of the vast coastline, that includes extensive outcrops of Yedoma (Pleistocene Ice-Complex Deposits, ICD) (e.g., Semiletov, 1999; Stein and Macdonald, 2004; Schirrmeister et al., 2011; Vonk et al., 2012,

Sanchez-Garcia et al., 2014). Insights into the sources and degradation status of TerrOC on the ESAS have been gained from applying isotope-based source apportionment models to the surface sediments (e.g., Semiletov et al., 2005; Vonk et al., 2010, 2012, 2014) and biomarkers for both surface sediments (e.g., Stein and Macdonald, 2004; Feng et al., 2013; Tesi et al., 2014) and POC in the water column (e.g., Charkin et al., 2011; Karlsson et al., 2011). Yet, despite increased awareness of potential changes in the Arctic carbon cycle, knowledge is still lacking on dispersal and accumulation of both TerrOC and marine organic carbon on the Arctic shelves, and whether any changes have occurred over the past century. Most studies have focused on surface sediments, and do not address this temporal dimension.

This study explores how sources and degradation status of organic matter have evolved over the last century and assesses whether recent changes in the Arctic carbon cycle are evident in the shelf sediment record. Our analysis focused on two sediment cores from the East Siberia Sea (ESS) that record up to the last 120 years of sediment accumulation. The cores were collected in different depositional regimes: one nearshore located outside the Kolyma estuary and the other one from the outer shelf about 600 km from the coastline (Fig. 1). To reconstruct a historical record of the terrigenous input to the ESAS and to compare temporal to spatial changes we developed a ^{210}Pb -based age model and measured down-core profiles of a suite of well-known terrigenous and marine biomarkers (solvent extractable high-molecular weight wax lipids and CuO oxidation products) as well as bulk carbon isotopes ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) at these two locations.

2. Materials and Methods

2.1. Study area

The East Siberian Sea (ESS) is the largest marginal sea in the Arctic Ocean (Stein and Macdonald, 2004, and citations therein), spanning an area of 987,000 km² that is bordered by the Laptev Sea along the western edge of the New Siberian Islands and the Chukchi Sea along Wrangel Island to the east. With a mean depth of 58 m and low bathymetric gradients, it also belongs amongst the shallowest shelf seas in the Arctic. The Indigirka and Kolyma are the main rivers discharging into the ESS (54 and 122 km³ per year, respectively; Stein and Macdonald, 2004). Pacific inflow, the Transpolar Drift and the Siberian Coastal Current are the main flow regimes in the ESS. Their intensities and directions vary strongly depending on predominant atmospheric pressure conditions (Stein and Macdonald, 2004). Marine primary production is constrained to the ice-free periods in summer, when sunlight can penetrate surface waters (Stein and Macdonald, 2004). Due to adverse climate conditions and protracted periods of ice-cover, lasting on average 10 months per year, the ESS remains relatively poorly explored and characterized.

2.2. Sampling

Sediment core samples were collected with a dual gravity corer GEMAX on the East Siberian Arctic Shelf onboard the *H/V Yakob Smirnitskyi* as part of the extensive International Siberian Shelf Study in 2008 (ISSS-08); for more information on the expedition, see Semiletov and Gustafsson (2009). More information on the ISSS-08 study areas can be found in Alling et al. (2010), Sánchez-García et al. (2011) and Vonk et al. (2012). The inner shelf station YS-37 (70.13°N, 168.01°E, labelled IS) was located at a water depth of 42 m; the outer shelf station YS-90 (74.67°N, 172.39°E, labelled OS) at a depth of 63 m (Fig. 1). The sediment cores had a total length of 15 cm (IS) and 17 cm (OS). They were sectioned into 1

cm thick intervals within 12 to 48 hours after sampling and stored at -18°C for the rest of the expedition. The samples were then freeze-dried at the Department of Applied Environmental Science at Stockholm University, Sweden. Surface sediments from IS and OS have been extensively characterized in earlier studies (e.g., Tesi et al., 2014; Vonk et al., 2012, 2010).

2.3. Geochronology

^{210}Pb measurements were carried out by gamma spectroscopy at the Radiation Research Division of the Risø National Laboratory for Sustainable Energy, Denmark. An n-type HPGe detector with Beryllium window was used. Samples (~10 g dry weight) were placed in plastic Petri dishes and counted for 20 to 50 h depending on their activity. Self-absorption of the 46 keV line was corrected for using the methodology of Cutshall et al. (1983). The relative error was 5% on average for ^{226}Ra , 25% for ^{137}Cs , and 12% for ^{210}Pb . All ^{210}Pb data of this study have previously been published in Vonk et al. (2012).

2.4. Bulk elemental and isotopic analyses

Homogenized subsamples were acidified in pre-combusted Ag capsules by adding 1 M HCl in order to remove inorganic carbonates prior to bulk elemental and isotopic analyses. The samples were dried at 60°C and the procedure repeated. Total organic carbon (TOC) and total nitrogen (TN) content (as mg/gdw), as well as the stable isotope composition of the organic carbon ($\delta^{13}\text{C}$ of OC) were determined at the Department of Geosciences at Stockholm University using a Carlo Erba NC2500 elemental analyzer connected via a split interface to a Finnigan MAT Delta V mass spectrometer. Stable isotopes and TOC and TN were measured simultaneously. The relative error was $< 1\%$. Stable isotope data are reported relative to VPDB using the $\delta^{13}\text{C}$ notation.

Radiocarbon analyses of prepared samples were conducted at the US National Ocean Sciences Accelerator Mass Spectrometry Facility of the Woods Hole Oceanographic Institution, USA, following their standard routines (Pearson et al., 1998). The relative error of the measurements is $< 0.5\%$. Radiocarbon data are reported using $\Delta^{14}\text{C}$ notation following (Stuvier and Polach, 1977).

2.5. Surface area analyses

Specific surface area (SA) analyses were performed with a micromeritics Gemini VII Surface Area and Porosity analyzer. Prior to analysis, subsamples of approximately 1 gdw were desalted by repeated mixing with 50 ml MilliQ water, centrifugation (20 min at 8000 rpm) and removal of supernatant water. Samples were subsequently freeze-dried, combusted for 12 h at 400 °C to remove all organic material, and gently cooled down to room temperature over 12 h. Just before analysis, the samples were degassed in a Micromeritics FlowPrep 060 Sample Degas System for 2 h at 200 °C under a constant flow of nitrogen. Each analysis was started by measuring the free space in the vial. Nitrogen was used as adsorbing gas. From 6-pressure-point measurements (relative pressure $p/p_0 = 0.05\text{--}0.3$, equilibration time 5 s) the specific surface areas were derived as in Brunauer et al. (1938). The instrumental error was 0.1–0.3 m²/gdw, which corresponds to a relative error of about 1%. The instrument performance was monitored with the surface area reference material Carbon Black (21.0 ± 0.75 m²/g) provided by Micromeritics.

