RESEARCH ARTICLE

Key Points:
- Molecular ^{14}C content of multiple terrestrial markers is compared in pan-arctic sediments
- Suberin- and cutin-derived diacids trace old and young terrestrial carbon separately
- New light is shed on terrestrial carbon sources and mobilization pathways in arctic basins

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Multimolecular tracers of terrestrial carbon transfer across the pan-Arctic: [14]C characteristics of sedimentary carbon components and their environmental controls

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Abstract Distinguishing the sources, ages, and fate of various terrestrial organic carbon (OC) pools mobilized from heterogeneous Arctic landscapes is key to assessing climatic impacts on the fluvial release of carbon from permafrost. Through molecular ^{14}C measurements, including novel analyses of suberin- and/or cutin-derived diacids (DAs) and hydroxy fatty acids (FAs), we compared the radiocarbon characteristics of a comprehensive suite of terrestrial markers (including plant wax lipids, cutin, suberin, lignin, and hydroxy phenols) in the sedimentary particles from nine major arctic and subarctic rivers in order to establish a benchmark assessment of the mobilization patterns of terrestrial OC pools across the pan-Arctic. Terrestrial lipids, including suberin-derived longer-chain DAs ($C_{24,26,28}$), plant wax FAs ($C_{24,26,28}$), and n-alkanes ($C_{27,29,31}$), incorporated significant inputs of aged carbon, presumably from deeper soil horizons. Mobilization and translocation of these "old" terrestrial carbon components was dependent on nonlinear processes associated with permafrost distributions. By contrast, shorter-chain ($C_{16,18}$) DAs and lignin phenols (as well as hydroxy phenols in rivers outside eastern Eurasian Arctic) were much more enriched in ^{14}C, suggesting incorporation of relatively young carbon supplied by runoff processes from recent vegetation debris and surface layers. Furthermore, the radiocarbon content of terrestrial markers is heavily influenced by specific OC sources and degradation status. Overall, multitracer molecular ^{14}C analysis sheds new light on the mobilization of terrestrial OC from arctic watersheds. Our findings of distinct ages for various terrestrial carbon components may aid in elucidating fate of different terrestrial OC pools in the face of increasing arctic permafrost thaw.

1. Introduction

Fluvial transport and erosion processes represent important pathways of carbon mobilization in the Arctic, with significant implications for regional and global carbon cycles [*Dittmar and Kattner*, 2003; *Vonk and Gustafsson*, 2013]. Arctic watersheds are characterized by heterogeneous landscapes, containing massive pools of terrestrial organic carbon (OC) with sharply contrasting ages, including modern surface vegetation and litter, pre-aged soil, and ancient permafrost both in deep soil horizons and in the form of Pleistocene Ice Complex Deposits (ICD, a.k.a., "Yedoma") [*Schirrmeister et al.*, 2011; *Vonk et al.*, 2012; *Hugelius et al.*, 2014]. Collectively, these carbon pools exceed the current inventory of carbon held in the atmosphere as CO_2. While the degradation and subsequent CO_2 release from fast cycling modern OC pools have little impact on the net atmospheric CO_2 level on decadal to centennial timescales, warming-induced mobilization and

carbon release from "cryo-locked" ancient OC may provide a positive feedback and further accelerate and amplify warming [*DeConto et al.*, 2012; *Holmes et al.*, 2013; *Schuur et al.*, 2015]. Distinguishing the reservoir size, age, and fate of various mobilized terrestrial carbon pools is hence key to improved understanding of the arctic carbon cycle and to assessing climatic impacts on permafrost carbon release via rivers/erosion.

