Biogeosciences, 12, 4841–4860, 2015
www.biogeosciences.net/12/4841/2015/
doi:10.5194/bg-12-4841-2015

Biogeosciences
Open Access

Multi-molecular tracers of terrestrial carbon transfer across the pan-Arctic: comparison of hydrolyzable components with plant wax lipids and lignin phenols

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Received: 16 February 2015 – Published in Biogeosciences Discuss.: 23 March 2015
Accepted: 31 July 2015 – Published: 14 August 2015

Abstract. Hydrolyzable 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 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 a changing climate. Here, we examine the molecular composition and source of hydrolyzable compounds isolated from sedimentary particles derived from nine rivers across the pan-Arctic. Bound fatty acids (b-FAs), hydroxy FAs, n-alkane-α,ω-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 ω-hydroxy FAs, mid-chain substituted acids, DAs, and hydrolyzable 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 sedimentary particles 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, hydrolyzable 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 Arctic rivers. 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 Arctic river sediments.

1 Introduction

The drainage basins of the Arctic rivers are estimated to contain 1100–1500 Pg of carbon, representing more than half of the global soil organic carbon (OC) reservoir (Hugelius et al., 2014), and are warming two to 3 times faster than other regions on Earth (IPCC, 2013). Fluvial transport currently delivers 25–36 Tg OC in the dissolved form into the Arctic Ocean annually (Raymond et al., 2007; Holmes et al., 2012), representing 5–7 % of the net primary production of the Arctic tundra (0.5 Pg C yr^{-1}; Chapin III et al., 2012). Fluxes of particulate OC (POC) are comparable in some rivers (such as Mackenzie and Colville) but are overall much smaller in Arctic fluvial systems (Stein and Macdonald, 2004). 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., 2015). 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 is a protective coating on vascular plant leaves, fruits, and seeds and suberin on roots and 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 hydrolyzable components of terrestrial organic matter (OM). Cutin and suberin are considered to be more resistant to microbial decomposition 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 for a broader assessment of the fate of mobilized terrestrial OC in the Arctic, including a significant pool (hydrolyzable carbon) that has received minimal scrutiny until now.

Here we utilize sedimentary particles 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}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 threefold: (1) to investigate the molecular composition and source of hydrolyzable 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 cold and semiarid climates in the drainage basins and 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

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

	Kalix	Ob’	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 to 71.02° N; 152.60° E[1]	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
Water depth (m)	13	< 2	< 2	< 2	8–11	< 2	NA	NA	NA	25
Forest coverage (%)[2]	60	30	49	84	21	31	2	2	51	63
Wetland coverage (%)[2]	20	11	3	1	3	1	NA	NA	14	18
Permafrost coverage[3]	5/15	2/24	33/55	79/20	100/0	100/0	100/0	100/0	23/76	16/66
Basin area (10^6 km^2)[4]	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^3 yr^{-1})[5]	10	427	673	588	54	136	19	19	208	316
Runoff (mm yr^{-1})[5]	417	145	263	245	159	209	317	317	251	181
Sediment yield (t km^{-2} yr^{-1})[6]	NA	6	2	8	36	19	6	6	72	74
TOC/POC flux (t km^{-2} yr^{-1})[6]	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[7]	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^{13}C–TOC (‰)[7]	−27.1	−27.4	−26.5	−25.0	−26.6	−26.7	−26.4	−26.7	−26	−26

NA: not available. [1] Combined surface sediments along a transect; [2] data from Revenga et al. (1998) and Ingri et al. (2005); [3] given as percent continuous / percent (discontinuous+sporadic+isolated) (Gustafsson et al., 2011; Holmes et al., 2013); [4] data from Gordeev et al. (1996); Holmes et al. (2002); Rachold et al. (2004) and Ingri et al. (2005); [5] data from Milliman et al. (1995); Stein and Macdonald (2004); Ingri et al. (2005) and Holmes et al. (2013); [6] 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); [7] Mass ratio of OC to total nitrogen (OC / N) and δ^{13}C values from Drenzek et al. (2007) for Mackenzie, van Dongen et al. (2008a) for GRARs and Vonk et al. (2008) for Kalix.

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

sub-Arctic Scandinavia into the Baltic Sea, which are all characterized by wetter climates, milder winters, and 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; Ingri et al., 2005). All rivers have comparable drainage-area-normalized fluxes of total organic carbon (TOC) and POC (Table 1; Stein and Macdonald, 2004; Ingri et al., 2005). Indigirka and Kolyma have higher sediment yields (36 and 19 t km^{-2} yr^{-1}, respectively) than the other Eurasian rivers (Stein and Macdonald, 2004). 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 August–September of 2004 and 2005, and from the Kalix in June 2005 on research vessel KBV 005 of the Umeå Marine Research Center (UMF, Norrbyn, Sweden). These sediments were mainly delivered by the annual spring freshet of the rivers and by coastal erosion during the past ∼ 20 years based on the sedimentation rate of 0.11–0.16 cm yr^{-1} (van Dongen et al., 2008a, b; Vonk et al., 2012), so their composition should not be so sensitive to the exact month of collection.

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 North American Cordillera 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 using a Smith–McIntyre grab sampler (Yunker et al., 1990). Previous radiocarbon analysis of marine biomarkers from the site implies deposition from recent years (Drenzek et al., 2007).

The Yukon River drains northwestern Canada and central Alaska in the United States into the Bering Sea with the second highest sediment yield (72 t km^{-2} yr^{-1}) in Arctic rivers (Guo et al., 2012). Its drainage basin is characterized by diverse ecosystems including forests, shrublands, tundra, and extensive areas of permafrost (Brabets et al., 2000). A sample of freshly deposited fine-grained fluvial sediment was collected from the Yukon near Pilot Station, Alaska during ice breakup in June 2007. The Pilot Station is considered to be the lowest reach of the river where streamflow is not affected by the Bering Sea and the outflow point for the entire Yukon River basin. 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 samples were collected from fresh mud that was deposited on the surface of river ice prior to ice breakup close to (within 40 km of) the river mouth in June 2007. As the majority of sediment is delivered from Arctic rivers during the freshet, the Colville samples are most likely an accurate reflection of the fluvial suspended load of sedimentary particles during the freshet and represent terrestrial OM transported to the river mouth.

The contrasting sampling strategies and sample types recovered from the various river systems (estuarine sediments for GRARs and Kalix vs. shelf edge sediments for Mackenzie and fluvial deposits near the river mouths for Yukon and Colville) may lead to varied contribution and concentrations of terrestrial, marine and relict carbon in the bulk OC. However, for locations where we have compared characteristics of the fluvial suspended load, or where appropriate data is available (i.e., Mackenzie; Vonk et al., 2015; Hussain et al., unpublished data), strong compositional similarities exist between suspended sediments and sediment deposits (on riverbank or riverbed). Therefore, observations described herein should be valid for the basin-scale comparison of the fate of various terrestrial OC biomarkers and their environmental controls, and we focus on the transformation and relative ratio of terrestrial components in the sedimentary OC only. Potential compositional variations induced by sampling methods are discussed in detail in the results.