2.6. Biomarker analyses

2.6.1. CuO oxidation products

CuO oxidations of sediment samples were carried out according to the method presented in Tesi et al. (2014), which is briefly summarized here. Microwave-assisted alkaline CuO

oxidation was carried out using an UltraWAVE Milestone 215 microwave. Homogenized subsamples containing 2–5 mg organic carbon (corresponding to 120–500 mg of sediment) were oxidized with 300 mg CuO and 50 mg ferrous ammonium sulfate under alkaline oxygen-free conditions (degassed NaOH solution, 8 wt%) at 150 °C for 90 min (Goñi and Montgomery, 2000).

Known amounts of *trans*-cinnamic acid and ethyl vanillin were added as recovery standards to the extracts. Samples were then acidified with concentrated HCl to pH 1 and extracted twice with ethyl acetate. Water was removed with anhydrous Na₂SO₄ and the solvent evaporated. The samples were re-dissolved in pyridine and derivatized with bis-trimethylsilyl-trifluoroacetamide (BSTFA) + 1% trimethylchlorosilane (TMCS). Target compounds were quantified on a gas chromatograph–mass spectrometer in full scan mode (GC–MS, Agilent) using a DB1-MS capillary column (30 m x 250 µm, 0.25 µm stationary phase thickness, Agilent J&W) with a temperature profile of initially 60 °C followed by a ramp of 5 °C/min until reaching 300 °C.

The quantification of lignin phenols, benzoic acids, and p-hydroxybenzenes was achieved by comparison to the response factors (key ions) of commercially available standards. For cutin-derived products, fatty acids and dicarboxylic acids the response factor of *trans*-cinnamic acid was used as in Goñi et al. (1998).

2.6.2. Solvent-extractable lipids

Solvent-extractable lipids were isolated and quantified according to the procedure presented in Vonk et al. (2008) and Karlsson et al. (2011). Homogenized subsamples of 3 gdw (equivalent to 20–50 mg OC) were Soxhlet-extracted for 24 h with 120 ml dichloromethane/MeOH (2:1, v/v). The extracts were further cleaned (water removal with anhydrous Na₂SO₄, sulfur removal with activated Cu) and then separated into a neutral and an

182 acid fraction using Bond-Elut cartridges (bonded phase NH₂, Varian). The neutral fraction
183 was further separated on activated Al₂O₃ columns into a polar and a nonpolar fraction. For the
184 three compound classes *n*-alkanes (neutral non-polar fraction), *n*-alkanols (neutral polar
185 fraction) and *n*-alkanoic acids (acid fraction) one internal standard, d50-tetracosane, 2-
186 hexadecanol and d39-eicosanoic acid respectively, was added to the sediment samples prior to
187 extraction.

188 All fractions were then analyzed by GC–MS with a DB5-MS capillary column (30 m x
189 250 µm, stationary phase thickness 0.25 µm, Agilent J&W) using the same temperature
190 program as for the CuO products. The polar and acid fractions were derivatized with BSTFA
191 + 1% TMCS prior to analysis. Quantification was performed using a 5-point calibration curve
192 with commercially available standards. All biomarker results are reported as loadings
193 (µg/m²), i.e. relative to the specific surface area.

3. Results and discussion

3.1. Geochronology and sediment surface area

In order to establish historical sediment records of organic matter input and degradation status an age model for dating the sediment cores is necessary. The radionuclide ^{210}Pb with a half-life of 22.2 years has been widely used for marine sediment dating on a timescale of 100 years (e.g., Nittrouer et al., 1979; Strobl et al., 1998). In undisturbed sediment cores with constant sedimentation rates the relationship between the natural logarithm of the unsupported fraction of ^{210}Pb , i.e. the difference in activity of ^{210}Pb and ^{226}Ra (termed excess ^{210}Pb), over compaction-corrected depth is expected to be linear, because the only change in activity is caused by radioactive decay (e.g., Cutshall et al., 1983). For the two cores used in this study, IS and OS, this linear correlation holds with a coefficient of determination (R^2) of 0.67 ($n = 15$, $p < 0.0002$) and 0.85 ($n = 9$, $p < 0.0004$), respectively (Supplementary Fig. S1). For OS, no excess ^{210}Pb could be detected below 9 cm depth, whereas for IS there is excess ^{210}Pb throughout the whole core, i.e. down to 15 cm depth.

Using the same ^{210}Pb data as in Vonk et al. (2012), and assuming a constant atmospheric ^{210}Pb input, the mass accumulation rates for IS and OS were determined (as in Appleby, 2008) to be 0.28 ± 0.07 and 0.24 ± 0.05 $\text{g}/\text{cm}^2/\text{year}$, respectively. These values translate into linear sedimentation velocities of 1.5 ± 0.4 and 1.4 ± 0.3 mm/year . The numbers agree with other results in Vonk et al. (2012) for the East Siberian Sea, but are slightly higher than the rates measured in the neighboring Laptev Sea by Strobl et al. (1998), which vary between 0.05 ± 0.02 and 0.24 ± 0.04 $\text{g}/\text{cm}^2/\text{year}$. The corresponding sediment records for IS (15 cm long) and OS (17 cm long) thus span a period of 90 and 120 years, and are therefore suitable for investigating changes in the ESS carbon cycling over centennial timescales.

The calculated rates are supported by ^{137}Cs data, which are often used to independently test the robustness of ^{210}Pb -derived accumulation rates (e.g., Strobl et al., 1998). According to

the ^{210}Pb chronology, ^{137}Cs activities steeply increased in the early 1960s and to a smaller extent again in the early 1990s, in agreement with the well-known transient events when the artificial radionuclide ^{137}Cs was released, i.e. nuclear bomb testing which started in 1954 with maximum fall-out in 1963 and the explosion of the nuclear reactor in Chernobyl in 1986 (Fig. 2B). Ongoing climate change is expected to cause increasing sediment transport to the Arctic Ocean (Syvitski, 2002). However, no significant change in the mass accumulation rates over the last century has been detected in either of the cores.

The mineral-specific surface area (SA) varies as a function of the sediment grain size and distribution/size of micro-pores to a first-order approximation. SA values range between 23–28 m^2/gdw for IS and between 18–25 m^2/gdw for OS (Fig. 2A). A trend towards finer material is observed starting 60 years ago (at 9 cm depth) for OS and 40 years ago (at 8 cm depth) for IS. During the last 20 years for OS (< 3 cm) and 10 years for IS (< 2 cm) a trend towards coarser sediments is detected. Since inorganic biogenic material is relatively low (< 7% dw) in these sediments (both as opal and carbonate) (Viscosi-Shirley et al., 2003) the influence of biogenic particles on SA values is expected to be negligible. Changes in SA can be attributed to changes in the energy balance of the system, where higher values, i.e. smaller grain sizes, reflect a decrease in energy (Dudarev et al., 2006). Within the same system SA values commonly increase with increasing distance from the shore (e.g., Coppola et al., 2007; Kuzyk et al., 2008), whereas here we find relatively coarser material on the outer shelf station. This indicates that the two stations may not be closely coupled by sediment transport. The distance between stations possibly results in different lateral transport times, different water circulation/water mass influences and different energy regimes driven by bottom currents and waves.

