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Contrasting composition of terrigenous organic matter in the dissolved, particulate and sedimentary organic carbon pools on the outer East Siberian Arctic Shelf

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Abstract

Fluvial discharge and coastal erosion of the permafrost-dominated East Siberian Arctic delivers large quantities of terrigenous organic carbon (Terr-OC) to marine waters. The composition and fate of the remobilized Terr-OC needs to be better constrained as it impacts the potential for a climate-carbon feedback. In the present study, the bulk isotope ($\delta^{13}C$ and $\Delta^{14}C$) and macromolecular (lignin-derived phenols) composition of the cross-shelf exported organic carbon (OC) in different marine pools is evaluated. For this purpose, as part of the SWERUS-C3 expedition (July-September 2014), sediment organic carbon (SOC) as well as water column (from surface and near-bottom seawater) dissolved organic carbon (DOC) and particulate organic carbon (POC) samples were collected along the outer shelves of the Kara Sea, Laptev Sea and East Siberian Sea. The results show that the Lena River and the DOC have a preferential role in the transport of Terr-OC to the outer shelf. DOC concentrations (740-3600 μg/L) were one order of magnitude higher than POC (20-360 μg/L), with higher concentrations towards to the Lena River plume. Depleted $\delta^{13}C$, modern $\Delta^{14}C$ and lignin phenols concentrations were all well correlated with DOC levels indicating a relatively young terrestrial contribution. In contrast, POC may have a preferential marine origin, as its concentrations were not correlated with isotope and terrestrial biomarker proxies. The $\delta^{13}C$ signatures in the three carbon pools varied from -23.9±1.9‰ in the SOC, -26.1±1.2‰ in the DOC and -27.1±1.9‰ in the POC. The $\Delta^{14}C$ values ranged between -395±83‰ (SOC), -226±92‰ (DOC) and -113±122‰ (POC). These stable and radiocarbon isotopes were also different between the Laptev Sea and the East Siberian Sea. Both DOC and POC showed a depleted and younger trend off the Lena River plume. The older and more enriched $\delta^{13}C$ signatures in the outer-shelf of the ESS suggest instead a greater influence of the sea ice coverage and the Pacific inflow from the east. Lignin phenols exhibited higher OC-normalized concentration in the SOC (0.10-2.34 mg/g OC) and DOC (0.08-2.40 mg/g OC) than in the POC (0.03-1.14 mg/g OC). The good relationship between lignin and $\Delta^{14}C$ signatures in the DOC suggests that a significant fraction of the outer-shelf DOC comes from "young" Terr-OC. By contrast, the slightly negative correlation between lignin phenols and $\Delta^{14}C$ signatures in POC, with higher lignin concentrations in older POC from near-bottom waters, may reflect the off-shelf transport of OC from remobilized permafrost in the nepheloid layer. Moreover, syringyl/vanillyl and cinnamyl/vannillyl phenols ratios presented distinct clustering between DOC, POC and SOC, suggesting that those pools are carrying different Terr-OC of partially different origin. Finally, 3,5-dihydroxybenzoic acid to vanillyl

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phenols ratios and p-coumaric acid to ferulic acid ratios, used as a diagenetic indicators, enhanced in POC and SOC. This suggests that the remobilized old OC from thawing permafrost, which is mainly transported within these pools, could experience less burial and more mineralization than believed earlier. Overall, DOC is strongly affected by the Lena River plume transporting young Terr-OC from topsoil and/or recently produced vascular pant material, while near-bottom POC and SOC preferentially carries off-shelf old OC released from thawing permafrost.

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1. Introduction

Studies of terrestrial organic carbon (Terr-OC) in the Arctic Ocean are receiving increasing interest due to concerns about the consequences on the carbon cycle by amplified climate change. The Eurasian Arctic Shelf is predicted to experience the highest increase in temperature on Earth, and its warming is even faster than predicted (Arndt et al., 2015; Zwiers, 2002). It has been suggested that these changes may translocate increasing amounts of Terr-OC to the coastal ocean (Vonk and Gustafsson, 2013). The Arctic tundra and taiga drainage basins represents roughly 50% of the global soil organic matter, much within shallow permafrost (Gorham, 1991; Tarnocai et al., 2009), and 10–20% of the global vegetation carbon with about 73% in Eurasia (McGuire et al., 2009; McGuire et al., 2010). Fluvial and erosional processes are expected to increase, as well as biomass cover, resulting in higher input fluxes and changing composition of Terr-OC to the continental shelf (Lantuit et al., 2013; Peterson et al., 2002; Sanchez-Garcia et al., 2014; Serreze et al., 2002). In addition, those mechanisms would enhance the remobilization of permafrost carbon, potentially constituting a climate-carbon positive feedback, in terms of CO_2 outgassing from degradation of thawing permafrost. Thus, it is essential to understand the sources, dynamical fate and composition of exported Terr-OC in order to assess its impact within the carbon cycle.

The fate of terrestrial OC in the marine system DOC, POC and SOC compartments is still a matter of debate. Some studies have indicated a conservative behavior of DOC in the Arctic Ocean with small influence on the ocean-atmosphere exchange of CO_2 (Amon and Meon, 2004; Dittmar and Kattner, 2003a; Köhler et al., 2003; McGuire et al., 2009), little or no degradation in microbial incubations (Amon and Meon, 2004), and high concentrations of lignin in the DOC pool (Amon and Benner, 2003; Amon et al., 2012; Lobbes et al., 2000). By contrast, others suggest that DOC is highly degraded by photochemical oxidation or microbial respiration in the water column or surface sediments (Alling et al., 2010; Benner and Kaiser, 2011; Hernes and Benner, 2003; van Dongen et al., 2008b). Investigations of the particulate compartment indicate that POC degrades much faster than DOC, and just a small fraction is transported off-shelf within the POC pool (Eglinton and Repeta, 2006; Sanchez-Garcia et al., 2011; van Dongen et al., 2008b). In addition, other processes on the wide and shallow Arctic shelves such as hydrodynamic sorting, deposition, resuspension and uptake by primary production may contribute to the dilution/dispersal of Terr-OC along the water and sediment dispersal system (Stein and Macdonald, 2004; Tesi et al., 2016; Tesi et al., 2014). It

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seems that different pools of Terr-OC have different behavior and fate during remobilization and transport. DOC and POC pools have much younger ^{14}C ages than the deposited sedimentary OC (Guo et al., 2007; Karlsson et al., 2016; Karlsson et al., 2011). Compound-specific radiocarbon analyses of lipid molecules and lignin phenols of surface sediments and POC from major river mouths in the Arctic revealed marked age offsets between different Terr-OC pools (Feng et al., 2013; Vonk et al., 2010). However, we still have a very limited understanding of the composition and cycling of Terr-OC in the Arctic Ocean.

The East Siberian Arctic Shelf (ESAS) is a particularly relevant region for investigating the distribution and fate of Terr-OC in the DOC, POC and SOC pools. The ESAS is the world's largest continental shelf and its adjacent basin is located in a region of continuous and discontinuous permafrost. The extensive ESAS is quite shallow (~50 m average depth) and receives massive amounts of Terr-OC. In the west, the Lena river and coastal erosion are the main inputs of OC (Laptev Sea and western East Siberian Sea, W-ESS) (Charkin et al., 2011; Salvadó et al., 2015; Semiletov et al., 2011; Tesi et al., 2014; Vonk et al., 2012). Alternatively, in the eastern East Siberian Sea (E-ESS, from ~160°E to eastwards) marine phytoplankton represents an important source of OC due to the influence of nutrient-rich Pacific inflow waters (Semiletov et al., 2005; Stein and Macdonald, 2004). Many investigations in the Arctic focused on characterizing the composition and fate of riverine OC (Amon et al., 2012; Benner et al., 2005; Elmquist et al., 2008; Goni et al., 2000; Lobbes et al., 2000; van Dongen et al., 2008a; Winterfeld et al., 2015), sedimentary OC in the ESAS (Bröder et al., Submitted; Karlsson et al., 2015; Salvadó et al., 2015; Tesi et al., 2014), and DOC and POC in the water column of the Eurasian Arctic Shelf (Alling et al., 2010; Sanchez-Garcia et al., 2011). This is, however, the first study that characterizes collectively the DOC, POC and SOC pools along the outer shelf. The present study uses carbon isotopes and macromolecular biomarkers to provide an extensive view of the composition and distribution of Terr-OC along the outer ESAS, with the objective to evaluate the sources, degradation and off-shelf transport of the DOC, POC and SOC pools.

2. Materials and methods

2.1 Study area

The ESAS is the widest, shallowest and, by area, largest continental shelf in the World Ocean. It comprises 40% of the Arctic shelf and 20% of the Acrtic Ocean (Stein and

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147 Macdonald, 2004). This study focuses on the outer shelf of ESAS seas (Laptev Sea and East
148 Siberian Sea) and the Kara Sea (Figure 1). The Kara Sea has an area of $880 \cdot 10^3$ km^2 and a
149 mean depth of 110 metres. It receives a large amount of fresh water mainly from the Ob river.
150 The Laptev Sea, between ~110ºE and 140ºE, covers almost $500 \cdot 10^3$ km^2 and has an average
151 water depth of 50 m. This sea receives large amounts of freshwater (~745 km$^3 \cdot$yr^{-1}) mainly
152 transported by the Lena river (566 km$^3 \cdot$yr^{-1}) (Cooper et al., 2008; Semiletov et al., 2000), but
153 most of the TerrOC that enters the Laptev Sea is coming from coastal erosion of late
154 Pleistocene ice complex deposits (Semiletov et al., 2011; Vonk et al., 2012). The East
155 Siberian Sea has an average water depth of 58 m, and is the largest and most ice-bound shelf
156 sea of the Arctic Ocean (Stein and Macdonald, 2004). It extends from 140ºE to 180ºE
157 covering an area of $987 \cdot 10^3$ km^2, and receives freshwater inputs from the Indigirka and
158 Kolyma rivers. This sea exhibits two physical and biogeochemical regimes. The eastern East
159 Siberian Sea (E-ESS, from ~160°E to ~180°E), which is influenced by the Pacific inflow
160 waters, and primary production represents an important source of OC (Semiletov et al., 2005;
161 Stein and Macdonald, 2004). And the western East Siberian Sea (W-ESS), between ~140°E
162 and ~160°E, where river runoff and coastal erosion of thawing permafrost supply the major
163 part of OC, but there is also a relatively high marine productivity, particularly in certain
164 polynya regions.