Compound-specific radiocarbon analysis (CSRA) of source-specific biomarkers is a powerful tool to investigate the age or residence time of various carbon pools in natural environments [*Eglinton et al.*, 1996, 1997]. Biomarkers typically make up a small fraction (<5%) of bulk OC, because the majority (up to 80%) of sedimentary OC has undergone complex interactions with each other and/or minerals during diagenesis and is molecularly uncharacterized or not extractable [*Hedges et al.*, 2000]. However, biomarkers faithfully preserve the isotopic signals of their carbon sources [*Eglinton et al.*, 1997; *Amelung et al.*, 2008], which can be used to constrain the behavior of OC components that make up a much higher proportion of bulk OC. Using CSRA, we have previously observed contrasting ages and mobilization pathways of two important groups of terrestrial molecular markers (higher plant leaf wax lipids and lignin-derived phenols) in the estuarine sediments of several Eurasian arctic rivers [*Gustafsson et al.*, 2011; *Feng et al.*, 2013a]. While lignin phenols receive significant inputs from surface carbon pools with relatively young ages, plant wax lipids are dominantly sourced from subsurface permafrost carbon pools characterized by much older ^{14}C ages. These results highlight the importance and urgent need of using multiple groups of tracers to accurately assess the fate of different terrestrial OC pools in the Arctic.

Cutin and suberin, which form protective coatings on vascular plant leaves and roots/bark [*Kögel-Knabner*, 2002], have been used to trace terrestrial OC in marine and lake sediments [*Goossens et al.*, 1989; *Gough et al.*, 1993; *Prahl et al.*, 1994; *Ishiwatari et al.*, 2005; *Tesi et al.*, 2014]. They have been found to be relatively resistant to microbial decomposition in soils [*Feng and Simpson*, 2008; *Feng et al.*, 2008] and may survive long-range fluvial transport better than solvent-extractable lipids. Cutin and suberin residues also display different degrees of association with mineral surfaces and may therefore differ in provenance and fate compared to other terrestrial components [*Gough et al.*, 1993]. Most recently, we have examined hydrolyzable compounds from the sedimentary particles of nine arctic and subarctic river systems [*Feng et al.*, 2015]. Hydroxy fatty acids (FAs) and *n*-alkane-α,ω-dioic acids [diacids (DAs)] originating from cutin and suberin made up 10–58% of the terrestrial biomarkers identified in the sediments (along with plant wax lipids, lignin, and hydroxy phenols), varying in both proportion and degradation extent as a function of vegetation cover and hydrogeographic conditions of the drainage basins [*Feng et al.*, 2015]. However, the ^{14}C characteristics of these different terrestrial biomarkers and their links to specific carbon pools—both within adjacent drainage basins and between different pan-arctic watersheds—remain to be determined. Quantifying radiocarbon in these components will be crucial for informed prediction and modeling of mobilization and subsequent fate of OC under changing conditions of the Arctic.

This study examined the ^{14}C contents of multiple biomolecular tracers of terrestrial OC in the fluvial deposits of, or estuarine and shelf sediments influenced by, nine different arctic and subarctic river systems. The objectives were (i) to better constrain the ages of OC mobilized from different terrestrial reservoirs and (ii) to assess the fate of various terrestrial OC components and hydrogeographic controls on their delivery across the pan-Arctic. The investigation involved radiocarbon characterization of a comprehensive suite of terrestrial marker compounds from the arctic sediments, and includes novel ^{14}C data for cutin- and suberin-derived DAs and hydroxy FAs, as well as for plant wax lipids, lignin, and hydroxy phenols.

2. Materials and Methods

2.1. Study Area and Sampling

Three North American arctic rivers (Mackenzie, Yukon, and Colville), five Great Russian Arctic Rivers (GRARs), and a subarctic Scandinavian river (Kalix) were included in this study (Figure 1), spanning large variations in hydrogeographic characteristics, vegetation, and permafrost coverage in the drainage basins (Table 1; see Text S1 in the supporting information for details). While these rivers are characterized by high dissolved OC fluxes and relatively low particulate OC (POC) fluxes, their sediment yield (normalized to basin area) is comparable to big tropical rivers such as Amazon (85 t km^{-2} yr^{-1}) and Congo (8.5 t km^{-2} yr^{-1}) [*Stein and Macdonald*, 2004]. The associated transport of POC has the potential to become a CO_2 source in climate changes [*Vonk and Gustafsson*, 2013].
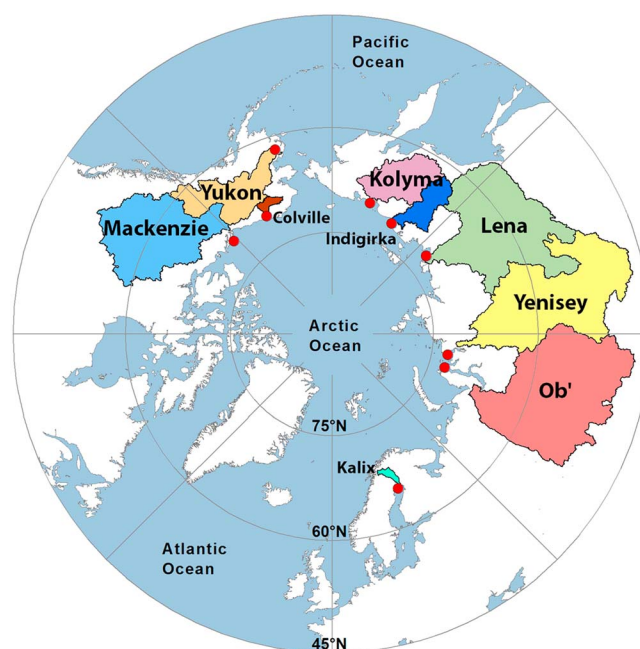
Figure 1. Sampling locations (red dots) and watersheds of the nine arctic and subarctic rivers.

