

Multi-molecular tracers of terrestrial carbon transfer across the pan-Arctic – Part 1

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# Multi-molecular tracers of terrestrial carbon transfer across the pan-Arctic – Part 1: Comparison of hydrolysable components with plant wax lipids and lignin phenols

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## Abstract

Hydrolysable organic carbon (OC) comprises a significant component of sedimentary particulate matter transferred from land into oceans via rivers. Its abundance and nature are however not well studied in the arctic river systems, and yet may represent an important pool of carbon whose fate remains unclear in the context of mobilization and related processes associated with changing climate. Here, we examine the molecular composition and source of hydrolysable compounds isolated from surface sediments derived from nine rivers across the pan-Arctic. Bound fatty acids (b-FAs), hydroxy FAs, *n*-alkane- $\alpha,\omega$ -dioic acids (DAs) and phenols were the major components released upon hydrolysis of these sediments. Among them, b-FAs received considerable inputs from bacterial and/or algal sources, whereas  $\omega$ -hydroxy FAs, mid-chain substituted acids, DAs, and hydrolysable phenols were mainly derived from cutin and suberin of higher plants. We further compared the distribution and fate of suberin- and cutin-derived compounds with those of other terrestrial biomarkers (plant wax lipids and lignin phenols) from the same arctic river sediments and conducted a benchmark assessment of several biomarker-based indicators of OC source and extent of degradation. While suberin-specific biomarkers were positively correlated with plant-derived high-molecular-weight (HMW) FAs, lignin phenols were correlated with cutin-derived compounds. These correlations suggest that, similar to leaf-derived cutin, lignin was mainly derived from litter and surface soil horizons, whereas suberin and HMW FAs incorporated significant inputs from belowground sources (roots and deeper soil). This conclusion is supported by the negative correlation between lignin phenols and the ratio of suberin-to-cutin biomarkers. Furthermore, the molecular composition of investigated biomarkers differed between Eurasian and North American arctic rivers: while lignin dominated in the terrestrial OC of Eurasian river sediments, hydrolysable OC represented a much larger fraction in the sedimentary particles from Colville River. Hence, studies exclusively focusing on either plant wax lipids or lignin phenols will not be able to fully unravel the mobilization and fate of bound OC in the arctic rivers.

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More comprehensive, multi-molecular investigations are needed to better constrain the land-ocean transfer of carbon in the changing Arctic, including further research on the degradation and transfer of both free and bound components in the arctic river sediments.

## 1 Introduction

The drainage basins of the arctic rivers are estimated to contain more than half of the global soil organic carbon (OC) reservoir (Tarnocai et al., 2009), and are warming two to three times faster than the other regions on Earth (IPCC, 2013). Fluvial transport currently delivers large amounts of terrestrial OC into the Arctic Ocean annually (Dittmar and Kattner, 2003; Semiletov et al., 2011), and the flux and nature of exported OC is projected to change in the coming decades (Holmes et al., 2013; Feng et al., 2013; O'Donnell et al., 2014). It is thus important to understand the transformation and preservation of terrestrial OC during land-ocean transfer in order to assess its fate and impact on regional and global carbon cycles.

The transport and fate of terrestrial OC in arctic riverine and estuarine sediments have been widely investigated, and two groups of molecular tracer compounds have typically been employed, i.e., plant wax lipids and lignin phenols (Yunker et al., 1993, 1995; Lobbes et al., 2000; van Dongen et al., 2008a, b; Vonk et al., 2010; Gustafsson et al., 2011; Karlsson et al., 2011; Schreiner et al., 2013; Winterfeld et al., 2014). By comparison, cutin- and suberin-derived ester-bound compounds have been much less extensively investigated and used to trace terrestrial carbon transfer in the Arctic (Zegouagh et al., 1996; Goñi et al., 2000; Tesi et al., 2014). Cutin and suberin are protective coatings on vascular plant leaves/fruits/seeds and roots/barks, respectively (Kögel-Knabner, 2002). While they are relatively minor contributors to plant biomass (much less than 10 %) as compared with lignin (~ 30 %), structures of cutin and suberin accumulate in plant litter and mineral soil during decomposition (Kögel-Knabner, 1993) and they are hence key hydrolysable components of terrestrial organic matter. Cutin

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and suberin are considered to be more resistant to microbial decomposition as compared with plant wax lipids (Feng et al., 2008; Feng and Simpson, 2008) and may thus survive longer-range fluvial transport. These different groups of compounds originate from various terrestrial biological sources (roots vs. leaves; woody vs. non-woody parts), potentially display varying degrees of association with mineral surfaces (Feng et al., 2005), and are hence expected to show different provenance and fate during the land-ocean transfer (Gordon and Goñi, 2003; Huguet et al., 2008; Mead and Goñi, 2008; Feng et al., 2013). Investigating their composition and distribution will allow a broader assessment of the fate of mobilized terrestrial OC in the Arctic, including a significant pool (hydrolysable carbon) that has received minimal scrutiny previously.

Here we utilize the surface sediments derived from nine major arctic and sub-Arctic river drainage basins to conduct a multi-tracer comparison of terrestrial OC composition and fate across the pan-Arctic. The investigated systems, including three North American arctic rivers (Mackenzie, Yukon, and Colville), five Great Russian Arctic Rivers (GRARs, namely Ob', Yenisey, Lena, Indigirka and Kolyma), and a sub-Arctic Scandinavian river (Kalix), exhibit varied hydrogeographic characteristics, vegetation and permafrost coverage in their respective drainage basins (Table 1). This comparison across different rivers facilitates an evaluation of controls on terrestrial OC transfer in various watersheds. This paper is the first of two stemming from the same study (the second paper focusing on the  $^{14}\text{C}$  age of individual biomarkers), and builds on prior investigations of lignin and plant wax characteristics in a subset of these rivers (Drenzek et al., 2007; van Dongen et al., 2008a; Feng et al., 2013). The objectives are three-fold: (1) to investigate the molecular composition and source of hydrolysable compounds from arctic and sub-Arctic riverine sediments, (2) to compare the distribution and fate of suberin- and cutin-derived OC vs. plant wax lipids and lignin phenols; and (3) to provide a benchmark assessment of the biomarker-based OC source and degradation indicators across the pan-Arctic.

## 2 Materials and methods

### 2.1 Study area and sampling

The three eastern GRARs (Lena, Indigirka and Kolyma) drain into the Laptev Sea (Lena) and the East Siberian Sea (Indigirka and Kolyma; Fig. 1), with a cold and semiarid climate in the drainage basins and a vast coverage (79–100 %) of continuous permafrost. This contrasts with the two western GRARs (Ob' and Yenisey) draining the west Siberian lowland into the Kara Sea and the Kalix River flowing through sub-Arctic Scandinavia into the Baltic Sea, which are all characterized by wetter climates, milder winters, and a much lower coverage of permafrost (Table 1). The GRAR drainage basins are characterized by various tundra and wetlands in the north and by forests in the south (FAO, 2001; van Dongen et al., 2008a). The Kalix watershed mainly consists of forests (60 %) and wetland (20 %; Hjort, 1971). All rivers have comparable drainage-area-normalized fluxes of total organic carbon (TOC) and particulate organic carbon (POC; Table 1; Stein and Macdonald, 2004; Ingri et al., 2005). A more detailed description of the drainage basins is provided elsewhere (van Dongen et al., 2008a; Vonk et al., 2008). Surface sediments (0–2 cm) were collected using a grab sampler from the GRAR estuaries during the second and third Russia–United States cruises (on H/V *Ivan Kireev*) in 2004 and 2005, and from the Kalix in 2005 on the research vessel “KBV005” from the Umeå Marine Research Center (UMF, Norrbyn, Sweden).

The Mackenzie River in North America is the largest fluvial source of both sediment and POC to the Arctic Ocean (Table 1). Its drainage basin spans the western alpine region of the Cordillera Mountains to the Canadian Shield and includes forests, swamps, grasslands, and permafrost soils. Previous studies have established that petrogenic OC, mainly supplied by immature bitumen, shales, or coals from the Devonian Canol formation, is actively cycling through the Mackenzie system (Yunker et al., 2002; Goñi et al., 2005; Drenzek et al., 2007). Surface sediments (0–2 cm) were collected from the Mackenzie shelf edge in July and August 1987 by a Smith–McIntyre grab sampler (Yunker et al., 1990).

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The Yukon River drains northwestern Canada and central Alaska in the United States into the Bering Sea. Its drainage basin is characterized by diverse ecosystems including forests, shrublands, tundra, and extensive areas of permafrost (Brabets et al., 2000). A river bank sediment sample was collected near Pilot Station, Alaska during ice breakup in June 2007. By comparison, the Colville River, originating in the Brooks Range in northern Alaska, is much smaller in terms of watershed area (Table 1), but is the largest North American river (both in terms of freshwater and sediment load) that exclusively drains continuous permafrost (Walker, 1998). It flows across the foothills of the Brooks Range and the adjacent arctic coastal plain to the Beaufort Sea and the watershed is characterized by dwarf and low shrub tundra, with mossy carpets and moist peaty soils (Walker et al., 2002). Two sediment samples were collected from the surface of the river ice when flood water was running over the ice in June 2007.

## 2.2 Bulk analyses

Bulk sediments were kept frozen at  $-20^{\circ}\text{C}$  after collection and freeze-dried prior to analysis. A small aliquot was used for TOC and bulk  $\delta^{13}\text{C}$  analyses at the UC Davis Stable Isotope Facility (for GRARs and Kalix) and the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution (for North American rivers).