165

166 **2.2 Sampling**

167 A comprehensive set of samples was obtained during July-August 2014 as part of the
168 international Swedish-Russian-US investigation of the Carbon-Climate-Cryospshere
169 Interactions in the East Siberian Arctic Ocean (SWERUS-C3) expedition onboard I/B Oden.
170 The first of two SWERUS-C3 2014 legs was an extensive 45-day campaign of complex
171 geophysical and hydrogeochemical sampling including at-sea analysis. The sample collection
172 for this study consisted of four types of samples along the outer ESAS (Figure 1): i) POC
173 from high volume filtration on 293 mm glass fibre filter (GF/F; Whatman Inc.) with a
174 nominal 0.7 µm cut-off, ii) POC from 47 mm Teflon filters, iii) DOC isolated with solid
175 phase extraction (SPE) cartridges, iv) surface sediment samples collected with a multicorer.

176 Surface and near-bottom waters (5m above bottom) were sampled and filtered through
177 high volume 293 mm GF/F filters (pre-combusted for 5h at 500ºC). Samples were filtered
178 either directly from the seawater intake (SWI) or by pumping water from 1000L tanks filled
179 from the SWI or from a submersible pump. The systems were connected to an electronic flow

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meter, in the flow path below the filter, and a pressure meter situated directly above the GF/F filter holder. We maintained the flow to about 8.5 $L \cdot min^{-1}$, and stopped filtering before the backpressure reached 1 bar to avoid cell lysing. After sampling of the particulate fraction, the GF/F filters were folded, put in a pre-combusted aluminium foil and stored at -20°. Since GF/F filters are not compatible with the alkaline hydrolysis of the CuO oxidation protocol to analyse lignin-derived phenols, POC samples were also obtained on 47 mm Teflon filters in order to analyse lignin-derived phenols in POC. We placed the Teflon filters in the filtration unit and applied a positive pressure flow with a peristaltic pump at a flow rate of 25 $ml \cdot min^{-1}$. POC samples in Teflon filters were folded in two, placed in petri dishes and stored frozen (-20°C) until laboratory analysis.

The dissolved fraction of organic matter was isolated by high-volume SPE cartridges containing 10 g of sorption material composed of octadecyl carbon moieties (C_{18}) chemically bonded to a silica support (C_{18}-SPE Mega-Bond Elut; Agilent) (Louchouarn et al., 2000). Cartridges were preconditioned with 5 resin volumes of methanol followed by 5 resin volumes of acidified (pH 2) Milli-Q Plus UV water. The water samples, previously filtered with GF/F, were acidified to pH 2 using reagent-grade concentrated HCl and pumped through the SPE cartridge with a peristaltic pump and silicone tubing. By this method, the water (~30L) was delivered directly into the headspace of the SPE cartridge and forced by pressure through the sorbent at a flow rate of 100 mL min^{-1}. Thereafter, we rinsed each SPE cartridge with 1L of acidified (pH2) Milli-Q Plus UV water to remove residual salts. Sample cartridges were packed in aluminum foil and stored at 4°C until further processing.

Sediment samples were collected with an 8-tube multicorer (Oktopus GmbH, Germany), which was developed to collect samples of the seabed with an undisturbed sediment-water interface. The liners were made of polycarbonate and were 60 cm long with a 10 cm diameter. The multicorer was deployed with full weight (head weight about 500 kg) at a speed of 0.5 m/s near the seabed. To increase recoveries, the multicorer was left for 1 minute on the seafloor. The cores were sectioned on low resolution (1cm intervals; shelf stations <200m water depth) or on high resolution (0.5cm intervals; slope and rise stations >200m water depth), and sediment samples were transferred into plastic bags and stored in the freezer (-20°C).

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213 **2.3 Bulk elemental and isotope analysis**

214 The analyses of organic carbon content, $\delta^{13}C$ and $\Delta^{14}C$ in the DOC, POC and SOC
215 pools have been described earlier (Karlsson et al., 2011; Louchouarn et al., 2000). Briefly,
216 DOC was determined onboard after GF/F filtration by high-temperature catalytic oxidation
217 (Shimadzu TOC-L_{CPH}). In the laboratory, SPE cartridges were eluted with 50 mL of
218 methanol. Then, we subsampled 0.5-1mL of the eluent, depending on DOC concentrations,
219 and placed it in smooth wall tin capsules for liquids (6 x 12 mm, Elemental Microanalysis,
220 Devon, UK). For organic carbon content and $\delta^{13}C$ composition of POC and SOC, GF/F filters
221 and surface sediment samples were subsampled and acidified with HCl (1.5M) to remove
222 carbonates. The analyses were performed in triplicates using a Carlo Erba NC2500 elemental
223 analyzer connected via a split interface to a Finnigan MAT Delta Plus mass spectrometer at
224 the Stable Isotope Laboratory of the Department of Geological Sciences at Stockholm
225 University. Some subsamples, after similar preparation steps, were analyzed for its
226 radiocarbon content ($\Delta^{14}C$) at the US-NSF National Ocean Sciences Accelerator Mass
227 Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution. Uncertainties of
228 $\Delta^{14}C$, $\delta^{13}C$, and OC analyses were ±0.002 (fraction modern error), ±0.1‰, and ±2% of the
229 measured OC content, respectively.

230

231 **2.4 Lignin phenols analysis**

232 The quantification of lignin-derived phenols in DOC (SPE eluents), POC (Teflon
233 filters), and SOC (surface sediment samples) was performed as described in detail by
234 Louchouarn et al 2000 and Tesi et al., 2014. Briefly, for the analysis of dissolved lignin, 5-15
235 mL of elution samples (1-2 mg OC equivalent) were reduced to dryness under a stream of
236 nitrogen in Teflon tubes. The dried samples were then oxidized under alkaline oxygen free
237 conditions (degassed NaOH solution, 8%) (Goni and Montgomery, 2000) with an addition of
238 10 mg of glucose to prevent superoxidation of the lignin polymer and spiked with recovery
239 standards (trans-cinnamic acid and ethyl vanillin). Samples were then acidified, extracted
240 twice with ethyl acetate and concentrated under vacuum at 60ºC. The same oxidation and
241 extraction procedure was also used for POC (Teflon filters) and SOC samples, but without
242 the addition of glucose in sediment samples.

243 Prior to the analyses, extracts were re-dissolved in pyridine and derivatized. Target
244 compounds were quantified on a gas-chromatograph mass spectrometer (GC-EI-MS, Agilent)

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using a DB1-MS capillary column (30m x 250µm, 0.25µm stationary phase thickness, Agilent J&W) for separation. Quantification of lignin phenols, benzoic acids, and p-hydroxybenzenes was achieved using the response factors of external standards. All reported concentrations of CuO oxidation products were reported in mg of biomarker per g OC.

3. Results and discussion

3.1 Elemental Composition and Distribution of DOC, POC and SOC

DOC in the water column of the outer ESAS during SWERUS-2014 expedition was one order of magnitude higher than POC. The DOC concentrations ranged from 740 to 3600 $\mu g \cdot L^{-1}$ (mean of 1400±790$\mu g \cdot L^{-1}$) and POC varied between 20 and 360 $\mu g \cdot L^{-1}$ (mean of 110±80$\mu g \cdot L^{-1}$) (Table 1, Figure 2A, Figure 3). Those values are in the same range as previous studies in the Siberian Arctic Seas (Alling et al., 2010; Benner et al., 2005; Sanchez-Garcia et al., 2011). Whereas DOC showed the highest values in surface waters of the Laptev Sea (2000±1100 $\mu g \cdot L^{-1}$), particularly off the Lena river mouth, POC concentrations were slightly higher in the Kara Sea (290±86$\mu g \cdot L^{-1}$) and the E-ESS (150±92$\mu g \cdot L^{-1}$) with no significant differences between surface and near-bottom waters. SOC values in surface sediments from the same stations presented higher concentrations in the E-ESS (1.32±0.42%), but also exhibited an increase in the Laptev Sea (1.21±0.26%) (Figure 3). This is in the lower range of what was previously reported in the inner-shelf of the ESAS (Charkin et al., 2011; Karlsson et al., 2015; Karlsson et al., 2011; Tesi et al., 2014; Vonk et al., 2012), suggesting either degradation of Terr-OC or sediment sorting during the across-shelf transport as discussed in Tesi et al. 2014 and Bröder et al. 2016. Alternatively, higher POC and SOC values in the E-ESS may be related to the higher marine productivity in that region due to the Pacific water influence (Semiletov et al., 2005; Stein and Macdonald, 2004).