2.2 Bulk analyses

Bulk sediments were kept frozen at $-20\,^{\circ}\mathrm{C}$ after collection and freeze-dried prior to analysis. A small aliquot of the Yukon and Colville samples were ground and used for TOC, total nitrogen and bulk δ^{13}C analyses at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at the Woods Hole Oceanographic Institution. The TOC, total nitrogen and δ^{13}C values of other sediments were derived from Drenzek et al. (2007) for Mackenzie, van Dongen et al. (2008a) for GRARs and Vonk et al. (2008) for Kalix.

2.3 Biomarker extractions

Total lipid extracts (TLEs) were obtained from freeze-dried sediments ($\sim$ 70–160 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 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. While microwave-assisted extraction is reported to show higher lipid yields than Soxhlet extraction, lipid composition (especially for saturated FAs) is very similar in both TLEs (Szentmihályi et al., 2002; Qu et al., 2011). Hence, lipid composition is unlikely to be affected by the extraction methods used here.

Hydrolyzable 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_{19} FA and C_{18} n-alkane was added as internal standards. Similar to the TLE analysis, neutral and acid fractions were then recovered from the hydrolyzed 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-α,ω-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_2 for further analysis.

Lignin and hydroxy phenols were further released from the dried hydrolyzed 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_2-bubbled NaOH solution (2 M) were loaded into vessels containing sediments (3–10 g) with $\sim$ 50 mg of TOC. All vessels were vacuum-purged with N_2 four times and oxidized at 150 °C for 1.5 h. The oxidation products were spiked with an internal standard (ethyl vanillin), extracted with ethyl acetate after acidification to pH 2 and concentrated under N_2 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 spectrometer (MS; 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 $3\,^{\circ}\mathrm{C\,min^{-1}}$ and helium was used as carrier gas ($1\,\mathrm{mL\,min^{-1}}$). 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_{18} *n*-alkane for *n*-alkanes, C_{19} 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 Data analysis

Relationships between the abundances of various biomarkers, biomarker-based parameters, sediment yield, 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) model was built 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. All ratios were expressed as proportions (with the numerator parameters repeated in the denominator), an arcsine transformation (calculation of the square root followed by the arcsine) was used to return this proportional data set to a normal distribution, and then data were autoscaled before PCA (Mos et al., 2006).

3 Results and discussion

3.1 Sediment bulk properties

Bulk chemical properties of the sedimentary particles 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 middle Mackenzie 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 δ^{13}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 C_{20}–C_{34} with C_{27} *n*-alkane being the most abundant in all samples (Fig. 2a and Table S1). 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 (C_{20}–C_{34}) ranged from 0.49 to $0.87\,\mathrm{mg\,g^{-1}}$ 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 (CPI_{25-33} as defined in Fig. 2; 7.3 and 6.9, respectively), whereas Mackenzie exhibited a C_{27} and C_{29} *n*-alkane predominance with the lowest CPI_{25-33} value of 2.3, corroborating the influence of petrogenic OC (Drenzek et al., 2007).

Solvent-extractable FAs in the Yukon and Colville sediments were dominated by even-numbered FAs in the range of C_{16}–C_{30} with C_{24} FA being the most abundant (Fig. 2b and Table S1). The concentration of higher-plant-derived HMW FAs (C_{20}–C_{30}) ranged from 0.67 to $0.68\,\mathrm{mg\,g^{-1}}$ OC in Colville and was much higher in Yukon ($1.19\,\mathrm{mg\,g^{-1}}$ OC) than in other sediments (Table S1). The CPI_{20-30} 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_{20}, especially C_{16}) FAs as compared with the others. As the Mackenzie sample was collected from the mid-shelf area, it is expected to receive higher contribution of algal or bacterial OC and hence LMW FAs (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 Hydrolyzable compounds

The acid fraction of the alkaline hydrolysis products yielded four major classes of compounds: b-FAs, hydroxy FAs (including α-, β-, ω-hydroxy FAs, and mid-chain substituted

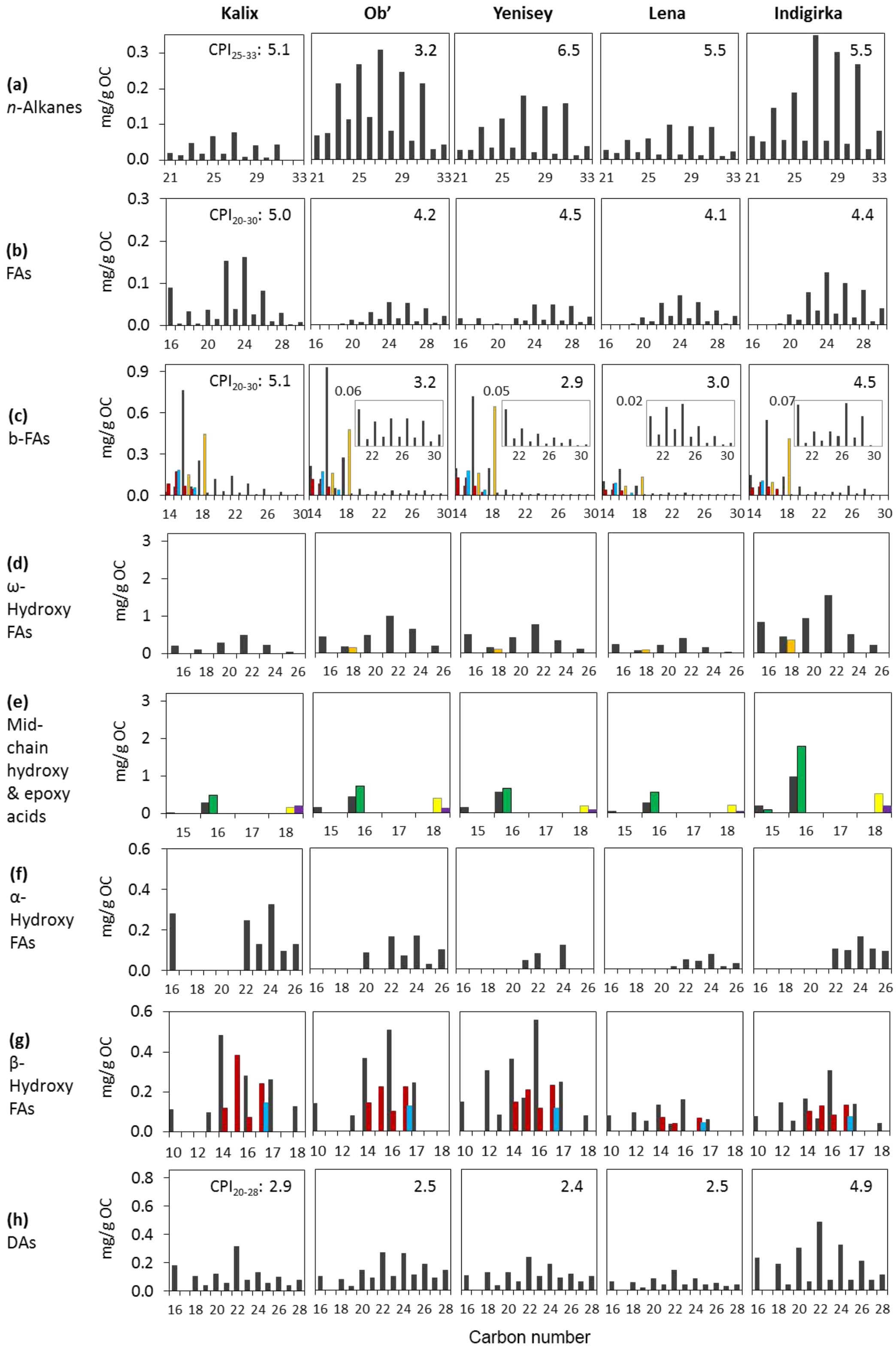
Kalix
Ob'
Yenisey
Lena
Indigirka
(a)
n-Alkanes
mg/g OC
0.0
0.1
0.2
0.3
CPI25-33: 5.1
3.2
6.5
5.5
5.5
21 25 29 33
(b)
FAs
CPI20-30: 5.0
4.2
4.5
4.1
4.4
16 20 24 28
(c)
b-FAs
0.0
0.3
0.6
0.9
CPI20-30: 5.1
3.2
2.9
3.0
4.5
0.06
0.05
0.02
0.07
22 26 30
14 18 22 26 30
(d)
ω-Hydroxy FAs
0 1 2 3
16 18 20 22 24 26
(e)
Mid-chain hydroxy & epoxy acids
15 16 17 18
(f)
α-Hydroxy FAs
0.0 0.2 0.4 0.6
16 18 20 22 24 26
(g)
β-Hydroxy FAs
10 12 14 16 17 18
(h)
DAs
0.0 0.2 0.4 0.6 0.8
CPI20-28: 2.9
2.5
2.4
2.5
4.9
16 18 20 22 24 26 28
Carbon number