## 2.3 Biomarker extractions

Total lipid extracts (TLEs) were obtained from freeze-dried sediments ( $\sim 70\text{--}160\text{ g}$ ) using dichloromethane / methanol (2 / 1) by soxhlet extraction (24 h; GRARs, Kalix and Mackenzie) or microwave-assisted reaction system (MARS, CEM Corporation; Yukon and Colville). The composition of solvent-extractable *n*-alkanes and *n*-alkanoic acids (fatty acids; FAs) was determined previously for the GRAR (van Dongen et al., 2008a), Kalix (Vonk et al., 2008) and Mackenzie sediments (Drenzek et al., 2007). Similarly, *n*-alkanes and FAs were purified and isolated from the TLEs of Yukon and Colville

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sediments using protocols as described previously (Galy et al., 2011). Briefly, TLEs were saponified with 0.5 M KOH in methanol / water (99 / 1; 70 °C, 2 h). “Neutral” and “acid” fractions were extracted with hexane and hexane / dichloromethane (4 / 1) at pH 7 and 2 (adjusted with HCl), consecutively. The latter fraction, containing FAs, was methylated with methanol / HCl (95 / 5; 70 °C, 12 h). Fractions containing alkanes and fatty acid methyl esters (FAMEs) were separated from the “neutral” and methylated “acid” fractions by liquid chromatography on a Pasteur pipette column filled with 1 % deactivated silica gel and eluted with hexane and hexane / toluene (1 / 1), respectively.

Hydrolysable lipids were released from the solvent-extracted residues (excluding the Mackenzie sample) by treatment with 1 M KOH in methanol / water (4 / 1; 100 °C, 3 h) using a microwave-assisted reaction system. The resulting solution was separated from the solid residue by centrifugation and the residue was washed with methanol / water (1 / 1) twice. A spike of C<sub>19</sub> FA and C<sub>18</sub> *n*-alkane was added as internal standards. Similar to the TLE analysis, “neutral” and “acid” fractions were then recovered from the hydrolysed solution with hexane and hexane / dichloromethane (4 / 1) at high (not acidified) and low pHs (pH 2, acidified with HCl), consecutively. The latter fraction, containing bound FAs (b-FAs) and specific biomarkers for cutin and suberin such as *n*-alkane- $\alpha$ ,  $\omega$ -dioic acids (DAs), and hydroxy FAs, was methylated with methanol / HCl (95 / 5; 70 °C, 12 h), extracted with hexane / dichloromethane (4 / 1), and concentrated under N<sub>2</sub> for further analysis.

Lignin and hydroxy phenols were further released from the dried hydrolysed residues using alkaline CuO oxidation on the microwave-assisted reaction system (Feng et al., 2013). For each sample, approximately 5 g of CuO, 0.6 g of ferrous ammonium sulfate, and 25 mL of N<sub>2</sub>-bubbled NaOH solution (2 M) were loaded into vessels containing sediments (3–10 g) with ~ 50 mg of TOC. All vessels were vacuum-purged with N<sub>2</sub> four times and oxidized at 150 °C for 1.5 h. The oxidation products was spiked with an internal standard (ethyl vanillin), extracted with ethyl acetate after acidification to pH 2 and concentrated under N<sub>2</sub> for further analysis.

## 2.4 Quantification and composition analysis

Small aliquots of the methylated “acid” fraction of hydrolysis products and lignin oxidation products were derivatized with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine (70 °C, 1 h) to yield trimethylsilyl (TMS) derivatives. The molecular composition of biomarkers (including *n*-alkanes, FAs, b-FAs, DAs, hydroxy FAs, lignin and hydroxy phenols) was examined on an Agilent 6890 Series gas chromatograph (GC) coupled to a mass spectrometry detector (Agilent Technologies, Santa Clara, CA, USA) using an Agilent DB-5MS column (50 m × 0.2 mm i.d., film thickness, 0.33 μm) for separation. Temperature increased from 100 °C (initial hold time, 2 min) to 300 °C at a rate of 3 °C min<sup>-1</sup> and helium was used as carrier gas (1 mL min<sup>-1</sup>). Spectra were obtained by scanning over the range 50–600 amu, with a cycle time of 1 s. Electron impact ionization (EI) at 70 eV was used for all analyses. Quantification was achieved by comparison with internal standards (C<sub>18</sub> *n*-alkane for *n*-alkanes, C<sub>19</sub> FA for other lipid compounds, and ethyl vanillin for phenols). Errors associated with the biomarker concentration data are typically < 10% based on replicate analysis of the same sediment sample.

## 2.5 Statistical analysis

Relationships between the abundances of various biomarkers, biomarker-based parameters, and vegetation coverage in the drainage basin were assessed using simple linear regression analysis. Correlation was considered to be significant at a level of  $p < 0.05$ . A principal component analysis (PCA) was further performed to investigate how the distribution of different biomarkers and source/degradation parameters related to each other and explained the compositional variance among different arctic river sediments.

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### 3 Results and discussion

#### 3.1 Sediment bulk properties

Bulk chemical properties of the surface sediments in the nine arctic and sub-Arctic rivers are listed in Table 1. The Kalix and Lena sediments had the highest (4.5%) and lowest (0.5%) OC content, respectively. The Mackenzie sediment, collected from the Mackenzie mid-shelf, had the lowest mass ratio of OC to nitrogen (OC/N; 4.7), consistent with significant inputs of petrogenic OC as well as contributions from marine OC (Goñi et al., 2005). All the other samples showed significantly higher OC/N ratios (from 10.0 to 15.9) and similar  $\delta^{13}\text{C}$  values ( $-25.0$  to  $-27.4\%$ ), indicating terrestrially dominated OC sources (see discussion in van Dongen et al., 2008a).

#### 3.2 Molecular composition and sources of biomarkers

##### 3.2.1 Solvent-extractable *n*-alkanes and FAs

Solvent-extractable *n*-alkanes in the Yukon and Colville sediments were dominated by odd-numbered homologues in the range of  $\text{C}_{20}$ – $\text{C}_{34}$  with  $\text{C}_{27}$  *n*-alkane being the most abundant in all samples (Fig. 2a and Table S1 in the Supplement). Their composition was similar to those in the GRAR (van Dongen et al., 2008a) and Kalix sediments (Vonk et al., 2008), revealing a predominance of terrestrial OC with very minor contributions from aquatic biomass or petrogenic (rock-derived) carbon. The concentration of higher-plant-derived high-molecular-weight (HMW) *n*-alkanes ( $\text{C}_{20}$ – $\text{C}_{34}$ ) ranged  $0.49$ – $0.87 \text{ mg g}^{-1}$  OC, lower than those of Indigirka and Ob' but similar to the others (Table S1). Among the investigated sediments, the Kolyma and Yukon samples had the highest values of carbon preference index for *n*-alkanes ( $\text{CPI}_{25-33}$  as defined in Fig. 2; 7.3 and 6.9, respectively) whereas Mackenzie exhibited a  $\text{C}_{27}$  and  $\text{C}_{29}$  *n*-alkane predominance with the lowest  $\text{CPI}_{25-33}$  value of 2.3, corroborating the influence of petrogenic OC (Drenzek et al., 2007).

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Solvent-extractable FAs in the Yukon and Colville sediments were dominated by even-numbered FAs in the range of C<sub>16</sub>–C<sub>30</sub> with C<sub>24</sub> FA being the most abundant (Fig. 2b and Table S1). The concentration of higher-plant-derived HMW FAs (C<sub>20</sub>–C<sub>30</sub>) ranged 0.67–0.68 mgg<sup>-1</sup> OC in Colville and was much higher in Yukon (1.19 mgg<sup>-1</sup> OC) than in other sediments (Table S1). The CPI<sub>20–30</sub> values showed a very narrow range in both Colville and Yukon sediments (5.1–5.2), similar to that in Kalix and higher than the rest (Fig. 2b), indicating a predominance of higher plant input in these two rivers. It is notable that FAs in the Mackenzie sediment had a much higher concentration of low-molecular-weight (LMW; < C<sub>20</sub>, especially C<sub>16</sub>) FAs as compared with the others, suggesting more algal or bacterial contributions to the sedimentary OC in the Mackenzie mid-shelf area (Yunker et al., 1995; Drenzek et al., 2007) as compared with sediments derived from estuaries (GRARs and Kalix) or within the river systems (Colville and Yukon).

### 3.2.2 Hydrolysable compounds

The acid fraction of the alkaline hydrolysis products yielded four major classes of compounds: b-FAs, hydroxy FAs (including  $\alpha$ -,  $\beta$ -,  $\omega$ -hydroxy FAs, and mid-chain substituted acids), DAs, and hydrolysable phenols (Table S1). Small amounts of steroids and terpenoids were also found, but not included in this study.

*b*-FAs: as compared with solvent-extractable FAs, *b*-FAs were dominated by LMW (C<sub>14</sub>–C<sub>19</sub>) homologues (with maxima at C<sub>16</sub>) with significant contributions from *iso*/*anteiso*-branched and mono-unsaturated counterparts (Fig. 2c). The concentration of HMW *b*-FAs (C<sub>20</sub>–C<sub>30</sub>) ranged from 0.08 mgg<sup>-1</sup> OC in Lena to 1.17 mgg<sup>-1</sup> OC in Colville 2, showing similar (in Kalix, Ob' and Colville) or lower (eastern GRARs and Yukon) values than HMW FAs from the same sediments. *b*-FAs exhibited similar CPI<sub>20–30</sub> values to FAs for Kalix, Indigirka and Kolyma and lower values for the rest of the rivers. In contrast to the FAs, the most abundant HMW *b*-FA varied, being C<sub>20</sub> *b*-FA in Ob', Yenisey, Kolyma and Colville 1, C<sub>24</sub> *b*-FA in Lena and Colville 2, C<sub>22</sub> *b*-FA in Kalix and C<sub>26</sub> in Indigirka. The marked difference in the molecular composition

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of these two types of lipids suggests varied sources in the surface sediments. While solvent-extractable FAs were mainly derived from higher plant waxes, b-FAs received much more inputs from bacterial and/or algal sources as indicated by the dominance of LMW homologues, the presence of branched and mono-unsaturated FAs, and slightly lower CPI<sub>20–30</sub> values. Such source variations have also been found for the solvent-extractable and hydrolysable lipids in other marine sediments (Zegouagh et al., 1996; Garcette-Lepecq et al., 2004).