The resulting bulk ratios in the DOC_{SPE} fraction indicate terrestrially dominated organic matter sources. The OC/TN (TN = organic nitrogen + inorganic nitrogen) of DOC_{SPE} ranged between 14 and 43 (mean of 28±8.4) without significant differences between surface and near-bottom waters (Table 1). Those ratios showed decreasing trends off the Lena river plume with higher ratios in the Laptev Sea and W-ESS. The same pattern and similar ratios were observed in the inner-shelf of the ESAS (Karlsson et al., 2016). Moreover, these values are in the same range as OC/TN ratios of DOC in Eurasian Arctic rivers, which varied between 23 and 69 (Lobbes et al., 2000), and the high OC/TN ratios (>40) of DOC collected

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277 from the Kara Sea (Köhler et al., 2003; Opsahl et al., 1999). Marine organic matter has
278 OC/TN values around 6-8 and terrestrial derived organic matter OC/TN ratios higher than 15
279 (Baldock et al., 1992; Hedges et al., 1986; Hedges and Oades, 1997). The OC/TN ratios in
280 the particulate and sedimentary compartments were much lower than in the DOC_{SPE}. Those
281 ratios ranged between 5 and 12 (mean of 7±1.7) in the POC and from 6 to 8 (mean of 7±0.5)
282 in the SOC. Similar OC/TN values were observed in the inner-shelf of the ESAS and Arctic
283 rivers in the particulate fraction (McClelland et al., 2016; Sanchez-Garcia et al., 2011).
284 However, these lower OC/TN ratios are at odds with e.g. δ^{13}C-OC and may be influenced by
285 selective degradation of labile carbonaceous forms (Hugelius and Kuhry, 2009), and/or
286 adsorption of inorganic nitrogen (e.g. ammonium) derived from decomposition of organic
287 matter (Sanchez-Garcia et al., 2011; Schubert and Calvert, 2001).

288

289 **3.2 Stable Carbon and Radiocarbon Isotopes**

290 The east-to-west extension of the depleted δ^{13}C signatures reflects a strong influence
291 of the Lena River (Figure 3), both in the Laptev Sea and the ESS. The δ^{13}C signatures in the
292 three carbon pools ranged from -23.9±1.9‰ in the SOC, -26.1±1.2‰ in the DOC_{SPE} and -
293 27.1±1.9‰ in the POC, with no significant differences between surface and bottom waters
294 (Tables 1, 2 and 3). The more depleted δ^{13}C-POC is consistent with marine productivity
295 using excess dissolved inorganic carbon (DIC) from the Lena river, which is more depleted
296 than marine DIC (Alling et al., 2012; Semiletov et al., 2016). This mechanism also explains
297 similarly depleted δ^{13}C-POC in the Lena plume far offshore in the Laptev Sea and ESS that
298 matched with depletion of other nutrients (Alling et al., 2010; Sanchez-Garcia et al., 2011).
299 The distribution of δ^{13}C-SOC was more homogeneous reflecting average over time in the
300 surface sediment regime. Only the concentration of DOC presented a good correlation with
301 δ^{13}C-DOC_{SPE} signatures, which indicates that higher concentrations of DOC come from
302 terrigenous sources (Figure 3).

303 The radiocarbon ages of DOC_{SPE} and POC showed a depleted and younger trend off
304 the Lena River plume. The Δ^{14}C signals ranged between -395±83‰ (SOC), -226±92‰
305 (DOC_{SPE}) and -113±122‰ (POC) presenting contrasting offsets between the Laptev Sea and
306 the East Siberian Sea, particularly in the E-ESS (Tables 1, 2 and 3; Figure 4). The older and
307 enriched δ^{13}C signatures in the outer-shelf of the ESS suggest the influence of sea ice
308 coverage and the Pacific inflow from the East. The more enriched Δ^{14}C signatures in POC
309 than in DOC are in accordance with previous studies in the Arctic Ocean (Griffith et al.,

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2012) and the Southern Ocean (Druffel and Bauer, 2000), which reflect a dominant marine source in the particulate carbon pool. The SOC pool does not present such marked west-east distribution of $\Delta^{14}C$ as observed in DOC_{SPE} and POC. The SOC also depicts older signatures near the New Siberian Islands. A recent study from the same area at the land-ocean interface presented older signatures in the POC than in the DOC (Karlsson et al., 2016), suggesting that thawing permafrost was transported preferentially within the POC pool. Therefore, our results support the hypothesis that remobilized permafrost preferentially settles out close to land, and then it is transported off-shelf through sediment resuspension-redeposition events. The older signals in the dissolved fraction of the ice-covered regions are consistent with a more recalcitrant OC in the dissolved pool of the Arctic Ocean (Follett et al., 2014; Griffith et al., 2012). It seems that the ice extent boundary works as a barrier that prevents the input of young DOC coming from the buoyant freshwater plume of the Lena river (Figure 4). It is important to point out that near-bottom waters presented more depleted and similar $\Delta^{14}C$ signatures in both DOC_{SPE} and POC (-258±94‰ and -250±83‰, respectively) than in surface waters (-213±93‰ and -57±86‰, respectively) (Figure 5; Tables 1 and 2). Those contrasting age offsets between surface and near-bottom waters, particularly for the POC fraction, may reflect the off-shelf transport of OC translocated over long distances from thawing permafrost.

DOC was the only carbon pool that presented good correlations with $\Delta^{14}C$ and $\delta^{13}C$ data (Figure 6). Those relationships are consistent with previous observations in the Arctic Ocean (Amon et al., 2012; Benner et al., 2004; Schreiner et al., 2013). The correlation between $\delta^{13}C$ and DOC (r^2=0.68) reflects the processes of the terrigenous DOC along the off-shelf transport, with more depleted signatures in higher DOC samples and enriched signatures in lower DOC concentrations. Processes such as hydrodynamic sorting, deposition, resuspension and uptake by primary production may contribute to the dispersal and processing of the OC in the ESAS. On the other hand, the relationship between $\Delta^{14}C$ and DOC (r^2=0.87) represents the source of the terrigenous DOC, where higher DOC samples are composed by young Terr-OC and lower DOC concentrations by old and refractory Terr-OC. Overall, these findings are direct evidence that a large proportion of DOC exported to the outer shelf comes from young and fresh vascular plant material.

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342 **3.3 Lignin-Derived Phenols**

343 Lignin-derived phenols are exclusively synthesized by vascular plants and account for
344 one third of the organic matrix of wood, grasses, needles, and herbage, therefore, they have
345 been extensively used to characterize the pathway of terrestrial matter in the marine
346 environment (Louchouarn et al., 1999; Pasqual et al., 2013; Tesi et al., 2014). The carbon-
347 normalized lignin content (mg/g OC) refers to the sum of vanillyl, syringyl and cinnamyl
348 phenols. DOC_{SPE} samples presented lignin concentration on the same order as the
349 corresponding underlying sediments (0.10-2.34 and 0.08-2.40 mg/g OC, respectively). By
350 contrast, the particulate carbon pool had slightly lower OC-normalized lignin concentrations
351 between 0.03 and 1.14 mg/g OC (Figure 4; Tables 1 and 2). Lignin levels in the SOC and
352 DOC pools are in agreement with previous studies in ESAS sediments (Karlsson et al., 2015;
353 Tesi et al., 2014) and the polar surface water of the Arctic Ocean (Benner et al., 2005). These
354 are the first POC-lignin data in the Arctic Ocean. Lignin concentrations exhibited contrasting
355 offsets in surface and near-bottom waters depending on the carbon pool. DOC_{SPE} presented
356 similar lignin concentrations in surface and near-bottom waters, except for the more
357 concentrated samples closer to the Lena river mouth. Conversely, POC showed enhanced
358 levels in all near-bottom water samples (from 0.17 to 1.14 mg/g OC), with even higher
359 concentrations than in the dissolved pool (from 0.16 to 0.91 mg/g OC) (Figure 2B; Tables 1
360 and 2). Those vertical lignin dissimilarities in the water column were not observed in the total
361 OC of the dissolved and particulate fractions. However, Δ^{14}C-OC also showed offsets in the
362 particulate pool. While DOC_{SPE} depicted similar Δ^{14}C signatures in both surface and near-
363 bottom waters, POC was much older in near-bottom waters. Hence, these findings suggest
364 that particulate old OC with high concentrations of lignin, probably coming from thawing
365 permafrost, is mainly transported off-shelf in near-bottom waters by resuspension and
366 remobilization of the SOC pool.

367 Lignin phenols exhibited decreasing OC-normalized concentrations with increasing
368 distance from the Lena river plume in all carbon pools and in both surface and near-bottom
369 waters (Figure 4). Previous studies in ESAS for other biomarkers have also reported
370 decreasing across-shelf trends of terrestrial organic matter with increasing distance from the
371 coast (Selver et al., 2015; Tesi et al., 2014). Several studies reported minimal degradation of
372 DOM across the broad Eurasian shelves (Dittmar and Kattner, 2003b; Kattner et al., 1999;
373 Köhler et al., 2003). With such a scenario, our off-shelf decreasing lignin concentrations in
374 DOC, POC and SOC pools may be interpreted to result from dilution with marine organic

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matter during transport and/or hydrodynamic sorting along the water and sediment dispersal system. However, other studies found that terrestrial DOC in this ESAS shelf sea system was degraded, with a first-order removal rate constant of 0.3 yr^{-1} (Alling et al., 2010). Recent studies also suggested high reactivity of lignin in rivers (Benner and Kaiser, 2011; Fichot and Benner, 2014; Ward et al., 2013) and in offshoreward direction across ESAS (Bröder et al., Submitted; Tesi et al., 2014). If this instead is the dominating process, the decreasing trend in the current study may also be due to degradation.