The GRAR and Kalix watersheds cover a continental climate gradient, being cold and semiarid in the east and having wetter and milder winters in the west. 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). 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 [*van Dongen et al.*, 2008a, 2008b; *Vonk et al.*, 2012]. Previous molecular and isotopic investigations revealed a predominance of terrestrial OC with very minor contributions from aquatic biomass or petrogenic (rock-derived) carbon into these estuarine sediments [*van Dongen et al.*, 2008a; *Vonk et al.*, 2008].

Among the North American arctic rivers, the Mackenzie River is the largest fluvial source of both sediment and POC to the Arctic Ocean (Table 1). 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]. Sedimentation rates on the shelf generally range from 0.01 to 0.3 cm/yr [*Macdonald et al.*, 1998], and previous radiocarbon analysis of marine biomarkers from the site implies very recent deposition [*Drenzek et al.*, 2007]. For Yukon River, a sample of freshly deposited fine-grained fluvial sediment was collected 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. The Colville River is the largest North American river (both in terms of freshwater and sediment load) that exclusively drains continuous permafrost [*Walker*, 1998]. Two sediment 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.

The contrasting sampling strategies and sample types recovered from the various river systems (estuarine sediments for GRARs and Kalix versus shelf edge sediments for Mackenzie and fluvial deposits near the river mouth for Yukon and Colville) may lead to varied contributions of terrestrial, marine, and relict carbon to the bulk OC. However, as the majority of sediment is delivered from arctic rivers during the freshet, the Yukon and Colville samples are most likely an accurate reflection of the fluvial suspended load during the freshet and represent terrestrial organic matter (OM) transported to the river mouth. Moreover, for locations where we have compared characteristics of the fluvial suspended load, or where appropriate data are available (Mackenzie, Colville) [*Schreiner et al.*, 2013; *Vonk et al.*, 2015; Hussain et al., unpublished data], strong compositional similarities exist between suspended sediments and sediment deposits. Importantly, as we focus exclusively on the ^{14}C characteristics of source-specific biomarkers (particularly terrestrial biomarkers), our approach is insensitive to other OC contributions. Therefore, we believe that the ^{14}C observations described herein are valid for the basin-scale comparison of the ages of various terrestrial OC pools and their environmental controls. It is yet worth mentioning that fluvial deposits may be under a stronger influence of local bank erosion but do not receive inputs from coastal erosion, which supplies ancient OC from subsea permafrost to estuarine and shelf sediments [*Vonk et al.*, 2012]. Potential variations induced by these processes on our molecular ^{14}C data are discussed in detail in the results.