The observed vertical changes for both cores correlate well with changing patterns in ocean currents, driven by changing atmospheric conditions as reported by e.g., Savelieva et al.

(2000). They observed a significant shift in the seasonal discharge of Siberian Rivers that occurred around 1970 caused by changes in the atmospheric climate in northeastern Siberia which led to changes in precipitation, air and soil temperatures in the river watersheds. In the late 1960s the North Atlantic Oscillation index (NAO), which is closely linked to the Arctic Oscillation, shifted from negative to positive values (e.g., Peterson et al., 2002). During negative NAO periods the Beaufort Gyre is more pronounced in contrast to positive conditions when coastal currents gain importance (e.g., Steele and Ermold, 2004) and thereby facilitate along-shelf/impede cross-shelf transport. This could explain the decrease in grain size after 1960 at least for the outer shelf as there is a weaker Beaufort Gyre current.

3.2. Sources of organic matter

In this section we present proxy data that are either normalized to the organic carbon content (OC) or to the mineral surface area (SA). OC-normalization provides information about the relative proportions of different components of the organic material. SA-normalization, on the other hand, is used to describe absolute changes over time of each of these fractions (assuming that the mineral-specific surface area does not change significantly during burial).

3.2.1. Bulk characteristics and dual-isotope source apportionment of carbon fractions

Typical values for total organic carbon (TOC) content in surface sediments from the East Siberian Arctic Sea range from 0.2–1.6 %OC with higher values close to the river outlets (Stein and Macdonald, 2004). The TOC values for surface sediments in the two cores examined here are 1.3 (OS) and 1.7 %OC (IS) (Fig. 2B), consistent with other data for this area (e.g., Semiletov et al., 2005; Vonk et al., 2010). Bulk TOC is systematically higher for IS (about 0.3–0.5 %OC more throughout the profile) than for the outer shelf core OS. Following

rather constant values around 0.7 (OS) and 1.2 %OC (IS) for the lower/older part of the cores, both cores show an exponential increase ($R^2 > 0.95$) in OC concentrations over the last 60 years towards the present day.

The Carbon/Nitrogen (C/N_{mol}) ratio may be used as an indicator for a terrigenous vs marine source of TOC as higher (i.e. vascular) plants have a higher ratio than marine organic matter. Substantial contributions of soil organic matter (Goñi et al., 1998) and inorganic nitrogen, for example from ammonium bound to clay minerals, however, can distort these results to artificially low numbers, especially if the TOC concentrations are low. For these data the plot of TN over TOC yields an intercept < 0 for OS and 0.004 for IS, indicating that there are likely no significant contributions of inorganic nitrogen (as in Hedges et al., 1988). The atomic C/N ratio data for OS (Fig. 2C) shift from 7.5 to > 9 in the top 9 cm of the core (i.e. approximately the last 60 years), whereas values for IS are around 9.7 for the whole core without substantial changes over time. These C/N results agree well with earlier measurements in the East Siberian Sea by Semiletov et al. (2005). The results for OS likely indicate a relative loss of marine organic matter with increasing depth. C/N ratios can also be altered to both higher and lower values during early diagenesis, however, and implications derived from this proxy should therefore be supported by additional data (e.g., Meyers, 1994).

The isotopic composition of the bulk organic carbon may also convey information about the source of organic matter (e.g., Fry and Sherr, 1984; Raymond and Bauer, 2001). The stable carbon isotope record ($\delta^{13}C$) shows a difference between IS with values between -26 and -25‰ and OS, ranging between -24 and -22‰ (Fig. 2D), indicative of a greater proportion of terrigenous, isotopically depleted organic matter in IS (similar to other shelf regions; e.g., Gordon and Goñi, 2004). No major changes in $\delta^{13}C$ over time are evident for IS, whereas OS displays an increase in $\delta^{13}C$ of $\sim 2\text{‰}$ from the beginning of the record towards

present day. This trend is consistent with preferential degradation of reactive, isotopically enriched, marine organic matter pools confirming the indications of the C/N ratio.

The radioactive carbon isotope (^{14}C) is widely used for dating organic material, as well as for source apportionment of carbon pools with different ages (for the marine carbon cycle; e.g., McNichol and Aluwihare, 2007). Radiocarbon data ($\Delta^{14}\text{C}$) for the two cores span a wide range from -300 to -600‰ , corresponding to conventional radiocarbon ages of 2950 to 7210 years (Fig. 2E). All $\Delta^{14}\text{C}$ values have been corrected for decay since time of deposition using the ^{210}Pb chronology. Down-core trends are similar to TOC concentrations for IS and are also consistent with a relative decrease of radiocarbon-enriched (i.e. freshly produced) marine material. For OS, $\Delta^{14}\text{C}$ values are increasingly less depleted from 80 years ago towards the present. The trend can also be explained by a greater proportion of (younger) marine OC in the upper portion of the record. Additional increases in $\Delta^{14}\text{C}$ after 1960 might be caused by elevated atmospheric ^{14}C concentrations due to nuclear weapon testing. Nevertheless, the $\Delta^{14}\text{C}$ data strongly suggest substantial supply of old terrigenous carbon, presumably released from thawing permafrost, to both cores, with this contribution most pronounced for the earlier portion of the sediment records and decreasing towards the present. The distinctive stable carbon isotope and radiocarbon profiles in each core imply that the composition of organic material and its accumulation are not closely coupled at the two locations. If the sampling locations were closely linked by rapid sediment transport, material of the same age should display similar $\delta^{13}\text{C}$ values.

In order to calculate the relative contributions of different OC sources, we applied a Monte Carlo based dual-carbon isotopic mixing model (Andersson, 2011, as applied earlier to the ESAS, e.g., Vonk et al., 2010, 2012). Three OC sources with distinct isotopic fingerprints (end member compositions) may be differentiated (see also Fig. 3A): erosion of ice-complex deposit permafrost, predominantly at the coast containing Pleistocene material that is very

depleted in $\Delta^{14}\text{C} = -940 \pm 84\text{‰}$, $\delta^{13}\text{C} = -26.3 \pm 0.63\text{‰}$ (labelled “ICD permafrost”); thawed terrigenous topsoil permafrost, i.e. organic carbon from the active layer, $\Delta^{14}\text{C} = -126 \pm 54\text{‰}$, $\delta^{13}\text{C} = -28.2 \pm 1.96\text{‰}$ (labelled “topsoil permafrost”); and marine/planktonic primary production, i.e. particulate organic matter, $\Delta^{14}\text{C} = 60 \pm 60\text{‰}$, $\delta^{13}\text{C} = -21 \pm 1\text{‰}$, (labelled “marine”).