Our results depicted a strong positive relationship between lignin phenols and total dissolved organic content within the 35 DOC_{SPE} samples analysed along the outer ESAS (r = 0.89) (Figure 7). There were also significant correlations between OC-normalized concentrations of lignin phenols and $\delta^{13}C$ (r = 0.66) and $\Delta^{14}C$ (r = 0.78) in the DOC_{SPE} pool. These data is consistent with the modern radiocarbon ages of DOC observed in Arctic rivers (Benner et al., 2004; Benner et al., 2005; Karlsson et al., 2016), which also demonstrated a general agreement between lignin phenols and $\Delta^{14}C$ signatures as traces of terrrigenous DOC. Lignin phenols were found in old OC from permafrost (Tesi et al., 2014). Compound-specific radiocarbon analyses of lignin phenols from sediments off major river mouths in ESAS indicated that those macromolecules were younger than sedimentary bulk OC (Feng et al., 2013). This is consistent with lignin compounds derived from both sources, and the higher lignin content from younger DOC_{SPE} likely coming from either recently produced vascular plant material or from contemporary topsoil. By contrast, the slightly negative correlation between lignin phenols and $\Delta^{14}C$ signatures in POC (r = 0.53) (Figure 7), with higher lignin concentrations in older POC, suggests that those macromolecules are coming from remobilized older permafrost carbon. Those results are consistent with previous findings indicating that OC from thawed permafrost is transported preferentially within the particulate carbon pool (Karlsson et al., 2016). There was no relationship between lignin content and bulk POC and SOC, which suggests that both pools are composed by a mixture of marine and terrestrial organic carbon. Taken together, whereas young Terr-OC is transported mainly within the dissolved fraction, near-bottom POC and SOC carries off-shelf preferentially old OC from remobilized permafrost.

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3.4 Biomarker indications of sources of DOC, POC and SOC

The ratios of individual or classes of lignin phenols are frequently used to infer the types of plants yielding the phenols and to what extent the organic matter has been oxidized. Vanillyl phenols (vanillin, acetovanillone and vanillic acid) are ubiquitous in lignin, while syringyl phenols (syringaldehyde, acetosyringone and syringic acid) derive only from angiosperms (Hedges and Mann, 1979; Spencer et al., 2008). Ratios of syringyl to vanillyl (S/V) phenols indicate contribution of angiosperm and gymnosperm vegetation to Terr-OC. Our low S/V ratios (from 0.14 to 1.05) indicate gymnosperm vegetation as the most important source of lignin (Figure 8A; Tables 1, 2 and 3). However, the high S/V ratios in the easternmost samples, particularly within the DOC and SOC, reflect a higher source apportion of tundra plants (Lobbes et al., 2000). Elevated values of S/V were also reported in sediments and dissolved organic carbon from the inner-shelf of the same study area (Karlsson et al., 2016; Tesi et al., 2014). The fact that the Indigirka and Kolyma watersheds are north of the Arctic Cirle with a general shift to flowering tundra plants could explain the elevated S/V ratios in the E-ESS.

Cinnamyl phenols (*p*-coumaric acid, ferulic acid) are predominantly found in herbaceous tissues, and the ratio cinnamyl over vanillyl (C/V) has been used to distinguish woody lignin from other sources (Goni and Hedges, 1992; Hedges and Mann, 1979). C/V ratios did not show a specific trend along the east to west data set. Similar results were observed previously in inner-shelf sediments and in the colloidal DOC fraction from the ESAS (Karlsson et al., 2016). As we also analysed lignin phenols in the particulate fraction, we could see that C/V ratios were slightly higher in POC (0.64±0.42) than in SOC (0.37±0.18) (Tables 1, 2 and 3), possibly reflecting more herbaceous plants or sphagnum moss source in the particulate pool and more woody lignin in the sedimentary carbon. However, those ratios should always be carefully interpreted as photooxidation and microbial degradation can alter the original compositions (Hedges and Prahl, 1993; Opsahl and Benner, 1995). Regarding the classical source plot of S/V versus C/V, our data set distributes along a line between angiosperm leaves and grasses and gymnosperm wood, suggesting that little amounts of non-woody angiosperm tissues are mixing with large amounts of gymnosperm woods in these samples (Figure 8A). Overall, this plot underlines distinct clustering between OC pools, suggesting that angiosperms are mainly transported by SOC and gymnosperms by POC.

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439 *p*-hydroxybenzoic acids (P) can originate from different sources, while *p*-
440 hydroxyacetophenone (Pn) has only been detected in terrigenous organic matter, particularly
441 in peat and sphagnum (Williams et al., 1998), while *p*-hydroxybenzaldehyde (Pl) and *p*-
442 hydroxybenzoic acid (Pd) can also derive from marine sources (Goni and Hedges, 1995). The
443 Pn/P ratios observed in DOC (0.08-0.37), SOC (0.06-0.17) and POC (0.02-0.14) indicate that
444 the OC in the dissolved pool is more terrestrial than in the particulate and sediment pools
445 (Tables 1, 2 and 3; Figure 9A). Those ratios present a slight east-to-west trend with higher
446 values off the Lena river plume. Similar trends and results were observed by Karlsson et al.,
447 2016 in the colloidal OC along the ESAS coast (0.15-30). Amon et al., 2012 characterized the
448 chemical composition of DOC in Arctic rivers and reported Pn/P ratios in the same range, for
449 instance, those ratios in the Lena, Indigirka and Kolyma rivers varied between 0.30 and 0.39.
450 It is important to point out that these findings are in agreement with the relationships of DOC
451 and $\Delta^{14}C$ and $\delta^{13}C$ presented above, which indicate that the DOC exported off-shelf is mainly
452 "young" and terrestrial. By contrast, P/V ratios presented an opposite trend with much higher
453 values in the POC than in the other carbon pools (Tables, 1, 2, 3). This distribution indicates
454 that POC is mainly composed by marine OC with enhanced concentrations in the E-ESS
455 reflecting the Pacific inflow from the East. Overall, these proxies

456

457 **3.5 Indicators of Terr-OC degradation across the OC continuum**

458 The relative abundances of some lignin phenols provide information about the
459 diagenetic alteration of Terr-OC. The acid/aldehyde ratios of syringyl (Sd/Sl) and vanillyl
460 (Vd/Vl) have been utilized as indicators of the relative degradation of the plant matter
461 contribution, as aldehydes degrade faster than corresponding acids (Goni and Hedges, 1992;
462 Hedges et al., 1986). However, some caution should be applied in the interpretation as source
463 signals are more varied than originally thought, and fractionation occurs during
464 leaching/adsorption processes (Benner et al., 1990; Hernes et al., 2007). Our data showed
465 Sd/Sl and Vd/Vl ratios higher in DOC_{SPE} (1.9±0.6 and 2.0±0.7, respectively), than in SOC
466 (0.9±0.2 and 1.1±0.3) and POC (0.4±0.1 and 0.5±0.2) indicating the presence of highly
467 oxidized lignin in the dissolved pool (Tables 1, 2 and 3; Figure 8B). It is important to notice
468 that the ranges of Sd/Sl and Vd/Vl ratios in this study were relatively broad and with clear
469 clusters between carbon pools. POC ratios were lower than the underlying sediments and the
470 dissolved carbon pool presented very high ratios (Figure 8B). Those ratios are in accordance
471 with previous studies in POC (Hernes and Benner, 2002; Lobbes et al., 2000; Winterfeld et

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al., 2015), sediments (Goni and Montgomery, 2000; Goni et al., 2005; Tesi et al., 2014) and DOC (Amon et al., 2012; Hernes and Benner, 2002; Lobbes et al., 2000), which also found higher ratios in the dissolved than in the particulate phase. The elevated Sd/Sl and Vd/Vl in the dissolved fraction, as well as the enhanced ratios in the SOC pool, may reflect leaching/adsorption processes (Hernes et al., 2007; Houel et al., 2006).

Another proxy commonly used to determine the degradation of Terr-OC is the ratio between 3,5-dihydroxybenzoic acid and vanillyl phenols (3,5-Bd/V) (Farella et al., 2001; Houel et al., 2006; Otto and Simpson, 2006; Prahl et al., 1994). Since 3,5-Bd is highly resistant to degradation (Dickens et al., 2007) while vanillyl phenols are very susceptible to degradation, higher values of 3,5-Bd/V are indicative of more degraded Terr-OC. Our results presented opposite patterns than the ones observed by Sd/Sl and Vd/Vl with higher 3,5-Bd/V ratios in POC (1.7±0.7) and SOC (1.0±0.6) and lower ratios in DOC_{SPE} (0.7±0.3) (Tables 1, 2 and 3; Figure 9B). These values are in accordance with those in DOC from ESAS rivers (0.4-0.7) (Amon et al., 2012) and the colloidal fraction from the ESAS land-ocean interface (0.4-0.8) (Karlsson et al., 2016). In addition, SOC ratios are consistent with those observed in surficial sediments from the same area (0.2-1.3) (Tesi et al., 2014). However, we could not find previous studies to compare our 3,5-Bd/V ratios in POC. The higher ratios in POC suggest that Terr-OC is more degraded in the particulate fraction than in the other carbon pools of the outer ESAS. We also should consider that macroalgal sources of 3,5-Bd might be significant in selected marine systems comprising minimal fractions of terrigenous organic matter (Goni and Hedges, 1995). The 3,5-Bd/V ratios in DOC_{SPE} and POC depicted a slightly increasing tendency in the eastern samples (Figure 9B). Previous studies in sediments and the colloidal fraction from the ESAS also reported the same trend (Karlsson et al., 2016; Tesi et al., 2014) reflecting the Pacific inflow from the east of more marine and/or degraded OC. We consider in our study that this degradation proxy is more reliable than Sd/Sl and Vd/Vl ratios as it is not affected by the leaching/adsorption processes between carbon pools. Therefore, the Terr-OC in the ESAS is more degraded in the POC and SOC pools.

Two cinnamyl phenols, *p*-coumaric acid (pCd) and ferulic acid (Fd), are additional CuO oxidation products of lignin that are particularly abundant in grasses and many herbaceous tissues. The two phenols differ by a presence of a methoxyl group, and this may explain the preferential degradation of ferrulic acid (Opsahl and Benner, 1998). Therefore, pCd/Fd ratio has been used as a diagenetic indicator (Amon et al., 2012; Houel et al., 2006). In this data set pCd/Fd ratios follow the same pattern as the ones observed in 3,5-Bd/V ratios

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505 with higher values in POC and SOC (Tables 1, 2 and 3; Figure 9C). This strengthens the
506 hypothesis that POC and SOC are more degraded than DOC.