Figure 2.

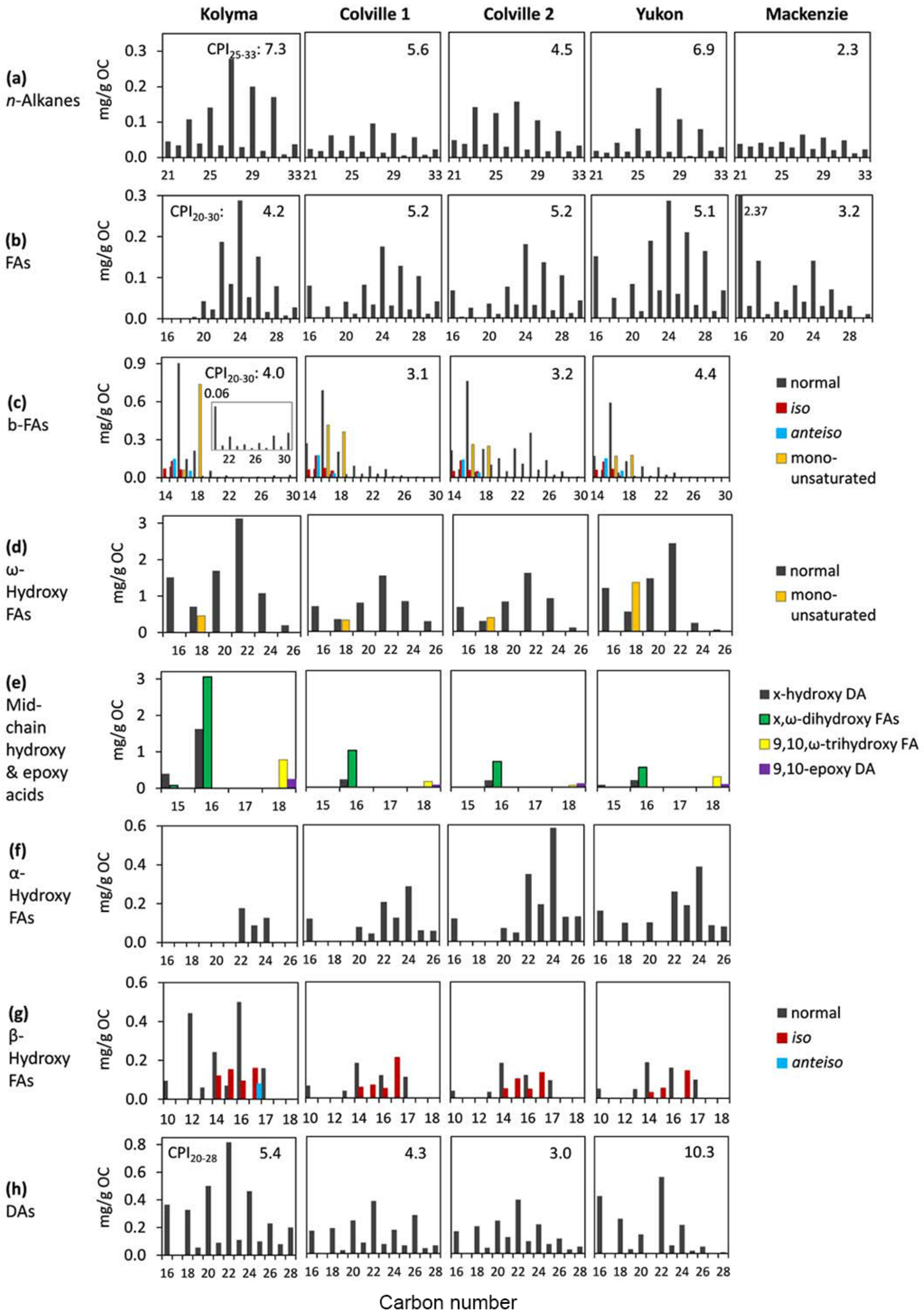

Figure 2. Abundances of solvent-extractable and hydrolyzable lipids in the pan-Arctic sedimentary particles, including n-alkanes **(a)**, fatty acids (FAs; **b**), bound fatty acids (b-FAs; **c**), ω-hydroxy FAs **(d)**, mid-chain hydroxy and epoxy acids **(e)**, α-hydroxy FAs **(f)**, β-hydroxy FAs **(g)**, and diacids (DAs; **h**). Carbon preference index (CPI) is defined as $\mathrm{CPI}_{25-33} = (\sum \mathrm{C}_{25,27,29,31,33} / \sum \mathrm{C}_{24,26,28,30,32} + \sum \mathrm{C}_{25,27,29,31,33} / \sum \mathrm{C}_{26,28,30,32,34})/2$ for n-alkanes, $\mathrm{CPI}_{20-30} = (\sum \mathrm{C}_{20,22,24,26,28,30} / \sum \mathrm{C}_{19,21,23,25,27,29} + \sum \mathrm{C}_{20,22,24,26,28,30} / \sum \mathrm{C}_{21,23,25,27,29,31})/2$ for FAs and b-FAs, $\mathrm{CPI}_{20-28} = (\sum \mathrm{C}_{20,22,24,26,28} / \sum \mathrm{C}_{19,21,23,25,27} + \sum \mathrm{C}_{20,22,24,26,28} / \sum \mathrm{C}_{21,23,25,27,29})/2$ for DAs. Data of solvent-extractable n-alkanes and FAs are derived from van Dongen et al. (2008a) for GRARs, Vonk et al. (2008) for Kalix, and Drenzek et al. (2007) for Mackenzie.