The end-members isotopic values for ICD permafrost and topsoil permafrost are taken from Vonk et al. (2012). The marine end-member values for $\delta^{13}\text{C}$ in that paper, largely based in Laptev Sea data, is too depleted for the current East Siberian Sea samples. Because the sampling location is farther east than most locations in Vonk et al. (2012) marine POC is likely to be more influenced by Pacific inflow with a more enriched stable isotope signature (compare with Semiletov et al., 2005). There is an ongoing discussion about the end-member stable isotope composition ($\delta^{13}\text{C}$ values) of marine organic matter in the Arctic Ocean (see e.g., Goñi et al., 2013); particulate organic matter (POC) derived from sea ice can be as enriched as -15 to -18‰ (Schubert and Calvert, 2001), but averaged values for POC collected in sediment traps on the Bering Sea shelf, which comprises the organic matter that is transported to the East Siberian Sea by the Pacific inflow, suggest a mean closer to -21‰ (Smith et al., 2002) for the eastern part of the ESAS (i.e. east of $\sim 160^\circ\text{E}$). Accordingly a value of $\delta^{13}\text{C} = -21 \pm 1\text{‰}$ was used for the marine fraction in this study. The mass balance equations were solved with a Monte Carlo simulation strategy (e.g., Andersson, 2011; Vonk et al., 2012), which allows comprehensive accounting for all uncertainties, including of the three end-member isotopic values. The three fractions were then converted into fluxes using the ^{210}Pb -based age model.

There are down-core variations in the relative contributions of the three OC sources as well as strong differences between the two locations. Overall fluxes are higher for IS as a result of its higher mass accumulation rate (Fig. 3B and C). The marine flux is relatively

higher for OS compared to IS (~61% in the top cm for OS, ~33% for IS). The flux of the marine OC fraction exponentially increases towards the present for both cores, consistent with trends in $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of the TOC. The topsoil permafrost fraction contributes only a small fraction in OS (~4–5%), while it contributes as much OC as the marine and ICD fractions for IS (~30%). However, in contrast to ICD, topsoil also increases exponentially towards the most recent portion of the record. This trend may reflect a recent increase in supply of topsoil permafrost toward the core top or loss over time/depth with diagenesis. Organic matter from ICD permafrost displays no significant trend over time for either core, but makes up the major component for IS (~37–58%). For OS it contributes as much as the marine fraction in the top 8 cm (~33–44%) and becomes the most important carbon fraction with depth (~52–62%).

A potentially complicating factor, particularly for OS source apportionment calculations, is the timescale of lateral transport of material prior to sediment sequestration on the outer shelf. Keil et al. (2004) estimated 1800 years for the lateral transport of 158 km along the Washington margin. For the 600 km distance between OS and the coastline the lateral transport time may therefore be on the order of several thousand years, although at present there are no constraints on this timescale. Nevertheless, it seems reasonable to assume significant ageing and thus radiocarbon depletion in organic matter during this cross-shelf transport. We performed a sensitivity analysis to explore potential effects of lateral transport time on the ^{14}C -based source apportionment (Table 1). We assumed a maximum transport time of 5000 years for OS, i.e. the time that has passed since the sea level reached the modern coast line in Arctic Siberia (Bauch et al., 2001), and adjusted both topsoil and ICD permafrost signatures to more depleted $\Delta^{14}\text{C}$ values to account for aging during transport. With these values we obtain increased contributions of the topsoil and correspondingly decreased contributions of the ICD permafrost organic matter. However, since the dual-isotope observations at OS are very close to a theoretical mixing line between marine and ICD end-

member (Fig. 3A), the topsoil permafrost contribution changes only slightly, from about 5% to about 7%, and the ICD permafrost contribution decreases from 48% to 44% (see Table 1). Given these considerations, ^{14}C -aging during lateral transport for the terrigenous sources appears to have a negligible effect on source apportionment assessments.

It is also important to bear in mind, however, that the marine OC end-member may also be subject to significant translocation and aging prior to sedimentation (e.g., Ohkouchi et al., 2002; Mollenhauer et al., 2005, 2007). Adjusting the radiocarbon signal of the marine contribution to an age as high as 3500 years as observed by Mollenhauer et al. (2007) for the Namibian shelf would certainly affect the results of these calculations even further. Such high ages for marine organic matter may have less impact on the Siberian Shelf due to the oxygenated waters associated with this region, whereas on the Namibian Shelf the strong oxygen minimum zone limits organic matter degradation during resuspension and redistribution.

Another source of uncertainty is the $\delta^{13}\text{C}$ value for the topsoil fraction. A recent study by Winterfeld et al. (2014) proposes $-26.6 \pm 1.1\text{‰}$ for the riverine, soil-derived particulate organic matter fraction in the Lena delta, whereas a mean value of $-29.3 \pm 1.7\text{‰}$ for Kolyma river POC is reported by McClelland et al. (2008). Extrapolating a $\delta^{13}\text{C}$ value for the riverine component from the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values of the Kolyma paleo-river samples in Vonk et al. (2010) results in $\delta^{13}\text{C}_{\text{topsoil}} = -29.3\text{‰}$. This value lies within one standard deviation of the value we have used in this study ($\delta^{13}\text{C}_{\text{topsoil}} = -28.2 \pm 2.0\text{‰}$). To further improve the quantitative source apportionment, both transport times and end-member isotopic signatures on the ESAS should be better constrained.

3.2.2. Biomarker indications of terrigenous organic matter sources

Molecular fossils of marine and terrigenous organic material carry complementary information that can help to constrain allochthonous and autochthonous OC contributions to Arctic continental margin sediments. In this investigation we examined both CuO reaction products and solvent-extractable lipids. By normalizing the measured biomarker amounts to the sediment surface area overshadowing signals caused by changes of the other OC fractions can be minimized. Lignin-derived phenols have been used in a wide variety of studies as a tracer of vascular plant-derived organic matter (e.g., Hedges and Mann, 1979a; Ertel and Hedges, 1984; Goñi and Hedges, 1995). They are commonly categorized according to their phenol type into vannillyl phenols (i.e. vanillin, acetovanillone, and vanillic acid; labelled V), syringyl phenols (i.e. syringaldehyde, aceto syringone, and syringic acid; labelled S), and cinnamyl phenols (i.e. p-coumaric and ferulic acids; labelled C). Total lignin represents the sum of these three groups. Cutin-derived hydroxy fatty acids (i.e., 16-hydroxyhexadecanoic acid; hexadecan-1,16-dioic acid; 18-hydroxyoctadec-9-enoic acid; 7- or 8-dihydroxy C₁₆ α,ω -dioic acid; and 8- or 9- or 10,16-dihydroxy C₁₆ acid) have been used in parallel with lignin phenols as tracer of TerrOC input (e.g., Hedges et al., 1988; Prahl et al., 1994; Goñi et al., 2000). These biomarkers trace the non-woody, soft tissues of plants, forming part of the cuticle in leaves and needles (Goñi and Hedges, 1990).