507 The strong relationship between lignin concentrations and the ^{14}C-age of DOC_{SPE} also
508 reflects the role of diagenetic processes. The younger the marine DOC is, the higher is the
509 concentration of lignin (Figure 7). Those relationships are consistent with previous
510 observations in the Arctic Ocean where the age of DOC decreased with increasing
511 concentration of lignin (Benner et al., 2004). These results suggest that a large proportion of
512 DOC exported to the outer shelf of the ESAS, off the Lena river, comes from recently
513 produced vascular plant material with little exposure to microbial degradation. Whereas most
514 of terrigenous POC settles out close to land and is transported through repeated cycles of
515 deposition and resuspension across the shelf, DOC is dispersed further out onto the EAS with
516 variable extends of conservative mixing.

517

518 **4. Conclusions**

519 This extensive study provides improved understanding on the sources and
520 composition of Terr-OC in the DOC, POC and SOC pools in the extensive outer ESAS. The
521 distribution of a wide variety of bulk ($\delta^{13}C$ and $\Delta^{14}C$) and macromolecular proxies (lignin-
522 derived phenols) reflects a strong influence of the Lena river on the outer shelf, both in the
523 Laptev Sea and the western ESS. These findings demonstrate that a large proportion of the
524 DOC exported off-shelf comes from "young" and fresh vascular plant material. The older and
525 more enriched $\delta^{13}C$ signatures in the E-ESS and its higher POC and SOC concentrations
526 suggest a greater influence of sea ice coverage and the Pacific inflow. The geochemical
527 proxies show dominance of marine sources in the POC pool. However, near-bottom waters
528 present more depleted $\Delta^{14}C$ signatures and higher concentrations of lignin, particularly for the
529 POC fraction. This may reflect the off-shelf transport of permafrost-derived OC in the
530 nepheloid layer, through repeated cycles of deposition and resuspension across the shelf. The
531 ratios of S/V indicate gymnosperm vegetation as the most important source of lignin, and
532 increasing S/V ratios in the easternmost samples reflect a relatively higher source
533 contribution of tundra plants. Moreover, the opposite trends in the Pn/P and P/V ratios
534 confirm the terrigenous source of DOC and the marine composition of POC, particularly in
535 the E-ESS. Taking together S/V and C/V ratios we observe distinct clustering between DOC,
536 POC and SOC, suggesting that those pools are carrying Terr-OC of partially different origin.
537 Regarding the degradation state of Terr-OC, lignin-phenols fingerprints are presenting

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538 contrasting results. While acid/aldehyde ratios are higher for DOC, possibly due to
539 fractionation during leaching, 3,5-Bd/V and pCd/Fd ratios were enhanced in POC and SOC,
540 suggesting degradation. If this hypothesis is true, the remobilized OC from permafrost, which
541 is mainly transported within these carbon pools, could experience less burial and more
542 mineralization than believed earlier. Overall, the high abundance of Terr-OC in the outer
543 ESAS, particularly in the dissolved and sedimentary carbon pools, is a clear indicator of the
544 magnitude of shelf to basin transport. Taken together, the results suggest that DOC, POC and
545 SOC are composed of partially different Terr-OC. While DOC is strongly affected by
546 buoyant freshwater plumes transporting young Terr-OC from topsoil and/or recently
547 produced vascular pant material, near-bottom POC and SOC carries off-shelf old OC released
548 from thawing permafrost.

549

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817 **Table 1. Composition of surface and near-bottom DOC samples collected in the outer Eurasian**
818 **Arctic Shelf.**

ID	Region	Lat	Long	DOC[1]	OC/TN	$\delta^{13}C$	$\Delta^{14}C$	Lignin[2]	S/V	C/V	Sd/Sl	Vd/Vl	3.5Bd/V
DOC-swi													
T-1	KS	79.8	67.9	880	14	-24.7		0.08	0.45	0.51	2.62	3.12	1.24
T-2	KS	81.7	75.3	910	15	-24.6		0.11	0.45	0.59	1.83	2.12	1.28
T-3	LS	81.3	109.4	810	18	-25.1		0.29	0.46	0.33	1.64	1.88	0.81
T-4	LS	81.0	112.9	1200	18	-25.4		0.19	0.43	0.32	2.04	2.40	0.85
1	LS	78.9	125.2	740	18	-24.9	-279	0.25	0.47	0.43	1.67	1.92	0.96
4	LS	77.8	126.7	1200	19	-25.9	-214	0.45	0.41	0.21	2.65	2.70	0.58
6	LS	77.1	127.4	1100	18	-26.0							
13	LS	76.8	125.9	1300	22	-26.3							
14	LS	76.9	127.8	1400	25	-26.8		0.51	0.37	0.19	1.75	1.99	0.41
23	LS	76.2	129.3	3400	43	-27.8		2.40	0.32	0.20	1.49	1.53	0.24
24	LS	75.6	129.6	3300	42	-27.9		2.05	0.31	0.17	1.62	1.49	0.29
25	LS	76.0	130.7	3600	43	-27.9	-19	2.01	0.31	0.15	1.85	1.71	0.26
26	LS	76.5	132.0	3400	40	-27.6							
27	LS	76.9	132.2	2200	36	-27.4							
28	LS	77.3	134.8	2650	39	-27.6	-90	1.22	0.33	0.17	1.64	1.69	0.33
29	LS	77.8	136.7	1700	33	-27.0							
39	W-ESS	77.7	141.4	2000	36	-27.4		0.80	0.34	0.23	1.69	1.38	0.46
40	W-ESS	77.6	145.8	2200	36	-27.2		0.70	0.36	0.25	1.99	1.78	0.34
41	W-ESS	77.0	148.3	1400	35	-29.0							
44	W-ESS	76.3	146.0	1300	26	-26.4	-160	0.41	0.43	0.33	1.93	1.74	0.51
45	W-ESS	76.4	148.1	1100	30	-26.9		0.31	0.48	0.43	2.81	2.99	0.71
46	W-ESS	76.4	149.9	935	25	-26.3							
48	W-ESS	76.5	150.8	995	22	-26.2		0.22	0.47	0.46	2.93	3.06	0.97
49	W-ESS	76.5	156.9	1300	23	-25.4		0.13	0.59	0.51	2.81	3.55	0.90
50	W-ESS	75.8	158.5	1100	21	-25.3	-262	0.16	0.55	0.49	3.09	3.07	0.98
52	E-ESS	74.1	160.6	880	24	-25.3	-288	0.13	0.38	0.14	0.65	1.01	0.61
56	E-ESS	74.6	161.9	920	21	-24.9							
57	E-ESS	74.4	163.7	850	23	-24.5		0.20	0.66	0.86	1.26	1.76	0.88
58	E-ESS	74.4	166.2	850	23	-24.7		0.15	0.54	0.49	3.47	3.77	1.26
59	E-ESS	74.4	168.5	750	25	-25.0							
60	E-ESS	73.4	169.5	850	21	-24.6	-268	0.23	0.68	0.70	1.57	1.91	0.64
61	E-ESS	74.1	170.9	890	26	-24.4	-278	0.20	0.64	0.80	2.28	2.81	1.48
63	E-ESS	74.7	172.4	820	27	-25.3		0.22	0.59	0.78	1.94	2.36	0.75
66	E-ESS	75.9	174.3	860	26	-26.0	-270	0.19	0.56	0.88	1.72	2.26	0.94
DOC-sub													
13	LS	76.8	125.9	1200	25	-26.7							
14	LS	76.9	127.8	1200	26	-26.5		0.24	0.52	0.55	2.50	2.54	0.70
23	LS	76.2	129.3	1200	30	-27.0							
25	LS	76.0	130.7	1100	35	-27.2		0.91	0.40	0.35	1.39	1.21	0.35
27	LS	76.9	132.2	1100	30	-26.3							
28	LS	77.3	134.8	1700	36	-27.4	-171	0.86	0.37	0.33	1.17	0.95	0.31
29	LS	77.8	136.7	920	33	-26.6							
39	W-ESS	77.7	141.4	2200	46	-28.6							
40	W-ESS	77.6	145.8	2000	36	-27.6		0.61	0.39	0.38	1.74	1.40	0.41
41	W-ESS	77.0	148.3	1500	42	-28.0							
44	W-ESS	76.3	146.0	1300	32	-27.4	-188	0.28	0.55	0.67	1.21	1.28	0.47
46	W-ESS	76.4	149.9	1100	19	-25.7							
48	W-ESS	76.5	150.8	990	26	-26.4		0.16	0.57	0.73	2.11	2.09	0.65
50	W-ESS	75.8	158.5	970	20	-26.9		0.20	0.58	0.69	1.41	1.73	0.63
52	E-ESS	74.1	160.6	940	20	-25.3	-307	0.19	0.66	0.74	1.18	1.44	0.71
56	E-ESS	74.6	161.9	910	21	-25.4							
59	E-ESS	74.4	168.5	720	20	-24.9							
60	E-ESS	73.4	169.5	870	20	-25.4	-366	0.26	0.68	0.72	1.16	1.45	0.57
63	E-ESS	74.7	172.4	820	18	-24.6		0.19	0.71	0.75	1.13	1.44	0.65

819 [1]DOC concentrations ($\mu g \cdot L^{-1}$)
820 [2]Lignin OC-normalized concentrations ($mg \cdot g^{-1}$ OC)
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822 **Table 2. Composition of surface and near-bottom POC samples collected in the outer Eurasian**
823 **Arctic Shelf.**