acids), DAs, and hydrolyzable phenols (Table S1). Small amounts of steroids and terpenoids were also found, but are not included in this study.

b-FAs

As compared with solvent-extractable FAs, b-FAs were dominated by LMW (C_{14}–C_{19}) homologues (with maxima at C_{16}) with significant contributions from *iso-*/*anteiso*-branched and monounsaturated counterparts (Fig. 2c). The concentration of HMW b-FAs (C_{20}–C_{30}) ranged from 0.08 mg g^{-1} OC in Lena to 1.17 mg g^{-1} 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_{20-30} values to FAs for Kalix, Indigirka and Kolyma and lower values for the rest of the rivers. In contrast to FAs, the most abundant HMW b-FA varied, being C_{20} b-FA in Ob', Yenisey, Kolyma and Colville 1, C_{24} b-FA in Lena and Colville 2, C_{22} b-FA in Kalix and C_{26} in Indigirka. The marked difference in the molecular composition of these two types of lipids suggests varied sources in the sediments. While solvent-extractable FAs were mainly derived from higher-plant waxes, b-FAs received much more input from bacterial and/or algal sources as indicated by the dominance of LMW homologues, the presence of branched and monounsaturated FAs, and slightly lower CPI_{20-30} values. Such source variations have also been found for the solvent-extractable and hydrolyzable lipids in other marine sediments (Zegouagh et al., 1996; Garcette-Lepecq et al., 2004).

Hydroxy FAs

Hydroxy FAs were the most abundant hydrolyzable compounds in the Arctic sediment samples examined. Among them, exclusively even-numbered ω-hydroxy FAs in the range of C_{16}–C_{26} were the dominant component (Fig. 2d), ranging from 1.16 mg g^{-1} OC in Lena to 8.78 mg g^{-1} OC in Kolyma, representing 14 % (in Kalix) to 50 % (in Yukon) of the total hydrolyzable lipids. The composition of ω-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 ($> C_{20}$) 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_{15}–C_{18} were also found in the sediments at slightly lower concentrations than ω-hydroxy FAs in Kalix and GRARs and in much lower abundances than ω-hydroxy FAs in Yukon and Colville (Fig. 2e). Among them, C_{15}, C_{16} mid-chain hydroxy DAs and C_{15}, C_{16} x, ω-dihydroxy FAs are considered to derive solely from cutin, whereas 9,10-epoxy C_{18} DA originates from suberin (Otto and Simpson, 2006a). By comparison, α-hydroxy acids in the range of C_{15}–C_{26} occurred in much lower abundances (0.22–1.61 mg g^{-1} OC; Fig. 2f). α-hydroxy acids have been found in the hydrolysis products of leaf waxes and wood, and in 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, β-hydroxy FAs were observed in the range of C_{10}–C_{20}, with branched homologues at C_{14}–C_{17} and maxima at C_{14}, C_{16} or i-C_{17} (Fig. 2g). These compounds showed similar concentrations to LMW b-FAs in Kalix and GRARs (0.82–2.75 mg g^{-1} OC) and lower abundances in Yukon and Colville sediments (0.77–0.89 mg g^{-1} OC). Similar compounds have been reported in the hydrolysis products of sediments from a freshwater lake (Goossens et al., 1989) and the Danube Delta (Garcette-Lepecq et al., 2004) and are considered to derive mainly from bound moieties in bacterial cell walls (Goossens et al., 1986). As the Yukon and Colville sediments were collected within the river (as riverbank sediment and ice deposits, respectively), they are expected to be mainly terrestrially sourced and contain less bacterial and/or algal OC as compared with the estuarine sediments of GRARs and Kalix.

DAs

DAs in the range of C_{16}–C_{28} represented 12–15 % of total hydrolyzable lipids in Arctic sediments, showing an even-over-odd predominance and maxima at C_{22} in all samples (Fig. 2h). DAs in sediments have several potential sources. First, medium- and long-chain (C_{16}–C_{28}) DAs predominating at C_{26} and C_{28} are found in seagrasses (Nichols et al., 1982). This molecular distribution is different from the DAs in our samples. Furthermore, it is well documented that phytobenthic species are either absent or only occur in low abundance in Arctic zones (Romankevich, 1984), and hence inputs from seagrasses are unlikely. DAs have also been suggested as oxidation products of FAs and/or ω-hydroxy FAs (Johns and Onder, 1975; van Bergen et al., 1998), where their distribution should parallel that of their precursors. This possibility can be ruled out as well because the molecular composition of DAs (C_{16}–C_{28} with maxima at C_{22}) does not match that of solvent-extractable FAs (with maxima at C_{24}), b-FAs (C_{14}–C_{30} with maxima at C_{20}, C_{22}, C_{24} or C_{26}), or ω-hydroxy FAs (only even-numbered in the range of C_{16}–C_{26}) from the same sediment. Hence, DAs in these Arctic sediments most likely originate from cutin and/or suberin of higher plants (Goñi and Hedges, 1990; Otto and Simpson, 2006a; Feng et al., 2010). Similar to ω-hydroxy FAs, the HMW ($> C_{20}$) DAs are considered to be specific to suberin in particular.

Hydrolyzable phenols

Other than lipids, alkaline hydrolysis released minor amounts of phenol moieties (Table S1). These phenols, ranging from 0.18 to 1.45 mg g^{-1} OC in total, amounted to < 6 % of lignin phenols released by CuO oxidation (see the section below) from the Kalix, GRAR and Yukon sediments and 9–13 % of lignin phenols from Colville. As hydrolyzable phenols are ester-bound in the sediments, they are considered to derive from the suberin macromolecule instead of "true" lignin, which is dominated by ether linkages (cf. Otto and Simpson, 2006a; 2007). Moreover, the concentration of hydrolyzable phenols was most significantly correlated with suberin biomarkers ($\sum$Suberin as defined in Section 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 mg g^{-1} OC) than in the North American ones (2.08–7.51 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 the East Siberian Shelf (receiving riverine inputs from Lena, Indigirka, and Kolyma; 0.3–38.2 mg g^{-1} OC; Tesi et al., 2014), in the sediment cores of Hudson Bay (0.4–14.6 mg g^{-1} OC; Kuzyk et al., 2008) and in the surface and suspended sediments from the Buor-Khaya Bay and Lena River (9.4–51.6 mg g^{-1} OC; Winterfeld et al., 2015) as well as from Beaufort Shelf and Mackenzie River (3.01–12.22 mg g^{-1} OC; Goñi et al., 2000, 2005). The Colville River sediments in this study had slightly less VSC (2.08–2.11 mg g^{-1} OC) as compared with Colville Delta surface sediments (4.1–14.6 mg g^{-1} OC; Schreiner et al., 2013). This difference may be attributed to OC source variations between the river and delta regions. Although mostly terrestrially sourced, the ice deposits near Colville River mouth may contain a higher proportion of easily degradable plant OC (such as carbohydrates) which dilutes lignin in the bulk OC.

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 (in the range of 2.90–6.72 and 0.96–2.70 mg g^{-1} OC, respectively) than in the North American rivers (1.13–1.87 and 0.26–0.70 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., 2015). Unlike VSC units, 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 environments (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., 2015).