There are no clear relationships between SA-normalized lignin and cutin loadings and ²¹⁰Pb-derived sediment age (Fig. 4C,D). Both groups of molecular marker highlight the contrast in organic matter composition between the inner and outer shelf sites, with biomarker loadings at IS that are about twenty times higher than at OS. This contrast can be explained by either hydrodynamic sorting of TerrOC (as in e.g., Kuzyk et al., 2008) and/or degradation during cross-shelf transport (Tesi et al., 2014). However, the input of either of these types of TerrOC appears not to have changed significantly over time.

While lignin phenols are primarily associated with woody tissues of vascular plants, long-chained (i.e. number of C atoms > 20) acyl lipids are derived from leaf waxes (Eglinton and Hamilton, 1967). As cutin acids, wax lipids thus trace another component of terrigenous organic matter than that traced by lignin phenols. Depth profiles for OS show no strong trends over time for either *n*-alkane and *n*-alkanoic acid loadings (Fig. 4C,D). For IS, however, there appears to be a slight increase in *n*-alkanes towards the core top, whereas HMW *n*-alkanoic acid loadings decreased by a factor of two over the last 100 years. The difference in *n*-alkane and *n*-alkanoic acid loadings between the two sites is about a factor of three to six, much lower than for lignin phenols and cutin acids (Fig. 4B–E). These findings agree qualitatively with results presented by Tesi et al. (2014). The contrasts between the biomarker classes as observed in their study may reflect either different source regions for the two depositional locations or, most likely, differences in degradation and/or sorting during lateral transport to the two sites. It is conceivable that hydrodynamic sorting results in settling of woody material (containing lignin phenols) closer to the coast while HMW wax lipids, presumably more associated with fine-grained sediments, are transported farther afield (Bianchi et al., 2007; Wakeham et al., 2009; Tesi et al., 2010). However, this process may not fully explain the difference between the behaviour of cutin acids compared to HMW wax lipids observed here, as both compound classes presumably trace similar plant components. Another explanation is the preferential degradation of lignin phenols and cutin acids compared to HMW lipids during transport, even though the down-core profiles of these biomarkers appear not to decrease significantly due to in-situ degradation. One possibility is that the degradation efficiency is higher under the oxic conditions prevailing during the many cycles of winnowing-focusing during the cross-shelf lateral transport (Keil et al., 2004), in contrast to the anoxic conditions that prevail below the top few millimeters of sediments on the East Siberian Arctic Shelf (e.g., Boetius and Damm, 1998). Furthermore, the time scales for degradation processes may be on

different orders of magnitude: about one century in-situ, but possibly several millenia during lateral transport. A third option explaining the observed contrasts is the decoupling of the two systems as discussed earlier. If the sediment cores reflect different TerrOC release timescales corresponding to distinctive cross-shelf transport times, their organic matter compositions may likely be different as well.

Comparing the abundance of lignin with cutin and/or HMW *n*-alkanes and *n*-alkanoic acids may address down-core changes in contribution from different terrigenous organic matter sources between woody vs soft tissue. The lignin/cutin ratio is slightly higher for IS and appears to decrease marginally with depth for both sites (Fig. 5A), possibly implying that cutin may be more recalcitrant than lignin. The lignin/(HMW *n*-alkanes and *n*-alkanoic acids) ratio is clearly lower for OS with no change over depth (Fig. 5B), whereas at the nearshore site (IS), the relative contribution of woody (traced by lignin) relative to soft OM tissues doubled toward the core top over the last 100 years. The latter suggests that lignin is preferentially degraded downcore, consistent with the hypothesis of preferential degradation of lignin phenols compared to HMW lipids during transport as discussed earlier. Another explanation would be a change in source material to more woody material, however, this is not echoed in the lignin/cutin ratio.

Low molecular weight (LMW) *n*-alkanes and *n*-alkanoic acids are biosynthesized in both marine and terrigenous organisms while the HMW counterparts are considered to be almost exclusively produced by (terrigenous) higher plants. The ratio of HMW to LMW *n*-alkanes and *n*-alkanoic acids are about three to five times higher for IS than for OS (Supplementary Fig. S2), which consistent with the other biomarker fingerprints suggests a greater influence of terrigenous organic matter at the station closest to the coast.

3.2.3. Lignin phenol fingerprints on sources of woody terrigenous organic matter

The relative distribution of different lignin phenols and other CuO oxidation products can shed additional light on sources and degradation of woody terrestrial organic matter. The ratio of syringyl (S) to vanillyl (V) phenols is informative regarding changes in the prevailing vegetation/biomass from where the OC was released, due to the fact that gymnosperm (nonflowering) plants do not produce syringyl phenols whereas angiosperm (flowering) plants do (Hedges and Mann, 1979b). Hence, a change to higher S/V values indicates a shift to higher lignin input by angiosperms. S/V ratios can also be lowered during early diagenesis due to preferential degradation of syringyl phenols by white- and brown-rot fungi during oxidative decay on land (Hedges et al., 1988). Under subaqueous conditions, however, no significant changes have been observed (Opsahl and Benner, 1995, and citations therein). The S/V values are overall low in both cores compared to typical values for angiosperm plant tissues (> 1 ; e.g., Hedges and Parker, 1976; Hedges and Mann, 1979b), suggesting either a predominance of gymnosperm carbon or previously ex-situ degraded material. While there is no clear depth trend for IS, the OS core reveals a trend to lower S/V values from 1890 to 1960, and thereafter a switch to instead increasing S/V towards the present day (Fig. 6A). This signal either implies first a trend to higher contributions by gymnosperms shifting around 1960 to an increasing proportion of angiosperm carbon or a change in the contribution of degraded material. The different trends and values further highlight the decoupling between the two stations, potentially reflecting different timescales for TerrOC release due to distinctive cross-shelf transport times. The shift observed between 1890 and 1960 at the outer shelf station would also imply a change in TerrOC source over this time period.

The ratio of cinnamyl over vanillyl phenols is used to discriminate between soft and woody tissues, because only non-woody vascular plants produce significant amounts of cinnamyl phenols, thus lower C/V values refer to more woody material (Hedges and Mann,

1979b). As the ratio may decrease with ongoing degradation (e.g., Opsahl and Benner, 1995) it should rather be viewed as a qualitative than a quantitative parameter. Values of C/V for both IS and OS are rather low compared to non-woody tissues (> 0.5, e.g., Hedges and Parker, 1976; Hedges and Mann, 1979b), and fairly stable with sediment depth (Fig. 6B) indicating that woody material may be the major source of lignin phenols over time. The lack of down-core trends implies no change due to in-situ degradation. The generally low C/V values, however, may also imply that lignin has been altered prior to burial.