ID	Region	Lat	Long	POC[1]	OC/TN	$\delta^{13}C$	$\Delta^{14}C$	Lignin[2]	S/V	C/V	Sd/Sl	Vd/Vl	3.5Bd/V
POC-swi													
T-1	KS	79.8	67.9	230	5.1	-26.9		0.16	0.37	0.70	0.29	0.40	1.93
T-2	KS	81.7	75.3	350	6.0	-24.7		0.21	0.42	1.58	0.35	0.59	2.72
T-3	LS	81.3	109.4	85	6.5	-28.2		0.71	0.14	0.25	0.33	0.27	0.95
T-4	LS	81.0	112.9	89	5.9	-28.0		0.58	0.31	0.77	0.27	0.45	2.26
1	LS	78.9	125.2	70	4.9	-28.6	14	0.13	0.31	0.50	0.45	0.42	1.45
4	LS	77.8	126.7	140	6.3	-28.8	11	0.14	0.32	0.65	0.48	0.57	3.05
6	LS	77.1	127.4	100	5.4	-26.8							
13	LS	76.8	125.9	51	5.4	-27.5							
14	LS	76.9	127.8	54	4.9	-27.9		0.44	0.30	0.38	0.32	0.33	1.62
23	LS	76.2	129.3	40	5.1	-29.0		0.72	0.46	0.44	0.78	1.09	0.72
24	LS	75.6	129.6	67	5.4	-28.4		0.57	0.44	0.21	0.64	0.97	0.38
25	LS	76.0	130.7	120	5.4	-30.2	5	0.17	0.43	0.29	0.60	0.85	0.66
26	LS	76.5	132.0	78	5.0	-29.5							
27	LS	76.9	132.2	96	5.1	-29.6							
28	LS	77.3	134.8	45	5.2	-29.3	-75	0.24	0.41	0.42	0.42	0.57	0.82
29	LS	77.8	136.7	58	5.1	-28.7							
39	W-ESS	77.7	141.4	69	8.1	-28.0		0.21	0.52	0.80	0.24	0.43	1.77
40	W-ESS	77.6	145.8	85	8.6	-28.5		0.12	0.32	0.39	0.39	0.44	1.24
41	W-ESS	77.0	148.3	66	7.0	-27.8							
44	W-ESS	76.3	146.0	63	7.9	-28.8	64	0.11	0.52	0.34	0.23	0.34	1.21
45	W-ESS	76.4	148.1	61	8.4	-27.5							
46	W-ESS	76.4	149.9	27	6.7	-27.5							
48	W-ESS	76.5	150.8	52	7.0	-27.3		0.06	0.33	0.59	0.39	0.63	1.61
49	W-ESS	76.5	156.9	140	9.1	-25.9		0.05	0.35	0.70	0.40	0.56	1.82
50	W-ESS	75.8	158.5	96	9.3	-25.6	-102	0.05	0.32	0.63	0.42	0.48	1.30
52	E-ESS	74.1	160.6	120	8.1	-24.4	-94	0.06	0.58	0.96	0.31	0.47	2.43
56	E-ESS	74.6	161.9	150	9.2	-24.0							
57	E-ESS	74.4	163.7	160	10.9	-23.0		0.05	0.32	0.73	0.31	0.52	2.11
58	E-ESS	74.4	166.2	60	7.3	-23.7		0.08	0.43	0.79	0.38	0.74	2.52
59	E-ESS	74.4	168.5	290	10.2	-27.4							
60	E-ESS	73.4	169.5	110	5.9	-25.4	-90	0.05	0.44	0.87	0.47	0.45	1.56
61	E-ESS	74.1	170.9	230	8.0	-24.9	-69	0.03	0.72	2.39	0.34	0.41	3.16
63	E-ESS	74.7	172.4	67	7.4	-24.4		0.08	0.43	0.36	0.47	0.39	0.98
66	E-ESS	75.9	174.3	20	6.7	-27.4	-240	0.20	0.60	0.48	0.33	0.41	1.45
POC-sub													
13	LS	76.8	125.9	38	6.7	-29.0							
14	LS	76.9	127.8	47	6.0	-30.9		0.36	0.60	0.89	0.30	0.57	2.32
23	LS	76.2	129.3	99	11.7	-27.2							
25	LS	76.0	130.7	130	10.1	-26.8		1.14	0.79	0.22	0.33	0.49	0.78
27	LS	76.9	132.2	54	7.9	-26.3							
28	LS	77.3	134.8	48	6.6	-28.1	-365	0.87	0.49	0.86	0.39	0.71	3.01
29	LS	77.8	136.7	60	6.4	-25.9							
39	W-ESS	77.7	141.4	93	6.9	-26.7							
40	W-ESS	77.6	145.8	52	7.2	-26.4		0.65	0.28	0.29	0.29	0.49	1.86
41	W-ESS	77.0	148.3	170	11.3	-27.5							
44	W-ESS	76.3	146.0	95	6.5	-28.1	-193	0.37	0.37	0.47	0.37	0.41	2.31
46	W-ESS	76.4	149.9	170	5.8	-25.8							
48	W-ESS	76.5	150.8	78	6.1	-26.2		0.31	0.36	0.47	0.25	0.42	1.60
50	W-ESS	75.8	158.5	170	6.3	-28.4		0.28	0.31	0.35	0.27	0.39	1.06
52	E-ESS	74.1	160.6	72	6.4	-27.1	-258	0.34	0.24	0.55	0.43	0.51	1.97
56	E-ESS	74.6	161.9	120	8.9	-25.9							
59	E-ESS	74.4	168.5	120	7.6	-26.4							
60	E-ESS	73.4	169.5	360	7.4	-27.5	-185	0.17	0.69	0.91	0.27	0.42	1.76
63	E-ESS	74.7	172.4	170	7.0	-25.0		0.17	0.59	0.63	0.23	0.34	1.88

824 [1]POC concentrations ($\mu g \cdot L^{-1}$)
825 [2]Lignin OC-normalized concentrations ($mg \cdot g^{-1}$ OC)

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826 **Table 3. Composition of surface sediment samples collected in the outer Eurasian Arctic Shelf.**

ID	Region	Lat	Long	Depth[1]	SOC[2]	OC/TN	$\delta^{13}C$	$\Delta^{14}C$	Lignin[3]	S/V	C/V	Sd/Sl	Vd/Vl	3.5Bd/V
SOC														
1	LS	78.9	125.2	-3120	1.0	7.1	-22.3	-418	0.58	0.72	0.34	0.62	0.89	0.62
4	LS	77.8	126.7	-2186	1.3	6.8	-22.5	-428	0.37	0.60	0.39	0.95	1.27	1.29
6	LS	77.1	127.4	-92	0.8	6.7	-23.2							
13	LS	76.8	125.9	-74	1.3	7.4	-24.1							
14	LS	76.9	127.8	-64	0.9	6.4	-24.3	-314	0.77	0.56	0.24	0.90	1.21	0.66
23	LS	76.2	129.3	-56	1.6	7.6	-25.0	-333	0.62	0.53	0.24	0.99	1.33	0.65
24	LS	75.6	129.6	-46	1.1	6.9	-24.8	-284	1.82	0.56	0.30	0.95	1.26	0.51
25	LS	76.0	130.7	-53	1.6	8.4	-25.5		2.35	0.56	0.31	0.81	0.95	0.34
26	LS	76.5	132.0	-52	1.2	7.9	-24.4	-441						
27	LS	76.9	132.2	-44	1.4	7.5	-24.2							
28	LS	77.3	134.8	-49	1.4	7.1	-23.8	-421	1.00	0.53	0.27	1.14	1.43	0.57
29	LS	77.8	136.7	-57	1.1	6.9	-23.4	-427						
39	W-ESS	77.7	141.4	-45	0.5	7.9	-24.0		0.77	0.48	0.20	0.91	1.17	0.59
40	W-ESS	77.6	145.8	-47	0.4	7.1	-23.7	-457	0.74	0.64	0.23	0.96	1.26	0.72
41	W-ESS	77.0	148.3	-40	0.3	7.7								
44	W-ESS	76.3	146.0	-43	1.2	7.9	-24.8	-484	1.41	0.55	0.39	0.73	0.97	0.51
45	W-ESS	76.4	148.1	-40	1.0	7.7	-24.4							
46	W-ESS	76.4	149.9	-40	1.1	7.2	-24.7	-463						
48	W-ESS	76.5	150.8	-40	1.4	7.4	-25.8	-345	0.28	0.50	0.29	1.17	1.23	1.26
49	W-ESS	76.5	156.9	-47	1.3	6.6	-23.6	-375	0.17	0.56	0.32	1.31	1.96	1.89
50	W-ESS	75.8	158.5	-44	1.2	6.7	-24.6	-523	0.54	0.50	0.21	0.92	1.20	0.69
52	E-ESS	74.1	160.6	-46	0.8	7.1	-23.9	-550	0.29	0.44	0.16	0.76	0.95	0.88
56	E-ESS	74.6	161.9	-48	1.1	7.3	-23.7							
57	E-ESS	74.4	163.7	-52	1.6	7.0	-24.2	-326	0.12	0.56	0.31	0.80	1.14	1.92
58	E-ESS	74.4	166.2	-54	1.7	7.5	-23.8	-296	0.10	0.72	0.52	0.78	1.43	2.38
59	E-ESS	74.4	168.5	-54	1.7	6.7	-23.5	-307						
60	E-ESS	73.4	169.5	-43	0.9	7.6	-24.0	-472	0.74	1.05	0.56	0.70	0.76	0.54
61	E-ESS	74.1	170.9	-51	1.8	7.0	-24.2	-318	0.25	0.85	0.81	0.91	1.03	0.86
63	E-ESS	74.7	172.4	-64	1.7	7.3	-22.7	-251	0.10	0.81	0.83	0.66	1.14	1.87
66	E-ESS	75.9	174.3	-239	0.8	5.6	-21.0	-448	0.10	0.76	0.41	0.34	0.53	1.38