3.3.1 Suberin and cutin inputs

Suberin- and cutin-specific biomarkers in the hydrolyzable products were summarized and calculated based on parameters developed by Otto and Simpson (2006a). Suberin biomarkers ($\sum\text{Suberin} = C_{20}$–$C_{26}$ ω-hydroxy FAs + C_{20}–C_{28} DAs + 9, 10-epoxy C_{18} DA) ranged from 1.39 to 8.93 mg g^{-1} OC while cutin biomarkers ($\sum\text{Cutin} = C_{15}$, C_{16} mid-chain hydroxy DAs + C_{15}, C_{16} x, ω-dihydroxy FAs) ranged from 0.81 to 5.16 mg g^{-1} OC in the pan-Arctic sediments (Table 3). $\sum$Cutin showed much higher concentrations in the Kolyma and Indigirka sediments, while $\sum$Suberin had the highest and lowest abundance in the Kolyma and Lena sediments, respectively. Comparison with other terrestrial biomarkers revealed that $\sum$Suberin was positively correlated with HMW FAs across the pan-Arctic transect ($p = 0.04$) whereas $\sum$Cutin was not (Fig. 3a). Conversely, lignin VSC was correlated with $\sum$Cutin (Fig. 3b; $p = 0.02$), but not with $\sum$Suberin or HMW FAs. Lignin, enriched in aromatic moieties, has distinct chemical structure, sorptive potentials and decomposition dynamics as compared with aliphatic structures such as suberin, cutin and FAs (Feng et al., 2005; Feng and Simpson, 2008). Hence, the observed correlations are not caused by similar preservation potentials or the chemical behavior of individual components. Instead, these suggest 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.,

Table 2. Abundances of lignin and hydroxy phenols in the pan-Arctic sediments (mg g^{-1} OC).

	Kalix	Ob'	Yenisey	Lena	Indigirka	Kolyma	Colville1	Colville2	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
p-hydroxybenzaldehyde	2.92	1.02	0.75	0.99	0.90	0.93	0.30	0.37	0.53	0.95
p-hydroxyacetophenone	1.32	0.75	0.43	0.50	0.44	0.81	0.11	0.12	0.21	0.22
p-hydroxybenzoic acid	2.49	2.36	1.72	2.18	3.03	3.06	0.72	0.66	1.12	0.70
p-hydroxy phenols (P)	6.72	4.13	2.90	3.67	4.36	4.80	1.13	1.15	1.85	1.87
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
Vanillyl phenols (V)	8.45	7.26	7.09	8.72	11.88	12.24	1.14	1.15	5.28	3.09
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
Syringyl phenols (S)	3.89	5.02	3.21	2.12	7.60	8.55	0.64	0.60	1.49	1.07
p-Coumaric acid (*p*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
Cinnamyl phenols (C)	2.01	1.09	0.86	0.58	1.89	1.98	0.43	0.33	0.74	0.17
Lignin phenols (VSC)	14.35	13.36	11.15	11.41	21.37	22.78	2.21	2.08	7.51	4.32

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

Indication	Proxy	Kalix	Ob'	Yenisey	Lena	Indigirka	Kolyma	Colville1	Colville2	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
	$\omega-C_{16}/\Sigma C_{16}$	0.18	0.26	0.27	0.21	0.22	0.23	0.33	0.39	0.51	NA
	$\omega-C_{18}/\Sigma C_{18}$	0.20	0.35	0.40	0.33	0.47	0.46	0.62	0.66	0.75	NA
Moss and peat input	$C_{25}/(C_{25}+C_{29})$ *n*-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
	*p*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	$(Ad/Al)_V$	0.58	0.76	0.81	0.76	0.79	0.71	0.70	0.59	0.66	0.47
	$(Ad/Al)_S$	0.82	0.58	0.50	0.60	0.55	0.62	0.99	0.83	1.10	0.99
	$(Ad/Al)_p$	0.85	2.33	2.31	2.21	3.38	3.28	2.40	1.78	2.12	0.74
FA preservation	HMW FAs / *n*-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_{20}–$C_{26}$$\omega$-hydroxy fatty acids (FAs) + C_{20}–C_{28} diacids (DAs) + 9,10-epoxy C_{18} DA; $\sum$Cutin = C_{15}, C_{16} mid-chain hydroxy DAs + C_{15}, C_{16} x,ω-dihydroxy FAs; ω-C_{16} / $\sum C_{16}$ or ω-C_{18} / $\sum C_{18}$ = ratio of C_{16} or C_{18} ω-hydroxy FA to the summation of C_{16} or $C_{18}$$\omega$-hydroxy FAs, DAs, and mid-chain hydroxy and epoxy acids; 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_{20}–C_{30}) to HMW *n*-alkanes (C_{20}–C_{34}); NA: not available.

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 ~ 1.6–1.7 in eastern GRARs to ~ 6.5 in Yukon (Table 3) and was positively correlated with both ratios of ω-C_{16} / $\sum C_{16}$ and ω-C_{18} / $\sum C_{18}$ (ratio of C_{16} or C_{18} ω-hydroxy FA to the summation of C_{16} or $C_{18}$$\omega$-hydroxy FAs, DAs, and mid-chain hydroxy and epoxy acids; Fig. 4a and b; $p < 0.001$ and 0.01, respectively). Ratios of ω-C_{16} / $\sum C_{16}$ and ω-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

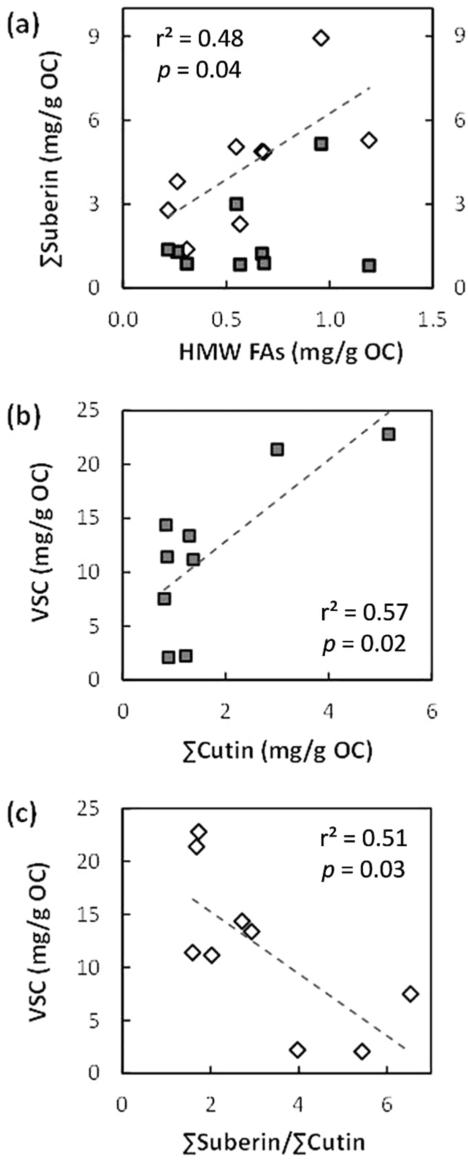

Figure 3. Correlations between the abundances of various terrestrial biomarkers in the pan-Arctic sediments. Open diamonds and filled squares in **(a)** represent suberin (∑Suberin) and cutin (∑Cutin) biomarkers, respectively (contents defined in Table 3). HMW FAs: high-molecular-weight fatty acids (C_{20}-C_{30}).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