*Hydroxy FAs*: hydroxy FAs were the most abundant hydrolysable compounds in the arctic sediment samples examined. Among them, exclusively even-numbered  $\omega$ -hydroxy FAs in the range of C<sub>16</sub>–C<sub>26</sub> were the dominant component (Fig. 2d), ranging from 1.16 mg g<sup>-1</sup> OC in Lena to 8.78 mg g<sup>-1</sup> OC in Kolyma, representing 14 % (in Kalix) to 50 % (in Yukon) of the total hydrolysable lipids. The composition of  $\omega$ -hydroxy FAs is very similar to those in soils and plant litter (Riederer et al., 1993; Rumpel et al., 2004; Otto and Simpson, 2006a; Feng et al., 2010), suggesting that they are mainly derived from higher plant cutin, suberin and epicuticular waxes. The HMW (> C<sub>20</sub>) homologues, in particular, are considered to be specific to suberin. As another main component of higher plant cutin and suberin, seven *mid-chain hydroxy and epoxy acids* in the range of C<sub>15</sub>–C<sub>18</sub> were also found in the sediments at slightly lower concentrations than  $\omega$ -hydroxy FAs in Kalix and GRARs and in much lower abundances in Yukon and Colville (Fig. 2e). Among them, C<sub>15</sub>, C<sub>16</sub> mid-chain hydroxy DAs and C<sub>15</sub>, C<sub>16</sub>  $\alpha,\omega$ -dihydroxy FAs are considered to derive solely from cutin, whereas 9,10-epoxy C<sub>18</sub> DA originates from suberin (Otto and Simpson, 2006a). By comparison,  *$\alpha$ -hydroxy acids* in the range of C<sub>15</sub>–C<sub>26</sub> occurred in much lower abundances (0.22–1.61 mg g<sup>-1</sup> OC; Fig. 2f).  $\alpha$ -Hydroxy acids have been found in the hydrolysis products of leaf waxes, wood as well as microalgae and seagrasses (de Leeuw et al., 1995; Volkman et al., 1998; van Dongen et al., 2000; Freire et al., 2002; Otto and Simpson, 2006a). They are hence not considered to be source-specific biomarkers.

Additionally,  *$\beta$ -hydroxy FAs* were observed in the range of C<sub>10</sub>–C<sub>20</sub>, with branched homologues at C<sub>14</sub>–C<sub>17</sub> and maxima at C<sub>14</sub>, C<sub>16</sub> or *i*-C<sub>17</sub> (Fig. 2g). These compounds



by ether linkages (cf. Otto and Simpson, 2006a, 2007). Moreover, the concentration of hydrolysable phenols was most significantly correlated with suberin biomarkers ( $\Sigma$ Suberin as defined in Sect. 3.3;  $p < 0.01$ ), and less so with lignin phenols ( $p = 0.04$ ), supporting the notion that they are mainly derived from suberin.

### 3.2.3 Lignin and hydroxy phenols

Eight phenols characteristic of lignin (vanillyl, syringyl, cinnamyl phenols (VSC); Hedges and Mann, 1979) were detected in much higher concentrations in the Eurasian rivers (11.15–22.78  $\text{mg g}^{-1}$  OC) than in the North American ones (2.08–7.51  $\text{mg g}^{-1}$  OC), including the universal and most abundant vanillyl phenols (vanillin, acetovanillone, vanillic acid), angiosperm-specific syringyl phenols (syringaldehyde, acetosyringone, syringic acid), and cinnamyl phenols found in non-woody tissues ( $p$ -coumaric acid, ferulic acid; Table 2). These concentrations fall within the range reported for lignin VSC in the surface sediments of East Siberian shelf (receiving riverine inputs from Lena, Indigirka, and Kolyma; 0.3–38.2  $\text{mg g}^{-1}$  OC; Tesi et al., 2014), in the sediment cores of Hudson Bay (0.4–14.6  $\text{mg g}^{-1}$  OC; Kuzyk et al., 2008) and in the surface and suspended sediments from Buor Khaya Bay and Lena river (9.4–51.6  $\text{mg g}^{-1}$  OC; Winterfeld et al., 2014) as well as from Beaufort shelf and Mackenzie river (3.01–12.22  $\text{mg g}^{-1}$  OC; Goñi et al., 2000, 2005). The Colville river sediments in this study had slightly less VSC (2.08–2.11  $\text{mg g}^{-1}$  OC) as compared with Colville delta surface sediments (4.1–14.6  $\text{mg g}^{-1}$  OC; Schreiner et al., 2013). This difference may be attributed to OC source variations between the river and delta regions.

Additionally, CuO oxidation released considerable amounts of  $p$ -hydroxy (P) phenols and 3,5-dihydroxybenzoic acid (3,5Bd) from all sediments, which also exhibited higher abundances in the Eurasian river sediments (ranging at 2.90–6.72 and 0.96–2.70  $\text{mg g}^{-1}$  OC, respectively) than in the North American rivers (1.13–1.87 and 0.26–0.70  $\text{mg g}^{-1}$  OC, respectively). Again, the abundances of these phenols fall within the range reported for the sediments of Beaufort shelf, Buor Khaya Bay, Lena and Mackenzie rivers (Goñi et al., 2000, 2005; Winterfeld et al., 2014). Unlike VSC units,

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these phenols may derive from protein and “tannin-like” compounds (Prahl et al., 1994; Goñi and Hedges, 1995; Goñi et al., 2000). In particular, it is found that the non-methoxylated hydroxy phenols (in particular, *p*-hydroxyacetophenone (Pn)) are enriched in *Sphagnum* (Erickson and Miksche, 1974; Lehto et al., 1985; Williams and Yavitt, 2003; Zaccone et al., 2008), and 3,5Bd, while absent in plant tissues, is most enriched in peat (Prahl et al., 1994; Goñi et al., 2000; Amon et al., 2012) and may indicate macrophytes (such as kelp) in certain environment (Kuzyk et al., 2008).

### 3.3 OC source and degradation parameters

Building on the above discussion, indicators of OM source and degradation stage are calculated using the aforementioned biomarkers (Table 3) and compared with the existing data (mainly on lignin phenols) on arctic sediments from the literature (Goñi et al., 2000, 2005; Kuzyk et al., 2008; Schreiner et al., 2013; Tesi et al., 2014; Winterfeld et al., 2014).

#### 3.3.1 Suberin and cutin inputs

Suberin- and cutin-specific biomarkers in the hydrolysable products were summarized and calculated based on parameters developed by Otto and Simpson (2006a). Suberin biomarkers ( $\sum \text{Suberin} = C_{20}\text{--}C_{26}$   $\omega$ -hydroxy FAs +  $C_{20}\text{--}C_{28}$  DAs + 9, 10-epoxy  $C_{18}$  DA) ranged from 1.39 to 8.93 mg g<sup>-1</sup> OC while cutin biomarkers ( $\sum \text{Cutin} = C_{15}$ ,  $C_{16}$  mid-chain hydroxy DAs +  $C_{15}$ ,  $C_{16}$   $\alpha,\omega$ -dihydroxy FAs) ranged from 0.81 to 5.16 mg g<sup>-1</sup> OC in the pan-Arctic sediments (Table 3).  $\sum \text{Cutin}$  showed much higher concentrations in the Kolyma and Indigirka sediments while  $\sum \text{Suberin}$  had the highest and lowest abundance in the Kolyma and Lena sediments, respectively. Comparison with other terrestrial biomarkers revealed that  $\sum \text{Suberin}$  was positively correlated with HMW FAs across the pan-Arctic transect ( $p = 0.04$ ) whereas  $\sum \text{Cutin}$  was not (Fig. 3a). Conversely, lignin VSC was correlated with  $\sum \text{Cutin}$  (Fig. 3b;  $p = 0.02$ ), but not with  $\sum \text{Suberin}$  or HMW FAs. This suggests that, similar to cutin acids, lignin is mainly

derived from surface litter and shallow soil, whereas suberin and HMW FAs incorporate significant inputs from belowground sources (i.e., roots and deeper mineral soils). This conclusion is in line with the relatively younger age of lignin phenols as compared to plant wax lipids in the Eurasian arctic river sediments (Gustafsson et al., 2011; Feng et al., 2013) and is further supported by the negative correlation between VSC and the  $\sum$ Suberin /  $\sum$ Cutin ratio (Fig. 3c;  $p = 0.03$ ), an indicator of the relative input of root/bark- vs. leaf-derived OC (Goñi and Hedges, 1990; Otto and Simpson, 2006a; Feng et al., 2010).

The  $\sum$ Suberin /  $\sum$ Cutin ratio increased from  $\sim 1.6$ – $1.7$  in eastern GRARs to  $\sim 6.5$  in Yukon (Table 3) and was positively correlated with both ratios of  $\omega$ - $C_{16}$  /  $\sum C_{16}$  and  $\omega$ - $C_{18}$  /  $\sum C_{18}$  (ratio of  $C_{16}$  or  $C_{18}$   $\omega$ -hydroxy FA to the summation of all  $C_{16}$  or  $C_{18}$  hydroxy FAs and DAs; Fig. 4a and b;  $p < 0.001$  and  $0.01$ , respectively). Ratios of  $\omega$ - $C_{16}$  /  $\sum C_{16}$  and  $\omega$ - $C_{18}$  /  $\sum C_{18}$  have been reported to increase with progressive cutin degradation in marine sediments, presumably due to the preferential degradation of cutin acids containing double bonds or more than one hydroxyl group (Goñi and Hedges, 1990). However, they also exhibit high values in fresh root tissues (Otto and Simpson, 2006a; Feng et al., 2010). The observed patterns may hence collectively suggest a higher input of root-derived OC in the sediments of North American arctic rivers relative to the GRARs and Kalix.