Comparison with published values reveals that the S/V and C/V lignin phenol fingerprints throughout these two ESS cores are remarkably similar to Kolyma DOM measured by Amon et al. (2012), even though the river DOM consists of much younger/fresher material according to $\Delta^{14}\text{C}$ data (Amon et al., 2012). Both cores are also similar to surface peat, ice-complex deposit and topsoil permafrost lignin end-members determined by Tesi et al. (2014), but distinctly different from the lignin signal from mosses, grasses and peat, that were compiled by Amon et al. (2012, references therein) (Fig. 6C).

3.3. Degradation status of down-core accumulated terrigenous organic matter

TerrOC degradation status in the two ESS sediment cores was investigated by the changes in the OC loadings for the topsoil and ICD fractions as obtained from the $\delta^{13}\text{C}$ - $\Delta^{14}\text{C}$ -based source apportionment calculations. Assuming the specific surface area is a conservative parameter, i.e. no dilution or dissolution of inorganic matter or change in mineralogy over time, down-core decreases in OC loadings can be attributed to degradation of that component (following the approach of Keil et al., 1997). The down-core profiles of topsoil OC loadings show a decrease over the top 6 cm for IS that may reflect in-situ degradation (Fig. 7A). For OS values are one order of magnitude lower and a similar trend over time is visible, albeit on a much smaller scale. The ICD fraction displays a contrasting behaviour (Fig. 7B). Values for

OS are lower than for IS, but only by less than a factor of three. For both cores there appears to be a trend to decreased loadings towards the present. These trends may suggest either more rapid degradation of the topsoil OC fraction relative to the ICD fraction or a longterm change of relative input for the two fractions that is not accounted for by SA normalization.

Information on the degradation status of TerrOC can also be obtained from both CuO reaction products and free lipids that reflect different TerrOC pools. Acid-to-aldehyde ratios for both CuO-derived syringyl and vanillyl phenols increase with ongoing degradation and have thus been commonly used as a proxy for the degradation status of lignin phenols (e.g., Ertel and Hedges, 1984; Hedges et al., 1988; Opsahl and Benner, 1995). For fresh material, Hedges et al. (1988) suggested values of 0.1–0.2, which is significantly lower than the values displayed by both cores ($[Ad/Al]_S$: 0.38–1.05 for OS, 0.56–0.67 for IS, Fig. S3A; $[Ad/Al]_V$: 0.52–1.61 for OS, 0.70–0.90 for IS, Supplementary Fig. S3B). No significant difference between the cores or down-core trends can be detected, which might be due to the already highly advanced degradation of the woody material prior to burial. Tesi et al. (2014) have reported no significant difference for CuO-derived acid to aldehyde ratios for both terrigenous end-members and surface sediments from the East Siberian Shelf ($[Ad/Al]_S$ ranging between 0.14–0.9; ($[Ad/Al]_V$ between 0.11–1.2), and argued that these ratios might have a limited use to constrain the degradation status of TerrOC in this area. Goñi et al. (2000) reached a similar conclusion for the Beaufort Shelf where the material transported by the Mackenzie River is already extensively degraded ($[Ad/Al]_S$ between 0.27 and 1.3; ($[Ad/Al]_V$ between 0.39 and 0.9),.

The ratio of CuO oxidation-derived 3,5-dihydroxybenzoic acid (3,5-Bd) to vanillyl phenols is used both as a tracer for mineral rich soil organic matter contrasting vascular plant debris (e.g., Prah et al., 1994; Dickens et al., 2007) and to determine the degree of degradation for TerrOC in sediments as 3,5-Bd/V increases with ongoing degradation (e.g.,

Hedges et al, 1988; Gordon and Goñi, 2004; Tesi et al., 2014). Its only known marine source is brown macroalgae (Goñi and Hedges, 1995), which is not present in the study area. Tesi et al. (2014) reported increasing 3,5-Bd/V ratios with increasing distance from the coast across the East Siberian Shelf, which agrees with the findings of this study (Fig. 8A). Values for OS vary between 1 and 4, whereas values for IS range between 0.3 and 0.5. These findings may imply that the TerrOC at OS is more degraded than at IS. However, no significant trends over time/down-core were detected. An alternative explanation could be that the relative contribution of mineral soil compared to plant litter is higher at OS than at IS, possibly resulting from preferential degradation of vascular plant debris or physical sorting during transport with plant litter settling closer to the coast.

Another approach to assess the TerrOC degradation status is provided by the vascular plant wax lipid data. The ratio of HMW *n*-alkanoic acids to *n*-alkanes decreases with ongoing degradation as the acids lose their functional groups. Similar to the lignin phenol acid/aldehyde ratios, no significant difference between OS and IS can be detected (Fig. 8B); however, while the signal for OS decreases with depth (from ~8 to ~4), for IS it seems to increase with depth (from ~4 to ~14), corresponding to more degraded wax lipids in the upper (most recent) part of the core. A possible explanation for these findings could be a change in HMW lipid input towards more degraded material over the last century in the coastal regime. Vonk et al. (2010) report HMW *n*-alkanoic acid-to-*n*-alkane ratios for surface sediments along the Kolyma paleoriver transect between 1 and 6 with no clear trend with increasing distance from the coast.

An additional degradation proxy derived from these measurements is the Carbon Preference Index (CPI), which describes the ratio of odd-to-even carbon chain lengths of HMW lipids. In fresh plant waxes, odd carbon numbered homologues predominate for alkanes, whereas even carbon numbered homologues dominate for fatty acids (Eglinton and

Hamilton, 1967). This preference is reduced with ongoing degradation and the CPI approaches 1 (Bray and Evans, 1961). The CPI for *n*-alkanes and *n*-alkanoic acids has been extensively applied to study degradation of plant waxes in sediments (for the ESAS, e.g., Fahl and Stein, 1997; Fernandes and Sicre, 2000; van Dongen et al., 2008; Vonk et al., 2010). For the two ESS cores in this study no trend over time is observed in the alkane CPI ($n = 21\text{--}31$, Fig. 8C), but OS CPI values are significantly lower (1.4–1.6) compared to those of IS (2.6–3). This implies more degraded HMW *n*-alkanes for the outer shelf; possibly as a consequence of degradation during protracted lateral transport. Alternatively, it may be a result of physical sorting in transit, if the material with a higher CPI is associated to the fraction settling closer to the coast. The acid CPI ($n = 20\text{--}30$), in contrast, suggest marginally more degraded material for IS than for OS (2.9–3.3 for IS and 3–4.4 for OS, Fig. 8D). For both cores there seems to be a small trend towards more degraded material in the core top. This is consistent with the trend observed for the ratio of HMW *n*-alkanoic acids to *n*-alkanes for IS (Fig. 8B).