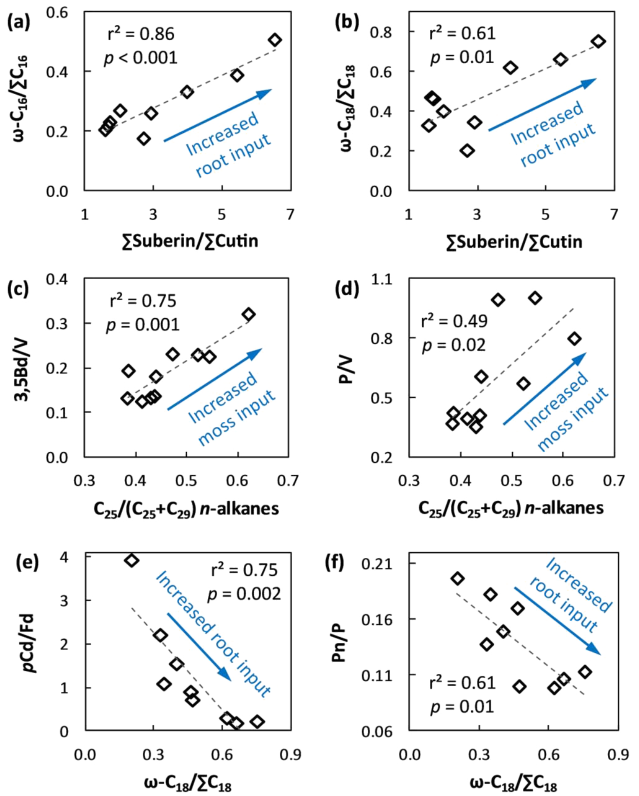

Figure 4. Correlations between the biomarker-based OC source parameters in the pan-Arctic sediments. Blue arrows indicate direction of change in the parameters with increased inputs of roots or mosses. See Table 3 for abbreviations and specific values.

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 range of sedimentary samples stemming from these Arctic rivers (Fig. 5a). In particular, both ratios of $\mathrm{C}_{25}/(\mathrm{C}_{25}+\mathrm{C}_{29})$ *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 (*p*Cd / 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 and peat indicators or with the wetland coverage, undermining their utility as source proxies for mosses and peat in the study area. Instead, both *p*Cd / Fd and Pn / P ratios decreased with increasing ratios of ω-$\mathrm{C}_{18}/\sum\mathrm{C}_{18}$ (Fig. 4e and f; $p = 0.002$ and 0.01, respectively). As discussed previously, the ω-$\mathrm{C}_{18}/\sum\mathrm{C}_{18}$ ratio may indicate the relative input of root OC, whereas elevated *p*Cd / 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 in the order of Kalix < GRARs < Yukon and Colville. The Pn / P ratio may be affected by such variations as well.

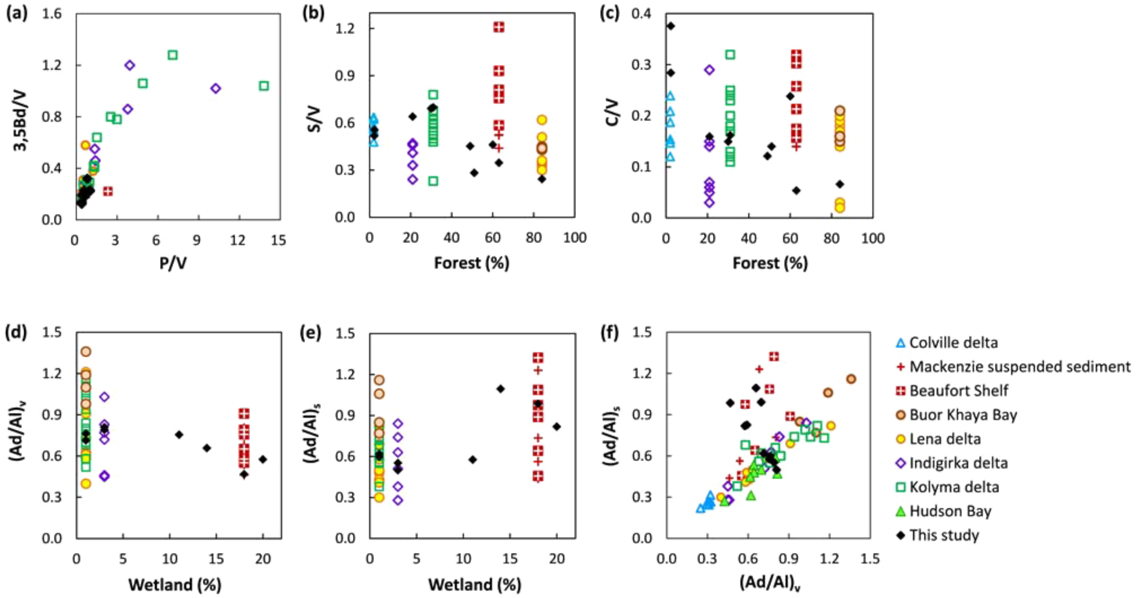

Figure 5. Comparisons of the lignin parameters from this study (black diamond) vs. published data in the pan-Arctic sediments (colored symbols). Original data are found in Schreiner et al. (2013) for Colville Delta sediments, Goñi et al. (2000, 2005) for Mackenzie River suspended sediments and Beaufort Shelf sediments, Winterfeld et al. (2015) 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.

3.3.3 Lignin source and degradation stage

Lignin source indicator S / V and C / V ratios ranged from 0.24 to 0.70 and from 0.05 to 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., 2015) 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 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 ($(\mathrm{Ad/Al})_\mathrm{v}$ and $(\mathrm{Ad/Al})_\mathrm{s}$, 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 ($(\mathrm{Ad/Al})_p$; Dittmar and Lara, 2001). These ratios are however also subject to variations induced by OC source alterations and dissolution processes (Benner et al., 1990; Hernes et al., 2007). 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., 2015) 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 breakup.