### 3.3.2 Indicators of moss and peat input

The ratio of  $C_{25} / (C_{25} + C_{29})$   $n$ -alkanes is used to indicate the relative input of *Sphagnum* mosses, which are particularly enriched in  $C_{25}$   $n$ -alkane (Baas et al., 2000; Nott et al., 2000; Pancost et al., 2002; Nichols et al., 2006; Vonk and Gustafsson, 2009). This ratio was highest in Kalix (0.62) and lowest in Indigirka (0.38; Table 3). Similarly, ratios of  $P/V$  and  $3,5Bd/V$  may indicate *Sphagnum* and peat inputs, respectively. These three parameters were positively correlated with each other in the pan-Arctic sediments analyzed in this study (Fig. 4c and d;  $p = 0.001$  and  $0.02$ , respectively), and the  $3,5Bd/V$  ratio generally increases with increasing  $P/V$  ratio in a broader

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range of sedimentary samples stemming from these arctic rivers (Fig. 5a). In particular, both ratios of  $C_{25} / (C_{25} + C_{29})$  *n*-alkanes and P / V increased with increasing wetland coverage in the drainage basin (Fig. 6a and b;  $p < 0.05$  and  $0.03$ , respectively). As *Sphagnum* mosses are most abundant in wetlands, such correlations corroborate the role of both ratios as moss indicators.

High ratios of *p*-coumaric acid to ferulic acid ( $pCd / Fd$ ) and *p*-hydroxyacetophenone to hydroxy phenols ( $Pn / P$ ) have also been reported for mosses and peat (Williams et al., 1998; Amon et al., 2012). However, neither ratio (Table 3) was correlated with the aforementioned moss/peat indicators or with the wetland coverage, undermining their utility as source proxies for mosses and peat in the study area. Instead, both  $pCd / Fd$  and  $Pn / P$  ratios decreased with increasing ratios of  $\omega$ - $C_{18} / \sum C_{18}$  (Fig. 4e and f;  $p = 0.002$  and  $0.01$ , respectively). As discussed previously, the  $\omega$ - $C_{18} / \sum C_{18}$  ratio may indicate the relative input of root OC, whereas elevated  $pCd / Fd$  ratios have also been reported in leaves and needles (Hedges and Parker, 1976; Hedges and Mann, 1979). Their negative correlation may hence point to an increasing proportion of root-derived OC over leaf/needle-derived OC in the watersheds of Kalix < GRARs < Yukon and Colville. The  $Pn / P$  ratio may be affected by such variations as well.

### 3.3.3 Lignin source and degradation stage

Lignin source indicator S / V and C / V ratios ranged from 0.24–0.70 and from 0.05–0.38, respectively (Table 3), generally within the range reported for the surface sediments of arctic rivers and deltas (0.23–2.09 and 0.02–0.32, respectively; Goñi et al., 2000, 2005; Kuzyk et al., 2008; Tesi et al., 2014; Winterfeld et al., 2014) and implying a predominance of gymnosperm wood-derived OC with minor inputs from angiosperms and non-woody tissues (Hedges and Mann, 1979; Goñi and Hedges, 1995). The Colville river sediments had particularly high C / V ratios (0.28–0.38), even as compared with the Colville delta sediments (0.12–0.24; Schreiner et al., 2013), likely due to OC inputs from tundra vegetation into riverine sediments, which is reported to show elevated C / V ratios (Ugolini et al., 1981). Both S / V and C / V were negatively

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correlated with the forest coverage in the drainage basins (Fig. 6c and d;  $p = 0.02$  and  $0.01$ , respectively), consistent with the dominance of gymnosperm woods in the forests of these arctic watersheds. Such correlations are however obscured by the scatter of the published S/V and C/V ratios for a wider range of sedimentary samples consisting of suspended river sediments to shelf deposits (Fig. 5b and c), because lignin phenol composition is subject to alteration during hydrodynamic sorting and diagenesis associated with land-ocean transfer processes (Opsahl, and Benner, 1995; Gordon and Goñi, 2003).

Lignin degradation through side chain oxidation (e.g., by white-rot decay) is typically assessed by the acid-to-aldehyde (Ad/Al) ratios of V and S phenols ( $(Ad/Al)_V$  and  $(Ad/Al)_S$ , respectively; Ertel et al., 1986; Hedges et al., 1988; Goñi and Hedges, 1992; Opsahl and Benner, 1995; Otto and Simpson, 2006b), while degradation of hydroxy phenols is also evaluated by the ratio of *p*-hydroxybenzoic acid to *p*-hydroxybenzaldehyde ( $(Ad/Al)_p$ ; Dittmar and Lara, 2001). Similar to the other lignin parameters, the Ad/Al ratios of V and S phenols in this study fall within the range reported for the surface sediments of arctic rivers and deltas elsewhere (Table 3; Goñi et al., 2000, 2005; Kuzyk et al., 2008; Tesi et al., 2014; Winterfeld et al., 2014) with the exception of the Colville sediments. The latter showed much higher Ad/Al values (0.59–0.70 and 0.83–0.99 for V and S phenols, respectively) as compared with the surface sediments of Colville delta (0.25–0.32 and 0.22–0.31 for V and S phenols, respectively; Schreiner et al., 2013), implying a more oxidized source of lignin (such as soil) for the sediments deposited over ice within the river. Alternatively, as delta sediment incorporates OC inputs throughout the year, its composition may be overwhelmed by the high input of relatively “fresh” lignin supplied from surface layers during freshet, whereas sediment deposits collected at the start of the ice breakup period incorporate more degraded OC from deeper soils that is accumulated within the river before ice breaking.

The  $(Ad/Al)_V$  and  $(Ad/Al)_p$  ratios were positively correlated (Fig. 7a;  $p = 0.01$ ) and showed higher values in the GRARs and Yukon relative to Kalix, Colville and

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Mackenzie (Table 3). Interestingly, both ratios were negatively correlated with the wetland coverage (Fig. 6e and f;  $p = 0.01$ ), implying that vanillyl and hydroxy phenols were less oxidized in wetland-dominated watersheds. As anoxic conditions in peat and wetlands are known to limit the activity of phenol-oxidizing enzymes (Freeman et al., 2001, 2004), our observations provide basin-scale evidence for suppression of phenolic compound oxidation in wetlands. Alternatively, the acidic phenols (i.e., vanillic acid and *p*-hydroxybenzoic acid) may have “leached” out in wetlands due to their higher solubility (Benner et al., 1990; Hernes et al., 2007), leading to lower Ad / Al values in the remaining sediments. Again, the correlation of Ad / Al values with wetland coverage is missing when extended to a wider range of sedimentary samples (Fig. 5d and e) where other environmental factors (such as hydrodynamic sorting patterns) likely overrule lignin oxidation.

In general, the  $(Ad/Al)_s$  ratio increases with increasing  $(Ad/Al)_v$  ratio for arctic sedimentary samples (Fig. 5f). Within our dataset, however, the  $(Ad/Al)_s$  ratio was negatively correlated with the  $(Ad/Al)_v$  ratio (Fig. 7b;  $p = 0.02$ ) and exhibited lower values in the GRAR sediments (Table 3). These contrasting patterns may be related to the scale of the values examined as our ratios also fit in the general pattern of the bigger dataset (Fig. 5f). Alternatively, the  $(Ad/Al)_s$  ratio in our samples increased with an increasing ratio of HMW FAs ( $C_{20}$ – $C_{30}$ ) to HMW *n*-alkanes ( $C_{20}$ – $C_{34}$ ) (HMW FAs / *n*-alkanes; Table 3; Fig. 7c;  $p = 0.001$ ), with the latter indicating enhanced FA preservation (van Dongen et al., 2008a). This relationship is counterintuitive and suggests that the  $(Ad/Al)_s$  ratio may be complicated by factors other than side chain oxidation alone in arctic drainage basins. As the  $(Ad/Al)_s$  ratio also increased with an increasing  $\sum$ Suberin /  $\sum$ Cutin ratio (Fig. 7d;  $p = 0.004$ ), we conclude that the acid-to-aldehyde ratio of syringyl phenols may be strongly influenced by the relative inputs of root/bark vs. leaf tissues. The  $(Ad/Al)_s$  ratio hence may more strongly reflect lignin source than its oxidation state in our sample set.

### 3.4 Variations in terrestrial OC composition and preservation across pan-Arctic river basins

To compare the distribution and degradation of terrestrial OC in the pan-Arctic sediments, a PCA model was performed based on the abundance of various groups of biomarkers (Table S1) and the biomarker-derived parameters (Table 3), respectively. The latter provides a better explanation of the variance (74% for the first and second principle component (PC) combined) among the nine rivers investigated (with Mackenzie excluded due to the absence of data on the hydrolysable compounds) and is hence presented here (Fig. 8). In agreement with the previous discussion, the  $(Ad/Al)_s$  ratio clustered with all the root-input indicators ( $\sum Suberin / \sum Cutin$ ,  $\omega-C_{16} / \sum C_{16}$  and  $\omega-C_{18} / \sum C_{18}$ ) in the fourth quadrant on the opposite side of the PC 1 axis to the other phenol-oxidation parameters ( $(Ad/Al)_v$  and  $(Ad/Al)_p$ ). Similarly, while all the moss- and peat-input indicators (including  $C_{25} / (C_{25} + C_{29})$  *n*-alkanes,  $P/V$ ,  $3,5Bd/V$ ,  $pCd/Fd$  and  $Pn/P$ ) plotted on the positive side of the PC 2 axis, the  $pCd/Fd$  and  $Pn/P$  ratios were on the opposite side of the PC 1 axis from the others. Root-input indicators were the largest contributors to PC 1 while moss-indicators contributed most to PC 2. Based on these parameters, the nine arctic rivers were grouped into three distinct clusters. Two North American rivers (Yukon and Colville) were separated from GRARs mainly by PC 1 due to higher root inputs to their sediments while Kalix River was separated from all the others by PC 2 due to a higher moss input.