Table 1. Sample Location, Drainage Basin Characteristics, and Bulk Sediment Properties of the Pan-Arctic Rivers

	Kalix	Ob'	Yenisey	Lena	Indigirka	Kolyma	Colville 1	Colville 2	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[a]	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
Sampling year/month	2005/06	2004–2005/ 08–09	2004–2005/ 08–09	2004–2005/ 08–09	2004–2005/ 08–09	2004–2005/ 08–09	2007/06	2007/06	2007/06	1987/07–08
Water depth (m)	13	<2	<2	<2	8–11	<2	na[b]	na	na	25
Salinity (‰)	<3	<3	<5	<1	15	16	na	na	na	31
Forest coverage (%)[c]	60	30	49	84	21	31	2	2	51	63
Wetland coverage (%)[c]	20	11	3	1	3	1	na	na	14	18
Permafrost coverage[d]	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)[e]	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)[f]	10	427	673	588	54	136	19	19	208	316
Runoff (mm/yr)[f]	417	145	263	245	159	209	317	317	251	181
Sediment yield[d] (t km^{-2} yr^{-1})[g]	2	6	2	8	36	19	6	6	72	74
TOC/POC flux[d] (t km^{-2} yr^{-1})[g]	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	1.8	0.9	1.2	1.6
δ^{13}C-bulk OC (‰)[h]	−27.1	−27.4	−26.5	−25.0	−26.6	−26.7	−26.4	−26.7	−26.0	−26.0
Δ^{14}C-bulk OC (‰)[i]	−74±37	−314±3	−175±3	−609±3	−527±3	−502±2	−515±2	−624±2	−324±3	−738
^{14}C age-bulk OC (year BP)[j]	570±250	3,000±35	1,500±30	7,500±60	6,000±50	5,600±50	5,750±35	7,800±45	3,090±35	10,700

[a]Combined surface sediments along a transect.
[b]na: not available.
[c]Data from *Revenga et al.* [1998] and *Ingri et al.* [2005].
[d]Given as % continuous; % (discontinuous + sporadic + isolated) [*Gustafsson et al.*, 2011; *Holmes et al.*, 2013].
[e]Data from *Gordeev et al.* [1996], *Holmes et al.* [2002], *Rachold et al.* [2004], and *Ingri et al.* [2005].
[f]Data from *Milliman et al.* [1995], *Stein and Macdonald* [2004], *Ingri et al.* [2005], and *Holmes et al.* [2013].
[g]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].
[h]Bulk 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.
[i]Values normalized for the year of measurement; BP: before present.
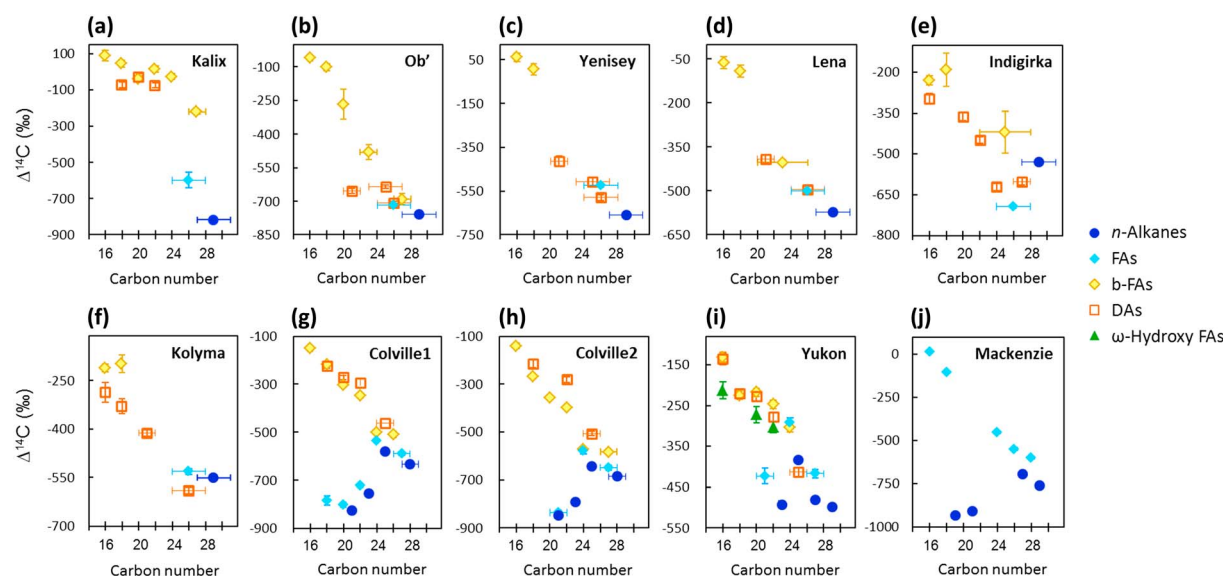
Figure 2. The $\Delta^{14}C$ values of ester-bound lipids in comparison with solvent-extractable lipids. All values are corrected for procedural blanks with the standard errors of analytical measurement propagated. The horizontal error bars represent the range of compounds being pooled for composite samples [odd-numbered *n*-alkanes, even-numbered fatty acids (FAs), bound FAs (b-FAs) and diacids (DAs), and $C_{23,25,27}$ DAs in Ob' and Yenisey]. Note that the *y* axes are not on the same scale. The $\Delta^{14}C$ values of *n*-alkanes and FAs in Mackenzie and six Eurasian arctic rivers are from *Drenzek et al.* [2007] and *Gustafsson et al.* [2011], respectively.