827 [1]Water depth (m)
828 [2]Percentage of sedimentary organic carbon
829 [3]Lignin OC-normalized concentrations ($mg \cdot g^{-1}$ OC)
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840 **Figures**

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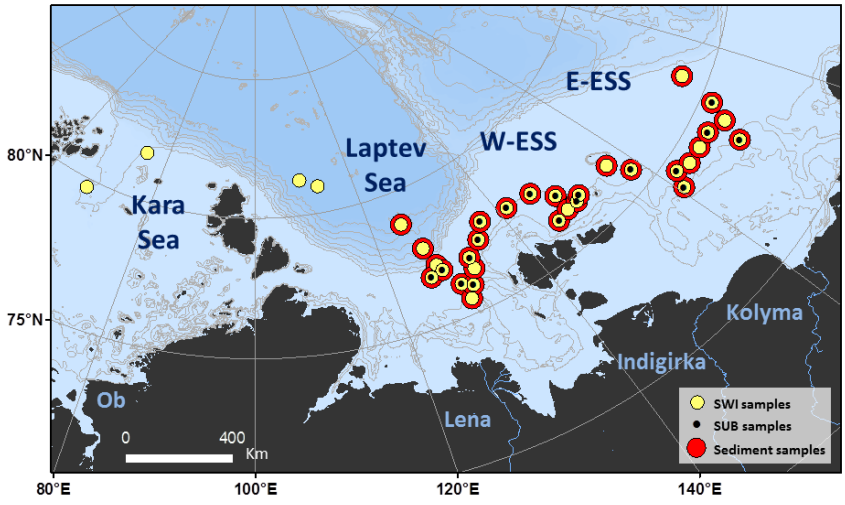

842

843 **Figure 1.** Map of the Eurasian Arctic Shelf including the Kara, Laptev and East Siberian seas
844 (E-ESS, eastern East Siberian Sea; W-ESS, western East Siberian Sea). SWI samples,
845 seawater intake samples (surface water samples at 8 m depth); SUB samples, samples
846 obtained by submersible pump (near-bottom water samples, 5 m above bottom).

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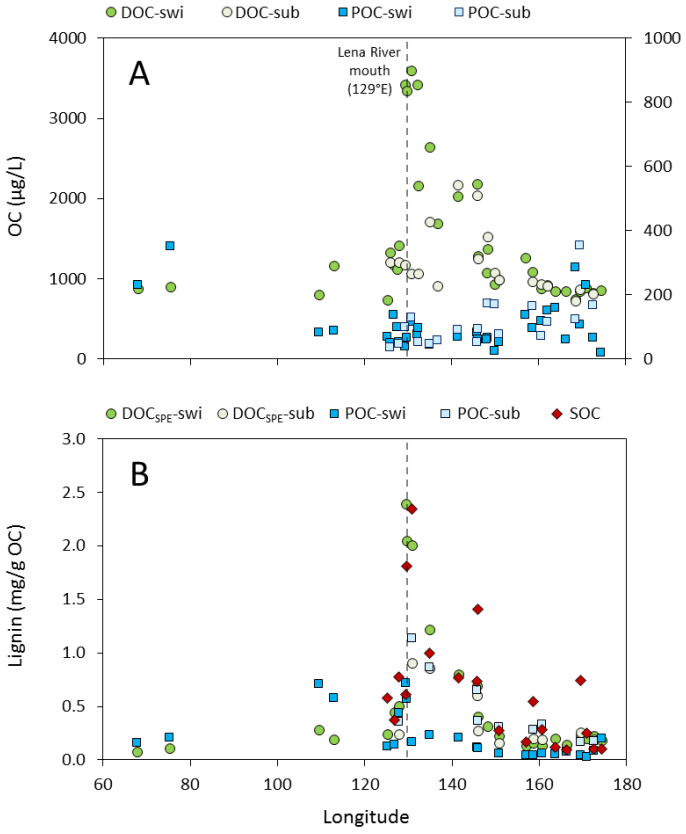

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848 **Figure 2.** Longitudinal distribution of organic matter content in water and sediment samples.
849 A) Organic carbon concentrations (µg/L) in DOC (green circles) and POC (blue squares). B)
850 Lignin concentrations (mg/g OC) in DOC_{SPE} (green circles), POC (blue squares) and SOC
851 (red diamonds); swi, seawater intake samples (surface water samples at 8 m depth); sub,
852 samples obtained by submersible pump (near-bottom water samples, 5 m above bottom).
853 Dash line indicate the latitude of the Lena River mouth.

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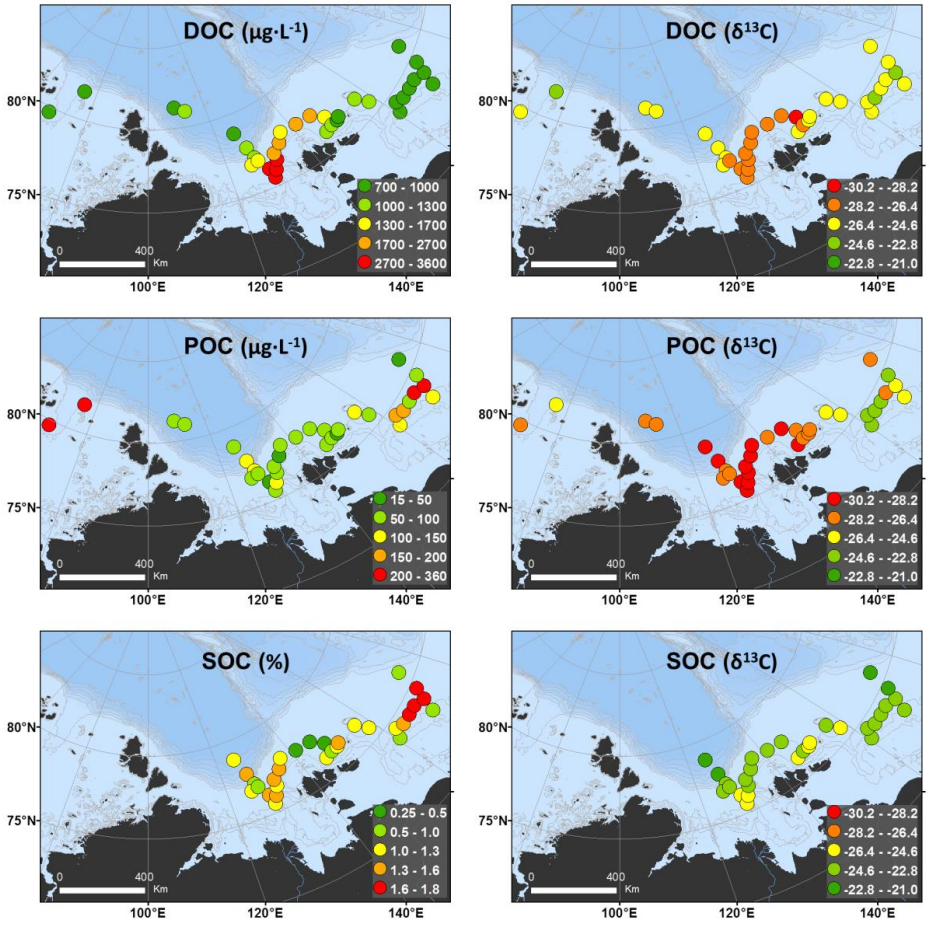

Figure 3. Spatial distribution of organic carbon concentrations and $\delta^{13}C$ signatures in the DOC, POC (surface water samples at 8 m depth) and SOC pools of the ESAS.

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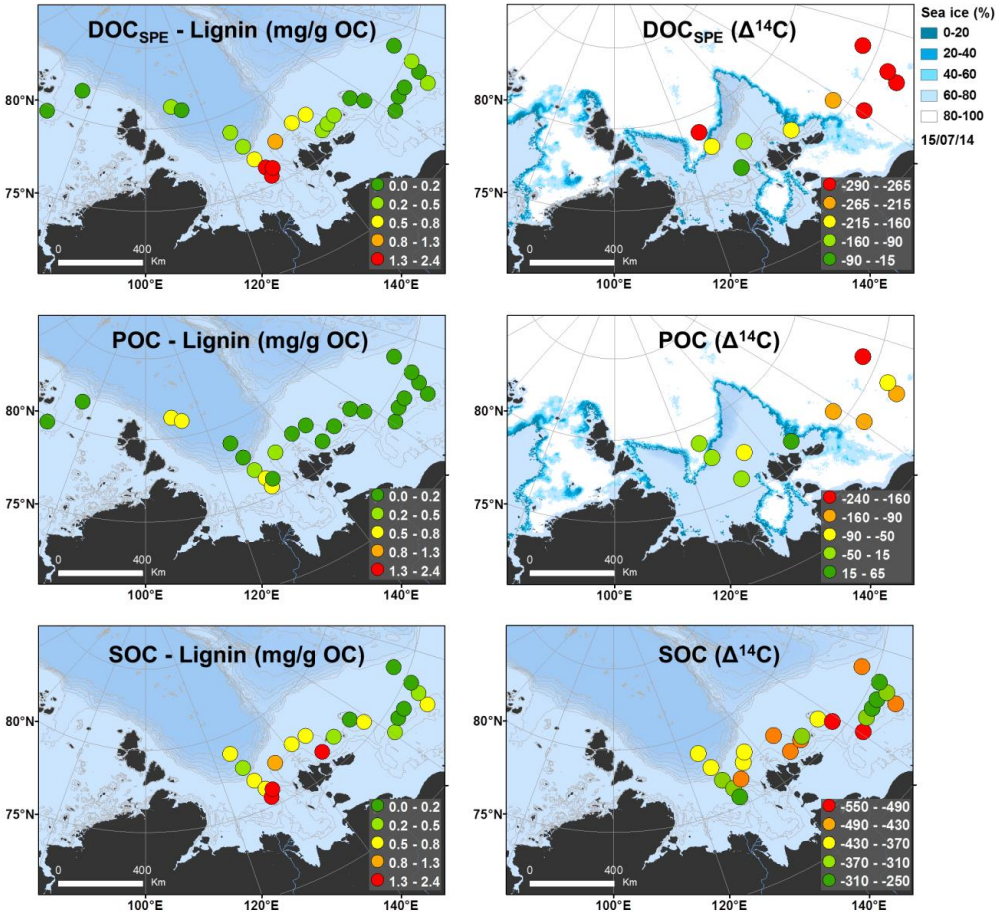

Figure 4. Spatial distribution of lignin (mg/g OC) and Δ^{14}C signatures in the DOC$_{SPE}$, POC (surface water samples at 8 m depth) and SOC pools of the ESAS. Sea ice (%) during the first sampling day in the ESAS (15/7/2015).