The relative proportion of various groups of higher-plant-derived biomarkers (including HMW *n*-alkanes, HMW FAs, HMW b-FAs,  $\sum Suberin$ ,  $\sum Cutin$ , lignin VSC, and hydroxy phenols) within the pan-Arctic sediments confirmed the PCA results (Fig. 9a). Lignin VSC was the dominating component in Eurasian river sediments, making up 52–62% of all the higher-plant-derived biomarkers analyzed, followed by hydroxy phenols (11–26%),  $\sum Suberin$  (8–20%), and  $\sum Cutin$  (3–12%). By comparison, the Colville and Yukon sediments were characterized by a much higher proportion of  $\sum Suberin$  (30–43%) and HMW FAs (6–7%) and a lower proportion of

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lignin VSC (18–43 %) and hydroxy phenols (10–11 %). This lends further weight to our previous conclusions based on the biomarker-derived ratios, and suggests that there is a greater proportional supply of belowground OC to the sediments of the North American arctic rivers relative to the GRARs and the Kalix river.

5 In terms of absolute abundances, Kalix had the highest concentration of higher-plant-derived biomarkers per gram of sediment ( $1.15 \text{ mg g}_{\text{sediment}}^{-1}$ ) among the eight arctic and sub-Arctic rivers (with Mackenzie excluded), followed by Kolyma and Indigirka (0.75 and  $0.54 \text{ mg g}_{\text{sediment}}^{-1}$  respectively). This pattern largely tracks the TOC content of these sediments (Table 1), which exerts a strong control over the abundance of  
10 biomarkers in sediments. When normalized to the TOC content, Kolyma and Indigirka had the highest overall sedimentary concentrations of higher-plant-derived biomarkers, approximately 1.5–3 times the amount found in the other rivers (Fig. 9b). This is consistent with the previous findings that plant-derived sterols (campesterol and  $\beta$ -sitosterol) were in much higher concentrations in these two rivers relative to the other  
15 GRARs (van Dongen et al., 2008a). These observations suggest that land-derived carbon is better preserved in eastern Siberia, probably due to the cold and dry climate in the drainage basins and/or a greater input of less degraded OC supplied by the widespread ice complexes (“Yedoma”) in the basins (Vonk et al., 2012; Sánchez-García et al., 2014). Alternatively, terrestrial OC may be less diluted by other carbon  
20 sources (such as marine or rock-derived OC) in eastern Siberian sediments (Semiletov et al., 2005; Dudarev et al., 2006). It is also notable that surface-derived OC, as represented by  $\Sigma$ Cutin and lignin VSC, was most abundant in the sediments of Kolyma and Indigirka, probably because surface runoff predominates as the mobilization pathways of terrestrial OC in these two continuous-permafrost-dominated watersheds  
25 (Feng et al., 2013). Such was however not true for the sediments from Colville River, whose watershed is fully covered by continuous permafrost as well. The difference may be explained by the varied vegetation coverage between these basins (as discussed below).

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Regardless of the geographic variations, hydrolysable components, including  $\sum$ Suberin,  $\sum$ Cutin, and HMW b-FAs, made up a significant fraction of the terrestrial OC buried in these arctic river sediments, amounting to 13 to 60 % of all the higher-plant-derived biomarkers analyzed. This was particularly true for the Colville sediments that were characterized by the lowest content of lignin, in line with the low forest coverage (2 %; Table 1) in the watershed. Accordingly, the Colville sediments had the highest content of  $\sum$ Suberin. This is probably related to the high tundra coverage in its watershed (Walker et al., 2002), as tundra has the highest root-to-shoot ratio of all terrestrial biomes (Jackson et al., 1996). Tundra is widely dispersed in the Arctic, and is expected to experience rapid change in response to regional climate variations (Schuur et al., 2009; Elmendorf et al., 2012). Our results suggest that the “bound” OC warrants greater attention both as an important (and even predominant) component of the carbon transferred from these landscapes into rivers and as molecular informants on biomass source and transport pathways.

#### 4 Conclusions and implications

Hydrolysable compounds, consisting of b-FAs, hydroxy FAs, DAs, and phenols, were a major component of the sedimentary OC exported from nine arctic and sub-Arctic river basins, and revealed distinct carbon sources vs. solvent-extractable lipids and lignin phenols. As compared with solvent-extractable FAs, b-FAs were influenced by bacterial and/or algal sources as indicated by the dominance of LMW homologues and the presence of branched and mono-unsaturated FAs. In contrast,  $\omega$ -hydroxy FAs, mid-chain substituted acids, DAs, and hydrolysable phenols were mainly derived from cutin and suberin of higher plants. Several parameters based on these biomarkers were used to investigate relative input of root- and moss-derived OC as well as OC degradation stages. Ratios of  $\omega$ -C<sub>16</sub> /  $\sum$ C<sub>16</sub> and  $\omega$ -C<sub>18</sub> /  $\sum$ C<sub>18</sub> were found to increase with increasing suberin / cutin ( $\sum$ Suberin /  $\sum$ Cutin) ratio, potentially providing a proxy for assessing fresh root input in these river sediments. Ratios of C<sub>25</sub> / (C<sub>25</sub> + C<sub>29</sub>)

*n*-alkanes and P/V increased with increasing wetland coverage in the drainage basin, corroborating their role as moss indicators. The Ad/AI ratios of both vanillyl and hydroxy phenols were negatively correlated with wetland coverage, probably reflecting the inhibited oxidation of phenolic compounds in these environments. The (Ad/AI)<sub>s</sub> ratio instead was sensitive to relative inputs of root/bark vs. leaf tissues and hence informed on lignin source rather than its oxidation state in the transect. These comparisons provide a benchmark assessment of the OC source and degradation indicators across the pan-Arctic.

Suberin-specific biomarkers were found to positively correlate with HMW FAs across the pan-Arctic sediments whereas lignin phenols were correlated with cutin-derived compounds. These correlations suggest that, similar to leaf-derived cutin, lignin is mainly derived from surface litter and soil, whereas suberin and HMW FAs incorporate significant inputs from belowground sources (roots and deeper soils). In addition, hydrolysable components displayed varied distribution patterns as compared with lignin or plant wax lipids in the pan-Arctic sediments, depending on the vegetation input and preservation in the drainage basins. While lignin dominates in the terrestrial OC transferred into the sediments of Eurasian rivers, hydrolysable OC mainly originating from suberin and cutin appears much more important in sediments derived from Colville watershed. Studies exclusively focusing on plant wax lipids or lignin phenols will fail to capture the diverse sources and sources involved in the mobilization and fate of OC in the arctic rivers. To better constrain land-ocean transfer of carbon in the changing Arctic, bound OC warrants greater attention both as an important component of sedimentary carbon mobilized by rivers and as molecular informants on biomass source and transport pathways.

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*Author contributions.* Ö. Gustafsson, R. M. Holmes, J. E. Vonk, B. E. van Dongen, I. P. Semiletov, O. V. Dudarev, M. B. Yunker and R. W. Macdonald collected samples. B. E. van Dongen and J. E. Vonk prepared samples for bulk organic carbon and stable isotope analyses. X. Feng conducted biomarker analysis with assistance of D. B. Montluçon and T. I. Eglinton. X. Feng prepared the manuscript with contributions from all co-authors.

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**Table 1.** Sample location, drainage basin characteristics and bulk sediment properties of the pan-Arctic rivers.

	Kalix	Ob <sup>a</sup>	Yenisey	Lena	Indigirka	Kolyma	Colville1	Colville2	Yukon	Mackenzie
Latitude; Longitude	65.44° N; 23.20° E	72.65° N; 73.44° E	72.61° N; 79.86° E	71.96° N; 129.54° E	72.06° N; 150.46° E– 71.02° N; 152.60° E <sup>a</sup>	70.00° N; 163.70° E	70.22° N; 150.98° W	70.22° N; 150.99° W	61.93° N; 162.88° W	70.17° N; 133.43° W
Forest coverage (%) <sup>b</sup>	60	30	49	84	21	31	2	2	51	63
Wetland coverage (%) <sup>b</sup>	20	11	3	1	3	1	NA	NA	14	18
Permafrost coverage <sup>c</sup>	5/15/80	2/24/74	33/55/12	79/20/1	100/0/0	100/0/0	100/0/0	100/0/0	23/66/11	16/29/55
Basin area (10 <sup>6</sup> km <sup>2</sup> ) <sup>d</sup>	0.024	2.54–2.99	2.44–2.59	2.40–2.49	0.34–0.36	0.65–0.66	0.06	0.06	0.83	1.75
Discharge (km <sup>3</sup> yr <sup>-1</sup> ) <sup>e</sup>	10	427	673	588	54	136	19	19	208	316
Runoff (mm yr <sup>-1</sup> ) <sup>e</sup>	417	145	263	245	159	209	317	317	251	181
TOC/POC flux (tkm <sup>-2</sup> yr <sup>-1</sup> ) <sup>f</sup>	1.4/0.099	1.1/0.14	1.8/0.066	1.9/0.49	1.2/0.47	1.5/0.48	4.6/2.6	4.6/2.6	3.0/1.07	2.1/1.1
OC (%)	4.5	0.9	1.9	0.5	1.5	1.7	1.78	0.85	1.16	1.56
OC/N <sup>g</sup>	10.9 ± 0.3	10.0 ± 0.1	10.5 ± 0.1	12.3 ± 0.8	14.7 ± 0.2	15.9 ± 1.2	12.8	13.7	15.5	4.7
δ <sup>13</sup> C-TOC (‰) <sup>g</sup>	-27.1	-27.4	-26.5	-25.	-26.6	-26.7	-26.4	-26.7	-26	-26

NA: not available.