2.2. Bulk Analyses

Bulk sediments were kept frozen at $-20°C$ after collection and freeze-dried prior to analysis. A small aliquot was used for total organic carbon (TOC) and bulk stable carbon isotope ($\delta^{13}C$) 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). Bulk ^{14}C analysis was all conducted at NOSAMS [see *Gustafsson et al.*, 2011].

2.3. Biomarker Extractions and Purification

Biomarkers were isolated from freeze-dried sediments (~70–160 g) via a sequential extraction scheme as described in *Feng et al.* [2015] and purified further for subsequent ^{14}C analysis (see Figure S1 in the supporting information). Briefly, solvent-extractable *n*-alkanes and FAs [ultimately converted to and analyzed as fatty acid methyl esters (FAMEs)] were purified and isolated from total lipid extracts (TLEs) previously for GRARs and Kalix [*Gustafsson et al.*, 2011] and Mackenzie [*Drenzek et al.*, 2007]. Similarly, *n*-alkanes and FAMEs were isolated from the "neutral" and methylated "acid" fractions of saponified TLEs from Yukon and Colville sediments using protocols as described previously [*Galy et al.*, 2011]. Saturated *n*-alkanes and FAMEs were further purified by eluting through an $AgNO_3$-impregnated silica column in hexane/dichloromethane (1:1) for subsequent isolation by preparative capillary gas chromatography (PCGC).

Hydrolyzable compounds were removed from the solvent-extracted residues (excluding the Mackenzie sample) with 1 M KOH in methanol/water (4:1, 100°C, 3 h) on a microwave-assisted reaction system (Figure S1). Bound FAs (b-FAs), suberin- and/or cutin-derived DAs, and hydroxy FAs were isolated from the "acid" fraction of the hydrolysis products, methylated with methanol/HCl (95:5; 70°C, 12 h), extracted with hexane/dichloromethane (4:1), and loaded onto a silica gel column (1% deactivated) for further separation. b-FAMEs and diacid dimethyl esters (DAMEs) were eluted with hexane/ethyl acetate (95:5), followed by hydroxy FAMEs eluting with hexane/ethyl acetate (4:1), and di- and tri-hydroxy FAMEs eluting with ethyl acetate in the end. b-FAMEs and DAMEs were further separated on an $AgNO_3$-impregnated silica column by elution with hexane and dichloromethane, respectively. Hydroxy FAMEs in one sample (Yukon) were also further purified by eluting through a $AgNO_3$-impregnated silica column with dichloromethane/ethyl acetate (1:1) for PCGC isolation.

Lignin and hydroxy phenols were released from the dried hydrolyzed residues using alkaline CuO oxidation on a microwave-assisted reaction system. The oxidation products were purified through two solid phase

extraction (SPE) cartridges (Supelco Supelclean ENVI-18 and Supelclean LC-NH$_2$ SPEs) before isolation on high pressure liquid chromatography (HPLC) [details in *Feng et al.*, 2013b].