The $(\mathrm{Ad/Al})_\mathrm{v}$ and $(\mathrm{Ad/Al})_p$ ratios were positively correlated (Fig. 7a; $p = 0.01$) and showed higher values in the

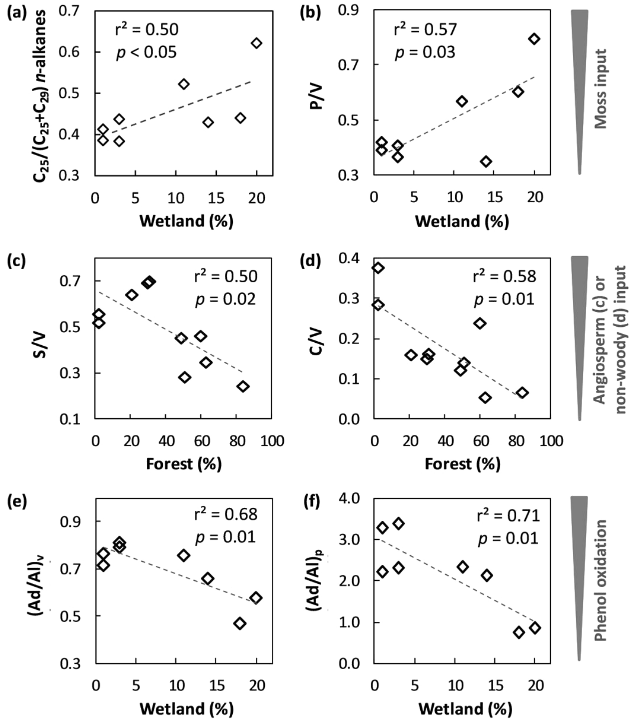

Figure 6. Influence of vegetation coverage on the OC source and degradation parameters in the Arctic watersheds. Panels **(a)** and **(b)** indicate more moss inputs at higher values. Panels **(c)** and **(d)** indicate more angiosperm and non-woody inputs, respectively, at higher values. Panels **(e)** 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.

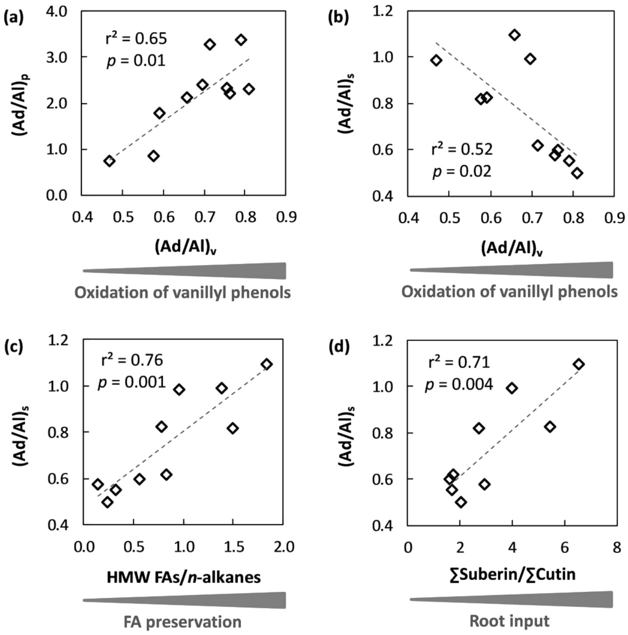

Figure 7. Relationships between the acid-to-aldehyde (Ad / Al) ratios and other OC parameters. Ratios of $(\text{Ad}/\text{Al})_\text{V}$, HMW FAs / *n*-alkanes and ∑Suberin / ∑Cutin increase with increasing oxidation of vanillyl phenols, FA preservation and root inputs, respectively. Refer to Table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

GRARs and Yukon relative to Kalix, Colville and 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 outweigh lignin oxidation.

In general, the $(\text{Ad}/\text{Al})_\text{s}$ ratio increases with increasing $(\text{Ad}/\text{Al})_\text{v}$ ratio for Arctic sedimentary samples (Fig. 5f) as diagenetic parameters in general. Within our data set, however, the $(\text{Ad}/\text{Al})_\text{s}$ ratio was negatively correlated with the $(\text{Ad}/\text{Al})_\text{v}$ 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 data set (Fig. 5f). Furthermore, the $(\text{Ad}/\text{Al})_\text{s}$ 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 $(\text{Ad}/\text{Al})_\text{s}$ ratio may be complicated by factors other than side-chain oxidation alone in Arctic drainage basins. As the $(\text{Ad}/\text{Al})_\text{s}$ ratio also increased with an increasing ∑Suberin / ∑Cutin ratio (Fig. 7d; $p = 0.004$), we postulate that the acid-to-aldehyde ratio of syringyl phenols may be strongly influenced by the relative inputs of root and bark vs. leaf tissues. The $(\text{Ad}/\text{Al})_\text{s}$ ratio hence may more strongly reflect lignin source than its oxidation state in our sample set. This effect is not obvious for the $(\text{Ad}/\text{Al})_\text{v}$ ratio likely because, unlike syringyl phenols that are specific to angiosperms, vanillyl phenols are universal in vascular plants and the Ad / Al variations as recorded by syringyl phenols in the root and/or bark vs. leaf of angiosperm may be obscured by inputs from gymnosperm tissues.

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 built based on the abundance of various groups of biomarkers (Table S1) and the biomarker-derived parameters (Table 3, with all ratios expressed as proportions), respectively. The PCA model is built on the relative ratio of (mainly) terrestrially derived biomarkers, and is not influenced by the varied inputs of marine and relict OC in different sedimentary samples. It also provides a better explanation of the variance (74.1 % for the first and second principal component (PC) combined; Fig. 8) among the nine rivers investigated (with Mackenzie excluded due to the absence of data on the hydrolyzable compounds). In agreement with the previous discussion, the $(\mathrm{Ad}/\mathrm{Al})_{\mathrm{s}}$ ratio clustered with all the root-input indicators ($\sum$Suberin / $\sum$Cutin, ω-C_{16} / $\sum C_{16}$ and ω-C_{18} / $\sum C_{18}$) in the lower right quadrant on the opposite side of the PC1 axis from the other phenol-oxidation parameters ($(\mathrm{Ad}/\mathrm{Al})_{\mathrm{v}}$ and $(\mathrm{Ad}/\mathrm{Al})_{p}$). 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) were plotted on the positive side of the PC2 axis, the pCd / Fd and Pn / P ratios were on the opposite side of the PC1 axis from the others. Root-input indicators were the largest contributors to PC1 while moss-input indicators contributed the most to PC2. 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 PC1 due to higher root inputs to their sediments, while Kalix River was separated from all the others by PC2 due to a much higher moss input. The latter observation is in accordance with the high coverage of wetland and, to a lesser degree, non-permafrost soils in the Kalix basin in comparison to other Arctic watersheds.

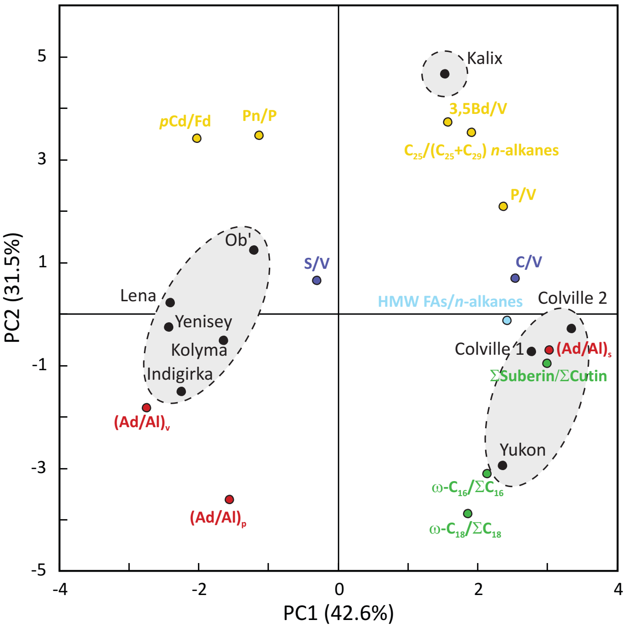

Figure 8. Principal component analysis (PCA) of biomarker-based parameters in the pan-Arctic river sediments. The PCA results are expressed as a biplot, where the distance and direction from the axis center has the same meaning for river samples and biomarker variables. The eight Arctic river samples (solid black circles) are grouped into three clusters as indicated by the shaded areas. Names and circles for variables (the biomarker-based source and degradation parameters) are colored according to their classic indications. Refer to Table 3 for abbreviations for the parameters.