<sup>a</sup> Combined surface sediments along a transect.

<sup>b</sup> Data from Revenga et al. (1998) and Ingri et al. (2005).

<sup>c</sup> Given as % continuous; % (discontinuous + sporadic + isolated); % non-permafrost (Gustafsson et al., 2011; Holmes et al., 2013).

<sup>d</sup> Data from Gordeev et al. (1996), Holmes et al. (2002), Rachold et al. (2004) and Ingri et al. (2005).

<sup>e</sup> Data from Milliman et al. (1995), Stein and Macdonald (2004), Ingri et al. (2005) and Holmes et al. (2013).

<sup>f</sup> Kalix data from Ingri et al. (2005), Colville data from McClelland et al. (2014), Yukon data from Guo et al. (2012), and the rest from Stein and Macdonald (2004).

<sup>g</sup> Mass ratio of OC to total nitrogen (OC/N) and δ<sup>13</sup>C values from Drenzek et al. (2007) for Mackenzie, van Dongen et al. (2008a) for GRARs and Vonk et al. (2008) for Kalix.

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**Table 2.** Abundances of lignin and hydroxy phenols in the pan-Arctic sediments ( $\text{mg g}^{-1}$  OC). Numbers in bold represent summed abundances of the corresponding phenols.

	Kalix	Ob'	Yenisey	Lena	Indigirka	Kolyma	Coville1	Coville2	Yukon	Mackenzie
3,5-dihydroxybenzoic acid (3,5Bd)	2.70	1.66	0.96	1.68	1.56	1.52	0.26	0.26	0.70	0.55
<i>p</i> -Hydroxybenzaldehyde	2.92	1.02	0.75	0.99	0.90	0.93	0.30	0.37	0.53	0.95
<i>p</i> -Hydroxyacetophenone	1.32	0.75	0.43	0.50	0.44	0.81	0.11	0.12	0.21	0.22
<i>p</i> -Hydroxybenzoic acid	2.49	2.36	1.72	2.18	3.03	3.06	0.72	0.66	1.12	0.70
<b><i>p</i>-Hydroxy phenols (P)</b>	<b>6.72</b>	<b>4.13</b>	<b>2.90</b>	<b>3.67</b>	<b>4.36</b>	<b>4.80</b>	<b>1.13</b>	<b>1.15</b>	<b>1.85</b>	<b>1.87</b>
Vanillin	4.06	3.11	2.94	3.64	4.58	5.17	0.58	0.63	2.76	1.70
Acetovanillone	2.04	1.80	1.76	2.30	3.68	3.38	0.15	0.15	0.71	0.59
Vanillic acid	2.34	2.35	2.38	2.78	3.62	3.69	0.41	0.37	1.81	0.79
<b>Vanillyl phenols (V)</b>	<b>8.45</b>	<b>7.26</b>	<b>7.09</b>	<b>8.72</b>	<b>11.88</b>	<b>12.24</b>	<b>1.14</b>	<b>1.15</b>	<b>5.28</b>	<b>3.09</b>
Syringaldehyde	1.73	2.51	1.75	1.13	3.90	4.20	0.27	0.28	0.58	0.45
Acetosyringone	0.75	1.06	0.58	0.32	1.55	1.75	0.11	0.09	0.28	0.17
Syringic acid	1.42	1.45	0.87	0.67	2.16	2.60	0.26	0.23	0.63	0.45
<b>Syringyl phenols (S)</b>	<b>3.89</b>	<b>5.02</b>	<b>3.21</b>	<b>2.12</b>	<b>7.60</b>	<b>8.55</b>	<b>0.64</b>	<b>0.60</b>	<b>1.49</b>	<b>1.07</b>
<i>p</i> -Coumaric acid ( <i>p</i> Cd)	1.60	0.56	0.52	0.40	0.78	0.93	0.10	0.05	0.13	0.09
Ferulic acid (Fd)	0.41	0.52	0.34	0.18	1.11	1.05	0.33	0.28	0.61	0.07
<b>Cinnamyl phenols (C)</b>	<b>2.01</b>	<b>1.09</b>	<b>0.86</b>	<b>0.58</b>	<b>1.89</b>	<b>1.98</b>	<b>0.43</b>	<b>0.33</b>	<b>0.74</b>	<b>0.17</b>
<b>Lignin phenols (VSC)</b>	<b>14.35</b>	<b>13.36</b>	<b>11.15</b>	<b>11.41</b>	<b>21.37</b>	<b>22.78</b>	<b>2.21</b>	<b>2.08</b>	<b>7.51</b>	<b>4.32</b>

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**Table 3.** Biomarker-based parameters of organic matter (OM) sources and degradation stages used in this paper.

Indication	Proxy	Kalix	Ob <sup>a</sup>	Yenisey	Lena	Indigirka	Kolyma	Coville1	Coville2	Yukon	Mackenzie
Inputs of suberin and cutin	$\sum$ Suberin	2.29	3.80	2.79	1.39	5.05	8.93	4.88	4.86	5.28	NA
	$\sum$ Cutin	0.84	1.30	1.37	0.87	3.00	5.16	1.23	0.89	0.81	NA
	$\sum$ Suberin / $\sum$ Cutin	2.72	2.93	2.03	1.60	1.68	1.73	3.98	5.44	6.54	NA
	$\omega$ -C <sub>16</sub> $\sum$ C <sub>16</sub>	0.18	0.26	0.27	0.21	0.22	0.23	0.33	0.39	0.51	NA
	$\omega$ -C <sub>18</sub> $\sum$ C <sub>18</sub>	0.20	0.35	0.40	0.33	0.47	0.46	0.62	0.66	0.75	NA
Moss and peat input	C <sub>25</sub> / (C <sub>25</sub> +C <sub>29</sub> ) <i>n</i> -alkanes	0.62	0.52	0.44	0.39	0.38	0.41	0.47	0.55	0.43	0.44
	P / V	0.80	0.57	0.41	0.42	0.37	0.39	0.99	1.00	0.35	0.60
	3,5Bd / V	0.32	0.23	0.14	0.19	0.13	0.12	0.23	0.22	0.13	0.18
	<i>p</i> Cd / Fd	3.91	1.08	1.53	2.19	0.70	0.89	0.29	0.17	0.21	1.23
	Pn / P	0.20	0.18	0.15	0.14	0.10	0.17	0.10	0.11	0.11	0.12
Lignin source	S / V	0.46	0.69	0.45	0.24	0.64	0.70	0.56	0.52	0.28	0.35
	C / V	0.24	0.15	0.12	0.07	0.16	0.16	0.38	0.28	0.14	0.05
Oxidation of phenols	(Ad / Al) <sub>v</sub>	0.58	0.76	0.81	0.76	0.79	0.71	0.70	0.59	0.66	0.47
	(Ad / Al) <sub>s</sub>	0.82	0.58	0.50	0.60	0.55	0.62	0.99	0.83	1.10	0.99
	(Ad / Al) <sub>p</sub>	0.85	2.33	2.31	2.21	3.38	3.28	2.40	1.78	2.12	0.74
FA preservation	HMW FAs / <i>n</i> -alkanes	1.49	0.14	0.24	0.56	0.32	0.83	1.38	0.78	1.83	0.96

Abbreviations:

$\sum$ Suberin = C<sub>20</sub>–C<sub>26</sub>  $\omega$ -hydroxy fatty acids (FAs) + C<sub>20</sub>–C<sub>28</sub> diacids (DAs) + 9,10-epoxy C<sub>18</sub> DA.

$\sum$ Cutin = C<sub>15</sub>, C<sub>16</sub> mid-chain hydroxy DAs + C<sub>15</sub>, C<sub>16</sub>  $\alpha,\omega$ -dihydroxy FAs.

$\omega$ -C<sub>16</sub> /  $\sum$ C<sub>16</sub> or  $\omega$ -C<sub>18</sub> /  $\sum$ C<sub>18</sub> = ratio of C<sub>16</sub> or C<sub>18</sub>  $\omega$ -hydroxy FA to the summation of all C<sub>16</sub> or C<sub>18</sub> hydroxy FAs and DAs.

P: *p*-hydroxy phenols.

V: vanillyl phenols.

S: syringyl phenols.

C: cinnamyl phenols.

3,5Bd: 3,5-dihydroxybenzoic acid.

*p*Cd: *p*-coumaric acid.

Fd: ferulic acid.

Pn: *p*-hydroxyacetophenone.

Ad / Al: the acid-to-aldehyde ratio of V, S and P phenols.

HMW FAs / *n*-alkanes = high-molecular-weight (HMW) FAs (C<sub>20</sub>–C<sub>30</sub>) to HMW *n*-alkanes (C<sub>20</sub>–C<sub>34</sub>).

NA: not available.