2.4. Isolation and ^{14}C Analysis of Individual Compounds

Selected lipid compounds (including *n*-alkanes, FAMEs, b-FAMEs, DAMEs, and hydroxy FAMEs), lignin, and hydroxy phenols were isolated for radiocarbon analysis. Among these samples, the ^{14}C contents of *n*-alkanes and FAMEs in the Mackenzie and Eurasian rivers were previously measured [*Drenzek et al.*, 2007; *Gustafsson et al.*, 2011], whereas the Δ^{14}C values of lignin and hydroxy phenols in Eurasian rivers are described in *Feng et al.* [2013a]. The ^{14}C contents of all other compounds are reported in this study for the first time, including *n*-alkanes and FAMEs in the Colville and Yukon sediments, hydrolyzable lipids (b-FAMEs, DAMEs, and hydroxy FAMEs) from all sediments (except Mackenzie), and lignin and hydroxy phenols in Mackenzie, Yukon, and Colville.

Briefly, lipid compounds were separated by PCGC consisting of a gas chromatograph (GC) system coupled to a Gerstel preparative fraction collector [see *Eglinton et al.*, 1996]. Hydroxy FAMEs were separated without derivatization using a DB-5MS column (30 m × 0.25 mm i.d., film thickness, 0.25 μm), whereas a DB-1 "mega-bore" column (30 m × 0.53 mm i.d., film thickness, 0.5 μm) was used for the other lipids. Phenolic compounds were separated on an Agilent 1200 HPLC system coupled to a diode array detector and a fraction collector using a Phenomenex Synergi Polar-RP column (4 μm × 4.6 × 250 mm) and a ZORBAX Eclipse XDB-C18 column (5 μm × 4.6 × 150 mm) [see *Feng et al.*, 2013b]. Approximately 5–150 μg C of individual compounds were collected after 20 injections on the PCGC or eight injections on the HPLC. Isolated compounds were eluted through a silica gel column (1% deactivated) to further remove potential column bleed with various solvents (hexane for *n*-alkanes, dichloromethane for FAMEs and b-FAMEs, dichloromethane/ethyl acetate (1:1) for DAMEs and hydroxy FAMEs, and ethyl acetate for phenols).

A small aliquot of the isolated compounds was used to check purity (as trimethylsilyl derivatives where necessary) on an Agilent 7890A GC coupled to flame ionization detection. All compounds were found to yield purities > 99%. In order to provide sufficient mass for reliable ^{14}C analysis, some lipid homologues were recombined (see Figure 2 and Table S1 for details).

Purified compounds were combusted under vacuum at 850°C for 5 h. The resulting CO_2 was cryogenically purified and quantified. A batch of CO_2 samples (~23–150 μg C; phenols from GRARs) was sent to NOSAMS, graphitized, and measured by accelerator mass spectrometry (AMS) [*Feng et al.*, 2013b]. The rest of the CO_2 samples (~10–75 μg C) were directly measured without graphitization on the miniaturized radiocarbon dating system at ETH Zürich using a gas feeding system [*Wacker et al.*, 2013]. Radiocarbon contents were corrected for the derivative carbon (where necessary) and reported as Δ^{14}C (‰) and conventional ^{14}C age. To assess procedural blanks, chemical extraction and PCGC or HPLC isolation were carried out with only solvents and reagents but no sample added. The PCGC or HPLC effluent was collected at time intervals corresponding to the retention time of targeted compounds, purified by the aforementioned procedures and quantified in a calibrated volume on the vacuum line. The resulting CO_2 from several blanks was pooled to determine a Δ^{14}C value, and we repeated the blank assessment over a period of 1.5 years. Procedural blanks yielded 1.8 ± 0.9 μg C with an F_m value of 0.44 ± 0.10 ($n = 5$) for 20 PCGC injections of lipid compounds and 2.5 ± 0.8 μg C with an F_m value of 0.21 ± 0.07 ($n = 5$) for eight HPLC injections of phenols, respectively. Neither the size nor the F_m value of procedural blanks was dependent on the elution or trapping time of compound, suggesting that silica gel column successfully removed potential column bleed (if any) from the isolated compounds and that compounds eluting later on the chromatography were not subject to more dead carbon contamination. All radiocarbon values are corrected for procedural blanks with the errors propagated. We measured aliquots of four different samples with varied sizes ranging 16–182 μg C (Table S2) at the two AMS facilities and did not observe a significant difference between radiocarbon contents of the same sample, also confirming the robustness of our blank correction.