The CPI proxies of HMW wax lipids have been widely employed to discern spatial differences in sources and degradation along the Eurasian Arctic Ocean margin. Stein and Macdonald (2004) report decreasing odd-even preference indices for HMW *n*-alkanes (chain lengths $n > 23$) in ESS surface sediments with increasing distance from the coast (mean values: 3.7 ($n = 8$) for estuary/deltaic, 3.3 ($n = 25$) for shelf/coastal, and 2.6 ($n = 6$) for the continental margin). These values are higher than the surface sediment values for coastal station IS (2.7) and outer shelf station OS (1.5). Van Dongen et al. (2008) analyzed surface sediments in five Russian Arctic River Estuaries for their lipid biomarker composition. For the Kolyma river outlet they obtained a CPI value of 7.3 for *n*-alkanes ($n = 25\text{--}33$) and 4.2 for *n*-alkanoic acids ($n = 20\text{--}30$), higher than the corresponding surface sediment values for IS (2.7 and 2.9). Vonk et al. (2010) measured *n*-alkanes and *n*-alkanoic acids CPI for surface sediments along the Kolyma paleoriver transect (using the same chain-length ranges as in this

study). Their alkane CPI decreases from 7.6 to 3.7 with increasing distance from the Kolyma river mouth. Acid CPI values span from 3.5 to 4.2 with no clear trend. Station IS is located approximately in the middle of this paleoriver transect and its CPI values are slightly lower, but agree fairly well with the data presented in Vonk et al. (2010). Station OS lies at approximately 300 km distance from the last station of their transect; the lower alkane CPI (1.5) is thus consistent with the observation of a decrease in alkane CPI with increasing distance from the coast. This very low value, however, might also be due to a background concentration of sedimentary rock-derived (petrogenic) *n*-alkanes, which are likely to have low CPI values (~1) if they experienced any thermal alteration. Given the low *n*-alkane loadings for OS (Fig. 4E), it is possible that there has been extensive removal of plant wax *n*-alkanes during cross-shelf transport, leaving a petrogenic signature behind.

3.4. Degradation status of marine organic matter

In addition to the terrigenous biomarkers discussed above, CuO oxidation yields products derived from proteins and lipids that can serve as tracers of marine/plankton inputs (Goñi and Hedges, 1995). Despite the fact that these products have been observed in Arctic terrestrial environments (Tesi et al., 2014), short-chain dicarboxylic and fatty acids (CuO-DAs and CuO-FAs) display clear exponential decay trends over time in both cores (Fig. 4B), suggesting a relatively fresh and reactive source of OC, presumably from marine phytoplankton. One particular fatty acid, a mono-unsaturated hexadecenoic acid (16:1FA), has been suggested as a more specific tracer of marine phytoplankton, as it likely derives from marine diatoms (Goñi et al., 2000). Tesi et al. (2014) studied CuO-derived 16:1FA (CuO-16:1FA) on several cross-shelf transects in the Laptev and East Siberian Sea and showed that the eastern regimes, where this study's sampling sites are located, displayed highest concentrations of CuO-16:1FA, likely reflecting biological productivity associated with the

nutrient-rich Pacific inflow to this area. By contrast, soil samples (ICD and topsoil) are characterized by extremely low 16:1FA concentrations (Tesi et al., 2014).

Both sediment cores in this study exhibit exponential decay trends for CuO-16:1FA concentrations over time/depth. From these data, half-lives for the traced carbon pools were determined using a simple, first-order kinetics model for their reactive fractions (Berner, 1964). These are defined as the difference between the measured concentration and the asymptotic concentration, which was determined by fitting an exponential decay curve to the measured values. The linear fits to the natural logarithm of both the CuO-16:1FA and the CuO-FAs reactive fractions over sedimentation age resulted in a half-life of 8 years for CuO-16:1FA and 14 (IS) to 17 years (OS) for the CuO-FAs (Fig. 9). The shorter half-life for CuO-16:1FA may be explained by its unsaturation, rendering it more labile.

The same model was applied to the bulk marine OC fraction, obtained from the $\delta^{13}\text{C}$ - $\Delta^{14}\text{C}$ -based source apportionment calculations (Fig. 3). Here it yields a half-life of 19 (IS) to 27 years (OS), see Fig. 10. As these values are derived from bulk measurements, they may be seen as more of an average marine OC pool, compared to the specific and rather labile CuO-FAs, and is therefore likely more recalcitrant. The combination of biomolecular tracer and bulk-OC fraction data constrain the half-life for degradation of the marine OC fraction in accumulating ESAS shelf sediments to between one and three decades. This agrees well with the observed overall decrease of TOC over time with an estimated half-life of 16–25 years, supporting the assumption of marine OC degradation as the main factor that affects TOC trends with time.

4. Conclusions

This study comprises the first down-core investigation of changes in the East Siberian Sea carbon cycling over the last century. A suite of terrigenous and marine biomarkers as well as

source-diagnostic bulk carbon isotopes were analyzed in two cores from different depositional regimes in this Arctic shelf sea: one close to the Kolyma estuary and the other one from the outer shelf.

The sediment mass accumulation rates were relatively uniform over the past century at both stations and did not confirm expected increasing trends due to global warming. Specific surface area measurements suggested that the two depositional regimes were not closely coupled with the outer shelf containing coarser grained sediments. The observed down-core decreases of TOC likely resulted from degradation of labile marine OC, as indicated by TOC/TN ratios, carbon stable and radioisotope data, as well as marine biomarkers, such as CuO oxidation products yielded by protein- and lipid-like material. From their exponential decrease with time, marine OC half-lives of 14–17 and 8 years were deduced, respectively. For the bulk marine OC fraction as calculated by the dual-carbon isotope source apportionment we obtained a half-life of 19–27 years which agrees well with the half-life of 16–25 years for TOC data, strengthening the assumption of a preferential degradation of marine OC. High $\Delta^{14}\text{C}$ ages of TOC implied a substantial input of pre-aged permafrost-released material as also suggested by dual-carbon isotope source apportionment. For more quantitative interpretations, however, improved constraints on end-member isotopic signals would be needed.

Biomarkers for terrigenous material revealed contrasting temporal trends among different OC pools. Lignin phenols, tracing the woody material of vascular plants, were relatively invariant with time, but were ten- to twentyfold higher for the near-shore station. Their composition suggested considerably degraded gymnosperm wood as a primary OC source. Cutin acids, tracing the wax lipids of vascular plants, showed a similar signal, whereas for long-chain acyl lipids, also associated with leaf waxes, the difference between the two stations was only a factor of three to six. Degradation proxies for TerrOC conveyed

contradictory messages: The CuO-derived ratio of 3,5-Bd/V and the HMW *n*-alkane CPI pointed to significantly more degraded TerrOC throughout the whole outer-shelf sediment core, whereas the HMW *n*-alkanoic acid CPI suggested slightly more degraded TerrOC for the coastal station with trends to more degraded material in the core top for both cores. This was supported for the inner-shelf sediment core by the ratio of HMW *n*-alkanoic acids to HMW *n*-alkanes.

Overall the differences in TerrOC biomarker concentrations between the inner and outer shelf sites were more pronounced than over time/down-core. Establishing whether this is due to contrasting source regions or hydrodynamic sorting processes and more efficient preferential degradation during lateral transport requires further investigation.