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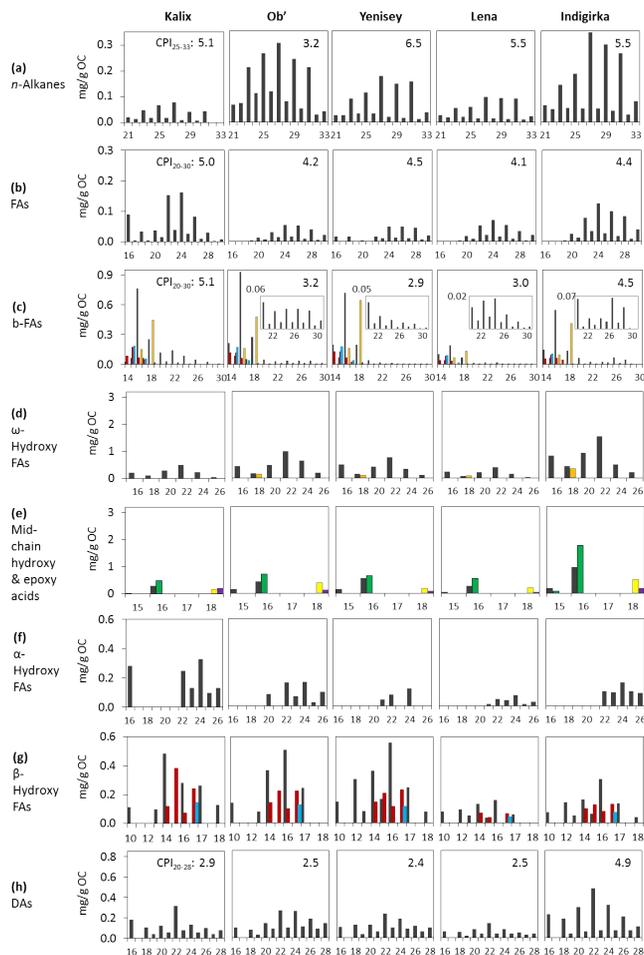


**Figure 1.** Sampling locations (red dots) and watersheds of the nine arctic and sub-Arctic rivers.

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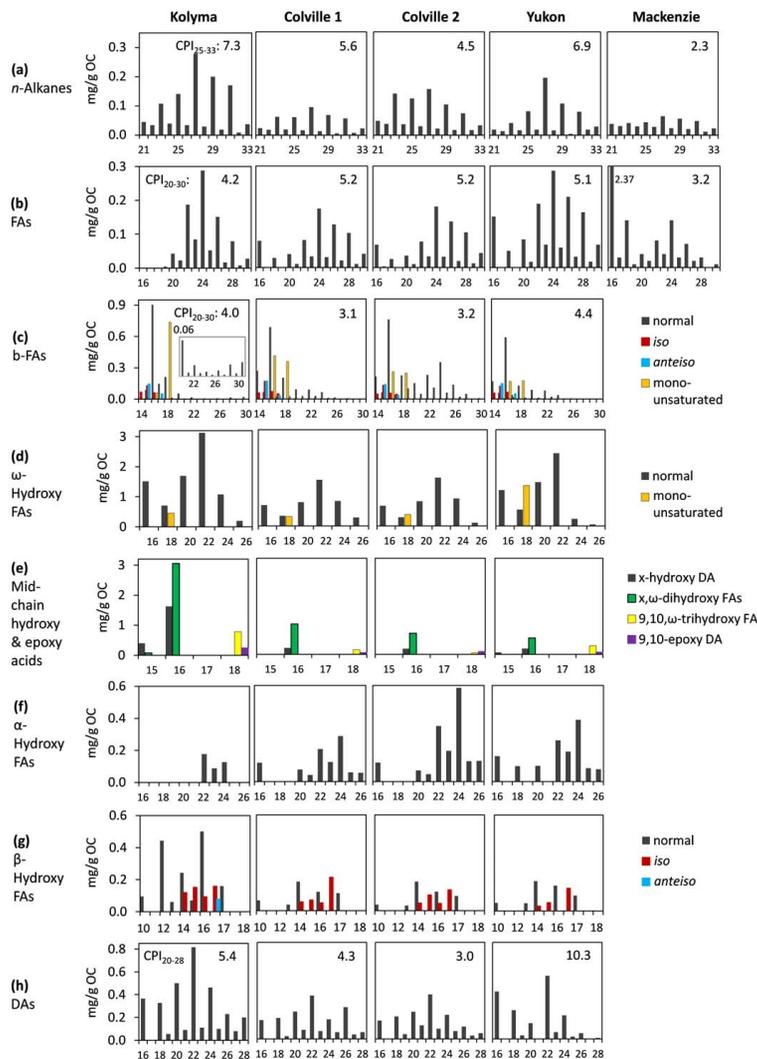
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**Figure 2.** Abundances of solvent-extractable and hydrolysable lipids in the pan-Arctic surface sediments. Carbon preference index (CPI) is defined as  $CPI_{25-33} = (\sum C_{25,27,29,31,33} / \sum C_{24,26,28,30,32} + \sum C_{25,27,29,31,33} / \sum C_{26,28,30,32,34}) / 2$  for *n*-alkanes,  $CPI_{20-30} = (\sum C_{20,22,24,26,28,30} / \sum C_{19,21,23,25,27,29} + \sum C_{20,22,24,26,28,30} / \sum C_{21,23,25,27,29,31}) / 2$  for fatty acids (FAs) and bound FAs (b-FAs),  $CPI_{20-28} = (\sum C_{20,22,24,26,28} / \sum C_{19,21,23,25,27} + \sum C_{20,22,24,26,28} / \sum C_{21,23,25,27,29}) / 2$  for diacids (DAs).

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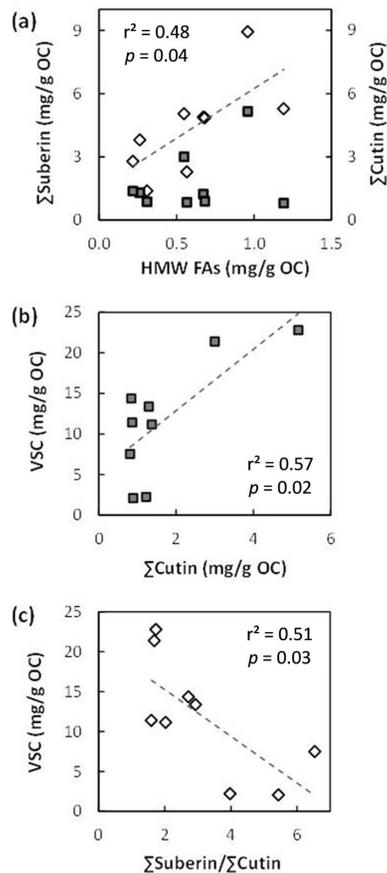
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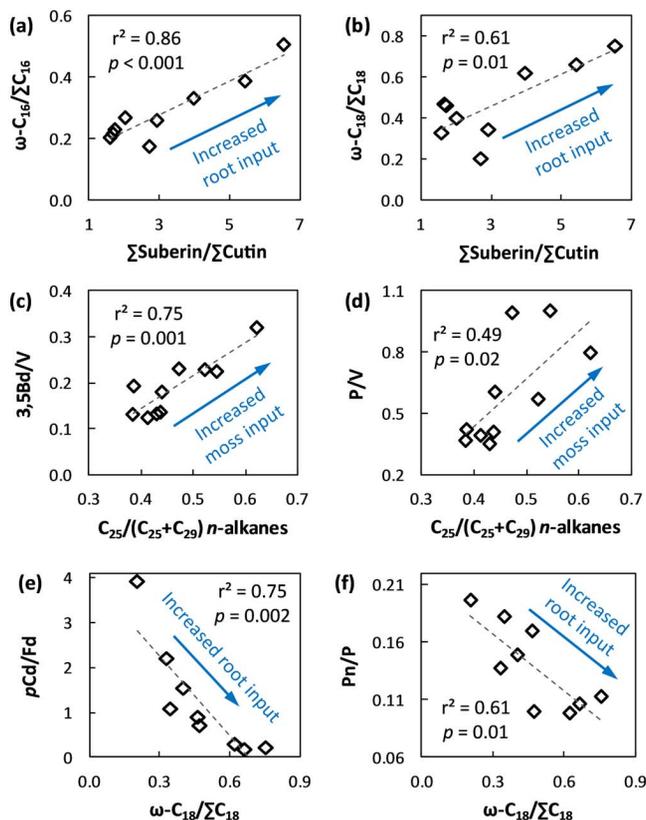
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**Figure 3.** Correlations between the abundances of various terrestrial biomarkers in the pan-Arctic sediments. Open diamonds and filled squares in (a) represent suberin ( $\Sigma$ Suberin) and cutin ( $\Sigma$ Cutin) biomarkers, respectively (contents defined in Table 3). HMW FAs: high-molecular-weight fatty acids ( $C_{20}$ – $C_{30}$ ). VSC: vanillyl, syringyl and cinnamyl lignin phenols.

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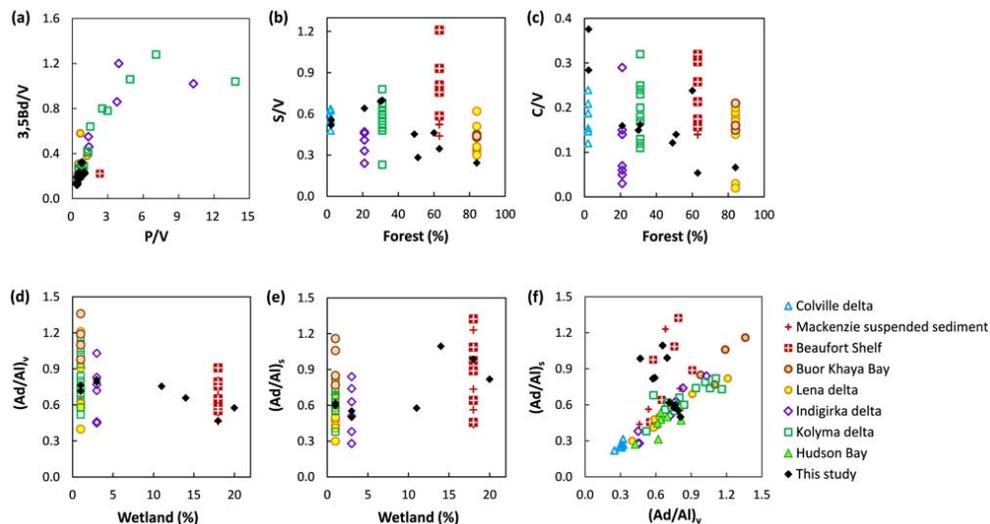


**Figure 4.** Correlations between the biomarker-based OC source parameters in the pan-Arctic sediments. Blue arrows indicate direction of change in the parameters with increased inputs of roots or mosses. See Table 3 for abbreviations and specific values.