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 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. As the Yukon and Colville samples were collected near the river mouth as riverbank and ice deposits, respectively, they had undergone a shorter transport journey and were subject to less hydrodynamic sorting relative to the estuarine sediments of the GRARs and Kalix, and the shelf edge sediment of Mackenzie. Although we did not conduct grain size analysis on these pan-Arctic sediments, the Yukon and Colville samples were possibly enriched with fine-grained materials derived from mineral soils in comparison with the coarser materials accumulated near river mouths and along shelves (Hedges and Mann, 1979; Keil et al., 1998). Such processes may contribute to the enrichment of belowground OC associated with fine-grained materials in the North American samples. Alternatively, the watersheds of Yukon and Colville have a higher coverage of tundra (Brabets et al., 2000; Walker et al., 2002). As tundra has the highest root-to-shoot ratio of all terrestrial biomes (Jackson et al., 1996), its wide distribution in the watershed is likely to increase the input of belowground OC to riverine export.

In terms of absolute abundances, Kalix had the highest concentration of higher-plant-derived biomarkers per gram of sediment (1.15 mg g^{-1} sediment) among the eight Arctic and sub-Arctic rivers (with Mackenzie excluded), followed by Kolyma and Indigirka (0.75 and 0.54 mg g^{-1} sediment respectively). This pattern largely tracks the TOC content of these sediments (Table 1), which exerts a strong control

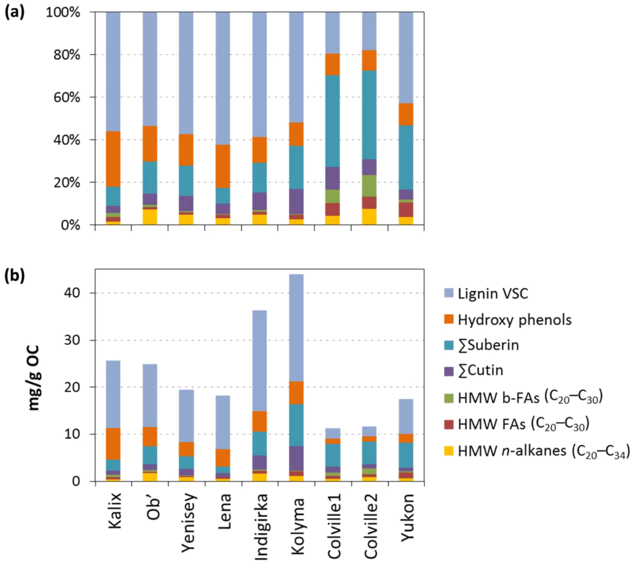

Figure 9. The relative proportion **(a)** and abundances **(b)** of various terrestrial biomarkers analyzed in the pan-Arctic sediments. VSC: vanillyl, syringyl and cinnamyl phenols; HMW: high-molecular-weight; b-FAs: bound fatty acids; $\sum$Suberin and $\sum$Cutin: suberin and cutin biomarkers as defined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

over the abundance of 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 β-sitosterol) were in much higher concentrations in these two rivers relative to the other 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 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 $\sum$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 (Feng et al., 2013). This was however not true for the sediments from Colville River, whose watershed is fully covered by continuous permafrost as well. Again, collected as ice deposits near the river mouth, the Colville sample may have integrated more belowground OC from local mineral soils. Alternatively, the difference may be explained by the high coverage of tundra in the Colville watershed.

Regardless of the geographic variations, hydrolyzable 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. As discussed previously, this is probably related to the high tundra coverage in its watershed (Walker et al., 2002) among other influences. 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

Hydrolyzable 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 monounsaturated FAs. In contrast, ω-hydroxy FAs, mid-chain substituted acids, DAs, and hydrolyzable 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 $\omega\text{-}C_{16}/\sum C_{16}$ and $\omega\text{-}C_{18} / \sum C_{18}$ 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 $C_{25} / (C_{25}+C_{29})$ *n*-alkanes and P / V increased with increasing wetland coverage in the drainage basin, corroborating their role as moss indicators. The Ad / Al 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 $(\text{Ad} / \text{Al})_s$ ratio instead was sensitive to relative inputs of root/bark vs. leaf tissues and hence described the 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, hydrolyzable 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, hydrolyzable 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 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 a molecular informant of biomass source and transport pathways.

The Supplement related to this article is available online at doi:10.5194/bg-12-4841-2015-supplement.

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.

Acknowledgements. Michael Schmidt and Michael Hilf are acknowledged for providing access to the GC/MS for biomarker analysis. We thank all colleagues from the International Siberian Shelf Study (ISSS) program for support including sampling. We also thank Jim McClelland for collecting the Colville sample, Rob Spencer for collecting the Yukon sample, and Greg Fiske for producing the map in Fig. 1. X. Feng acknowledges support from the Chinese National Key Development Program for Basic Research (2014CB954003, 2015CB954201). The ISSS program is supported by the Knut and Alice Wallenberg Foundation, headquarters of the Russian Academy of Sciences, the Swedish Research Council, the US National Oceanic and Atmospheric Administration, the Russian Foundation of Basic Research (#13-05-12028, 13-05-12041), the Swedish Polar Research Secretariat and the Nordic Council of Ministers (Arctic Co-Op and TRI-DEFROST programs). Collection of the Mackenzie sediment samples was supported by Fisheries and Oceans Canada and Indian and Northern Affairs Canada as part of the NOGAP B.6 project. Ö. Gustafsson acknowledges an Academy Research Fellow grant from the Swedish Royal Academy of Sciences. I. P. Semiletov and O. V. Dudarev thank the Government of the Russian Federation (#2013-220-04-157) for support as well as A. I. Khanchuk personally. T. I. Eglinton acknowledges support from Swiss National Science foundation (SNF) grant no. 200021_140850, and grants OCE-9907129, OCE-0137005, and OCE-0526268 from the US National Science Foundation (NSF), the Stanley Watson Chair for Excellence in Oceanography, and ETH Zurich. J. E. Vonk is thankful for support from NWO Rubicon (#825.10.022) and Veni (#863.12.004). B. E. van Dongen is thankful for support from the UK NERC (NE/I024798/1). R. M. Holmes acknowledges support from NSF 0436118, NSF 0732555, and NSF 1107774. X. Feng thanks WHOI for a postdoctoral scholar fellowship and for postdoctoral support from ETH Zurich. The National Thousand Young Talents recruiting plan of China and Institute of Botany are acknowledged for start-up support to X. Feng.

Edited by: N. Ohkouchi

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