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Figure captions

Fig. 1. Sampling locations in the East Siberian Sea. The IS station (YS-37) is situated close to the shore and the Kolyma river mouth at 42 m water depth, while the OS station (YS-90) is located on the outer shelf approximately 600 km from the coastline at 62 m water depth. OS is relatively more influenced by Pacific inflow, IS by the Siberian coastal current.

Fig. 2. Surface area and bulk organic matter composition of the two radiochronologically dated sediment cores. (A) The specific surface area (SA) of both cores reveals a shift from coarser to finer material over the last century with a coarser core top. A significant offset between the two locations indicates that the marine and coastal regimes of this study are not closely coupled. (B) Total organic carbon (TOC) decreases with time for both cores. The sediment depths, i.e. dates, where the artificial radionuclide ^{137}Cs signals peak are indicated on the right axis. Anthropogenic ^{137}Cs release events, i.e. nuclear bomb testing in the early 1960s and the explosion of the nuclear reactor in Chernobyl in 1986, have been recorded in the sediment and serve as an independent validation of ^{210}Pb -derived chronologies. (C) The lower C/N ratio for the upper (more recent) part of OS is likely reflecting degradation of marine organic matter. (D, E) Carbon isotopes show a relatively greater marine contribution to TOC (visible in the enriched values) for OS that decrease over time. $\Delta^{14}\text{C}$ data translates to TOC ages of about 3400 and 3000 years for IS and OS, respectively, in the surface sediment and 6200 and 7200 years at the base of each core.

Fig. 3. (A) Dual-carbon isotopic composition for both cores (surface sediments has larger symbols) as well as dual-carbon isotope end-member values for marine, ice-complex deposit permafrost and topsoil permafrost for source apportionment calculations. (B) IS and (C) OS OC fluxes attributed to the three carbon sources.

Fig. 4. A suite of molecular biomarkers tracing various OC sources. (A) TOC normalized to surface area, displaying a decrease with depth for the top half of each core. (B) CuO oxidation-derived short-chained fatty acids are mostly associated to bacteria and algae. For both cores an exponential decrease over time indicates relatively rapid degradation of this labile compound group. (C, D) Lignin and cutin trace vascular plants; lignin makes up the woody part, while cutin is part of the leaf waxes. A significant difference between the low values for OS and higher values for IS is visible for both compound classes. No clear trends over time are detected. (E, F) High-molecular-weight (HMW) *n*-alkanes and *n*-alkanoic acids are also constituents of vascular plant waxes and display the same difference between IS and OS although on a smaller scale (factor 3–6 compared to factor 10–20 for lignin and cutin). For IS HMW *n*-alkane loadings appear to decrease with increasing depth, while HMW *n*-alkanoic acids increase.

Fig. 5. Molecular biomarker ratios tracing different OC sources. Overall values are higher for IS than for OS, indicating that either cutin and HMW *n*-alkanes and HMW *n*-alkanoic acids survive cross-shelf transport more efficiently than lignin or the two stations are affected by different source regions.

Fig. 6. The ratios of different lignin-derived phenol types convey information about the lignin source. (A) Ratios of syringyl to vanillyl phenols are linked to different TerrOC sources. Higher values indicate higher contributions of angiosperm plants. For OS there appears to be a trend to more gymnosperm lignin input for sedimentation years of 1880 to 1960, which is reversed in the following years. No significant trend is detected for IS. (B) A high cinnamyl to vanillyl phenols ratio is used as an indicator for more woody material while low ratios indicate a higher contributions of soft tissues. Neither of the cores displays a significant trend over time. (C) Comparison of S/V and C/V lignin phenol ratios with the end-members for different Arctic plants, river dissolved organic matter (DOM), as compiled from different

studies by Amon et al. (2012, citations therein, here marked with ¹); ice-complex deposit and topsoil permafrost as determined by Tesi et al. (2014, here marked with ²). The boxes indicate typical ranges of S/V and C/V for different vascular plant tissues in different locations (e.g., Goñi et al., 2000). The lignin compositions in both cores cluster near gymnosperm wood and needles and agree well also with ice-complex deposit, topsoil permafrost and Kolyma DOM but far away from signals characterizing grasses, mosses and peats.

Fig. 7. Source apportionment of the two TerrOC fractions normalized to specific surface area reveals differential down-core changes of the two carbon pools, which either reflects relatively faster degradation of topsoil-derived OC than ICD-derived OC or a long-term change in relative delivery. The same trends are apparent in both systems; for OS topsoil OC on a much smaller scale.

Fig. 8. Degradation proxies for different TerrOC pools. Triangles point to proxy values that correspond to more degraded material. (A) The difference between IS and OS for CuO-derived 3,5-Bd/V ratios suggest more degraded TerrOC for OS than for IS with no change over depth. (B) The HMW *n*-alkanoic acid to *n*-alkane ratio does not show a significant difference between IS and OS, however, the ratio seems to increase with depth (corresponding to less degraded wax lipids in the deeper part of the core) for IS, while for OS the ratio seems to decrease with depth. (C, D) The Carbon preference index (CPI) for HMW *n*-alkanes displays a significant difference between more degraded alkanes for OS and less for IS with no visible trend over time, whereas the CPI for HMW *n*-alkanoic acids shows slightly more degraded material for IS than for OS with a trend to more degraded alkanic acids towards the core top.

Fig. 9. Clear linear correlations are detected between sediment layer age and the natural logarithm of the reactive fractions of each of the following: the marine fraction as calculated

1010 in the dual carbon isotope source apportionment approach (labelled $\delta^{13}\text{C}$ - $\Delta^{14}\text{C}$ -marine), the
1011 phytoplankton tracing CuO-derived 16:1FA (labelled CuO-16:1FA) and of all CuO oxidation-
1012 derived FA concentrations (labelled all CuO-FA). From the linear fit the half-life of the
1013 respective carbon pools is determined to be 8 to 19 years for IS, and 8 to 27 years for OS.
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Figure 1

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1033 **Table 1.** Results of the source apportionment calculations with and without correction for a theoretical reservoir time of 5000 years for TerrOC
 1034 for the outer-shelf station OS. Medians from the Monte-Carlo simulations for the relative contributions to TOC of the three sources topsoil
 1035 permafrost (topsoil), ice-complex deposit permafrost (ICD) and marine primary productions (marine) are shown.

²¹⁰ Pb-derived sedimentation year	no transport			5000 years lateral transport		
	topsoil	ICD	marine	topsoil	ICD	marine
2002	5.4%	33%	61%	8.3%	28%	62%
1997	5.1%	36%	57%	8.1%	31%	59%
1985	4.6%	40%	54%	7.4%	36%	55%
1971	4.3%	44%	50%	7.0%	40%	51%
1949	4.0%	52%	42%	6.6%	48%	43%
1932	4.1%	55%	40%	6.6%	51%	40%
1915	4.5%	55%	39%	7.3%	51%	40%
1900	4.5%	57%	37%	7.3%	52%	38%
1889	4.7%	62%	32%	7.5%	57%	34%

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