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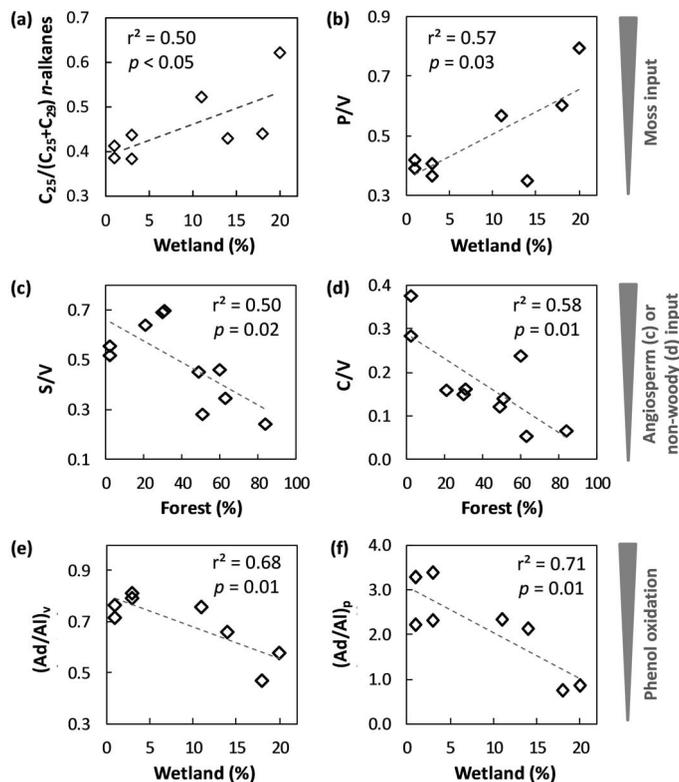
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**Figure 5.** Comparisons of the lignin parameters from this study (black diamond) vs. published data in the pan-Arctic sediments (colored symbols). Original data are found in Schreiner et al. (2013) for Colville delta sediments, Goñi et al. (2000, 2005) for Mackenzie river suspended sediments and Beaufort shelf sediments, Winterfeld et al. (2014) for Buor Khaya Bay sediments (receiving Lena River), Tesi et al. (2014) for Lena, Indigirka and Kolyma delta sediments and Kuzyk et al. (2008) for surface sediments of Hudson Bay.

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**Figure 6.** Influence of vegetation coverage on the OC source and degradation parameters in the arctic watersheds. (a and b) indicate more moss inputs at higher values. (c and d) indicate more angiosperm and non-woody inputs, respectively, at higher values. (e and f) indicate a more oxidized state of vanillyl and *p*-hydroxy phenols, respectively, at higher values. Refer to Table 3 for abbreviations and detailed values. Note that the Colville data are not included for the absence of information on its wetland coverage.

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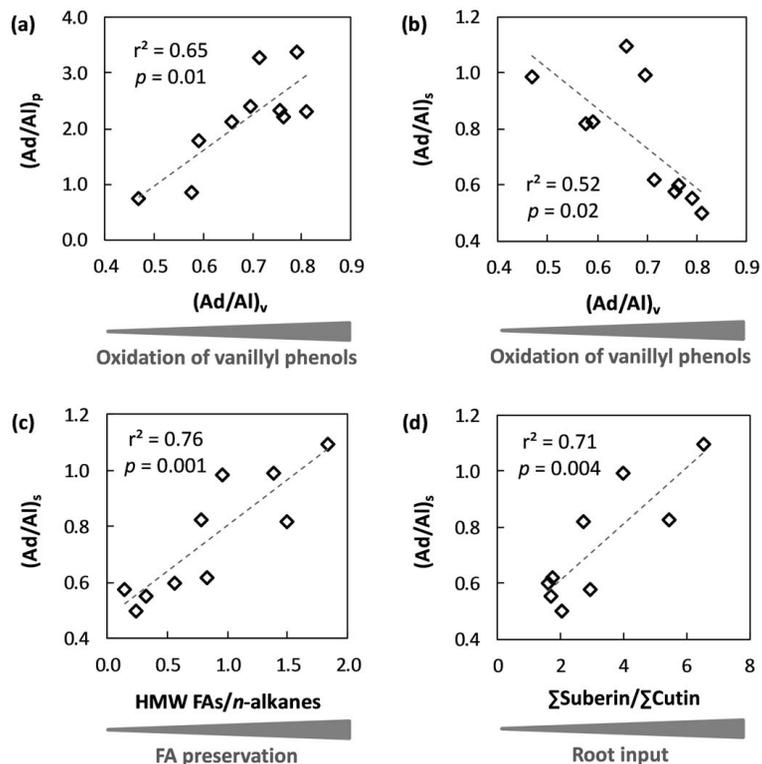
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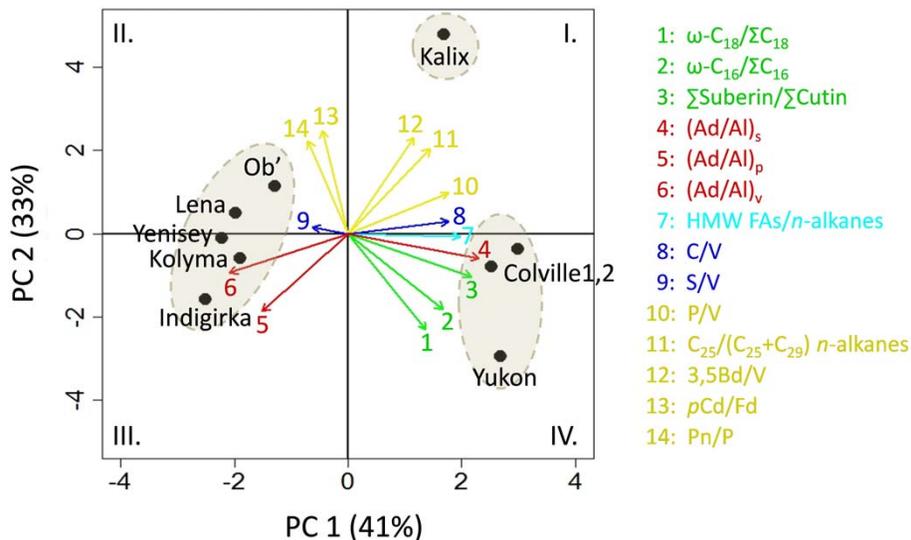
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**Figure 7.** Relationships between the acid-to-aldehyde (Ad / Al) ratios and other OC parameters. Ratios of  $(Ad/Al)_v$ , HMW FAs/*n*-alkanes and  $\Sigma$ Suberin /  $\Sigma$ Cutin increase with increasing oxidation of vanillyl phenols, FA preservation and root inputs, respectively. Refer to Table 3 for abbreviations and detailed values.

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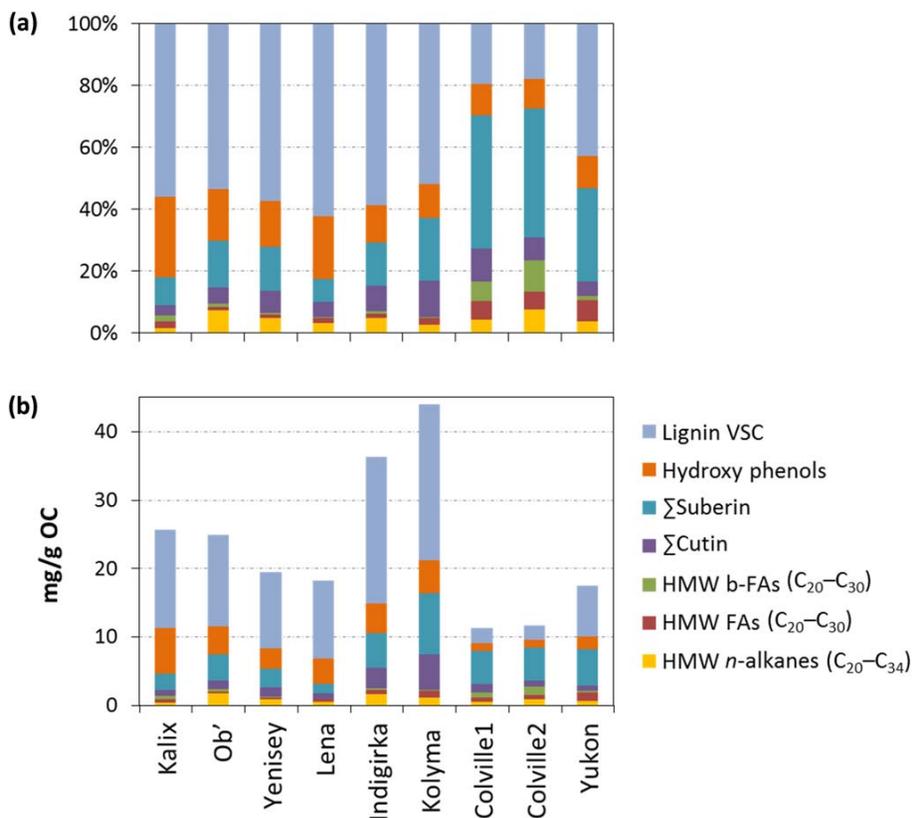
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**Figure 8.** Principle component analysis (PCA) of biomarker-based parameters in the pan-Arctic river sediments. The eight arctic rivers are grouped into three clusters as indicated by the shaded areas. Numbers represent biomarker-based source and degradation parameters as colored according to their classic indications. Refer to Table 3 for the abbreviations and detailed values of the used parameters.

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**Figure 9.** The relative proportion **(a)** and abundances **(b)** of various terrestrial biomarkers analyzed in the pan-Arctic sediments. VSC: vanilyl, syringyl and cinnamyl phenols; HMW: high-molecular-weight; b-FAs: bound fatty acids;  $\Sigma$ Suberin and  $\Sigma$ Cutin: suberin and cutin biomarkers as defined in Table 3.