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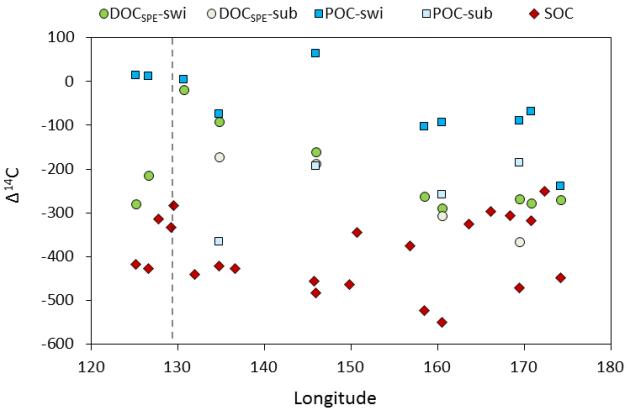

Figure 5. Longitudinal distribution of $\Delta^{14}C$ signatures in DOC_{SPE} (green circles), POC (blue squares) and SOC (red diamonds); swi, sea water intake samples (surface water samples at 8 m depth); sub, samples obtained by submersible pump (near-bottom water samples, 5 m above bottom). Dash line indicate the latitude of the Lena River mouth.

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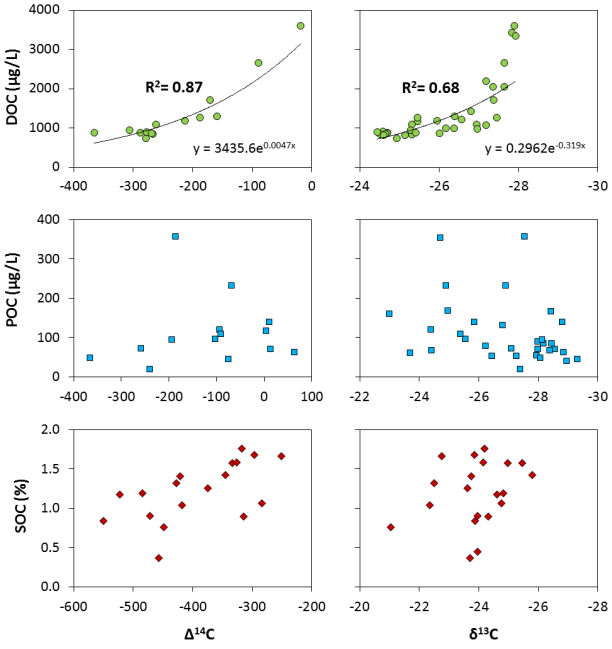

Figure 6. Relationships between organic carbon and $\Delta^{14}C$ and $\delta^{13}C$ signatures in the DOC (green circles), POC (blue squares) and SOC (red diamonds).

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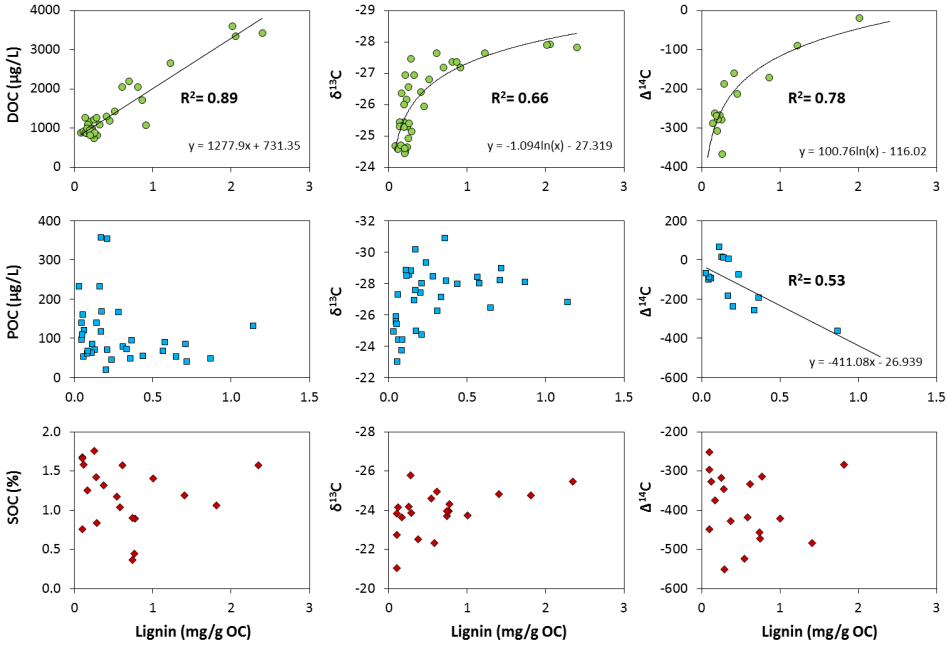

Figure 7. Correlations between lignin concentrations (mg/g OC) and organic carbon, $\delta^{13}C$ and $\Delta^{14}C$ signatures in DOC (green circles), POC (blue squares) and SOC (red diamonds).

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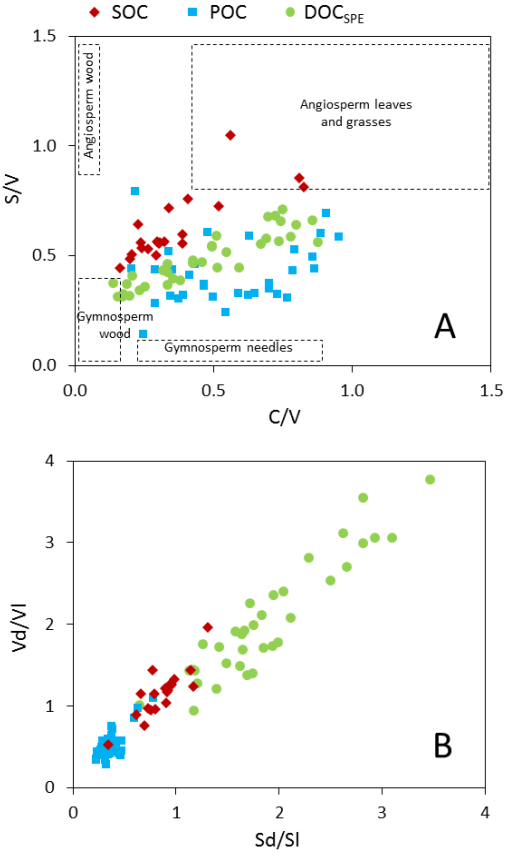

Figure 8. Lignin-phenols ratios in DOC_{SPE} (green circles), POC (blue squares) and SOC (red diamonds). A) Classical source plot of syringyl/vanillyl (S/V) vs. cinnamyl/vannillyl (C/V). B) The acid/aldehyde ratios of syringyl (Sd/Sl) vs. vanillyl (Vd/Vl).

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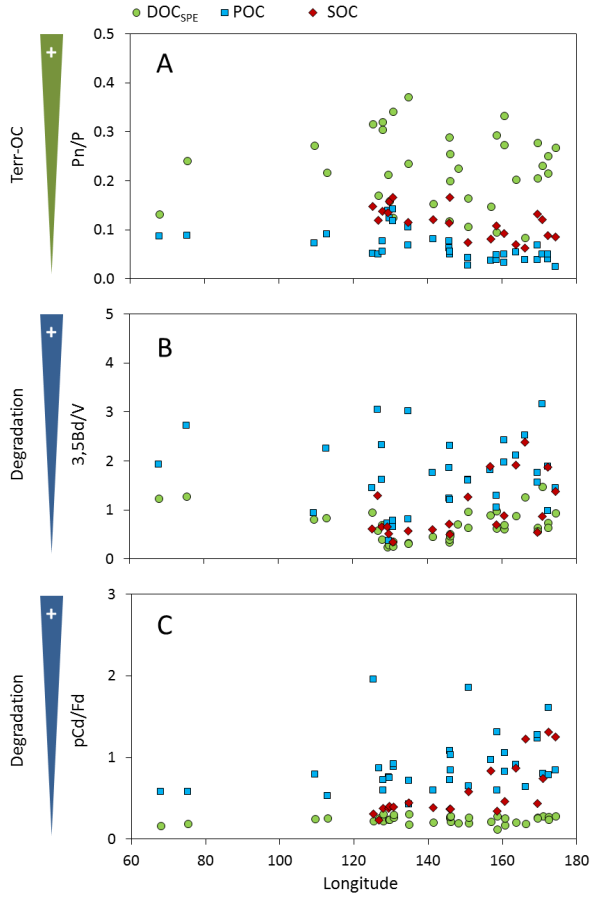

Figure 9. Lignin proxies of Terr-OC and relative degradation state of DOC_{SPE} (green circles), POC (blue squares) and SOC (red diamonds). A) hydroxyacetophenone/*p*-hydroxybenzoic acids (Pn/P). B) Ratios between 3,5-dihydroxybenzoic acid and vanillyl phenols (3,5-Bd/V). C) Ratios between *p*-coumaric acid and ferulic acid (pCd/Fd).