2.5. Statistical Analysis

A *t* test was used to compare the ^{14}C content of different biomarkers. Simple linear regression analysis was used to assess correlations between the radiocarbon composition of various biomarkers and sedimentary OC properties. Nonlinear (logarithmic) correlations were also used to assess "threshold" phenomena in

describing correlations between drainage basin characteristics and the ^{14}C contents of biomarkers. The main drainage basin parameters investigated as explanatory variables include basin area, POC flux, runoff rate, and the coverage of forest, wetland, and continuous permafrost in the watershed (Table 1). Discharge is found to be correlated with basin area for the river systems studied and is hence not included as an independent basin parameter in the correlation analyses. Differences or correlations are considered to be significant at a level of $p < 0.05$, and the r^2 values are used to compare the explanatory power of the variables.

3. Results and Discussion

3.1. Sediment Bulk Properties and ^{14}C Contents

Bulk geochemical properties of the sediments in the nine arctic and subarctic rivers are listed in Table 1. The Kalix and Lena sediments had the highest (4.5%) and lowest (0.5%) OC content, respectively. All sediments showed relatively similar bulk δ^{13}C values ($-25.0‰$ to $-27.4‰$), indicating terrestrially dominated OC sources [e.g., *van Dongen et al.*, 2008a]. Δ^{14}C values of bulk OC ranged from $-74‰$ in Kalix to $-738‰$ in Mackenzie, corresponding to conventional radiocarbon ages of 570 to 10,700 years before present (BP). This wide age span of bulk OC from the nine pan-arctic rivers clearly implies that different terrestrial OC pools are mobilized from different arctic watersheds. The biomarker-specific ^{14}C contents presented in the next section provide more detailed information on the sources and ages of the mobilized terrestrial OC.

3.2. ^{14}C Characteristics of Individual Lipid Compounds in Arctic Rivers

The Δ^{14}C values of solvent-extractable *n*-alkanes and FAs are compared with those of ester-bound lipid compounds (b-FAs, DAs, and ω-hydroxy FAs) isolated from the same river sediments (Figure 2). The Δ^{14}C values were measured for composite samples of $C_{27,29,31}$ *n*-alkanes and $C_{24,26,28}$ FAs, respectively, for the six Eurasian arctic (and subarctic) rivers [*Gustafsson et al.*, 2011] (Figures 2a–2f), whereas individual *n*-alkanes and FAs were measured in the North American arctic samples (Figures 2g–2j) [the Mackenzie data from *Drenzek et al.*, 2007]. Overall, *n*-alkanes displayed very low Δ^{14}C values in all pan-arctic rivers, ranging from $-932‰$ to $-383‰$. The Δ^{14}C values of $C_{27,29,31}$ *n*-alkanes increased eastward from $-818‰$ to $-530‰$ in the estuarine surface sediments across the Eurasian Arctic. In the North American arctic sediments, shorter-chain ($C_{19,21,23}$) *n*-alkanes displayed even more depleted Δ^{14}C values than their longer-chain homologues, suggesting OC input from petrogenic sources, as was observed in the surface sediments elsewhere [*Feng et al.*, 2013b]. However, in contrast to the Washington Margin sediment [*Feng et al.*, 2013b], C_{25} *n*-alkane was younger than the C_{27} and C_{29} counterparts in the Colville and Yukon sediments. As C_{25} *n*-alkane is particularly enriched in *Sphagnum* mosses [*Baas et al.*, 2000; *Pancost et al.*, 2002; *Vonk and Gustafsson*, 2009] and is relatively high abundant in these sediments [*Feng et al.*, 2015], the younger age of C_{25} *n*-alkane relative to typical plant wax *n*-alkanes ($C_{27,29}$) may reflect input of modern OC from contemporary mosses and peat that are abundant in the North American arctic watersheds.

Longer-chain ($>C_{24}$) FAs displayed a roughly similar range of Δ^{14}C values (from $-719‰$ to $-292‰$) as the *n*-alkanes ($>C_{25}$) across the pan-Arctic. The ^{14}C distribution with respect to carbon numbers was also similar between FAs and *n*-alkanes in the Colville and Yukon sediments (Figures 2g–2i) in that shorter-chain ($C_{18,20,22}$) FAs were more depleted in ^{14}C than $C_{26,28}$ FAs and had similar Δ^{14}C values to C_{21} and C_{23} *n*-alkanes in Colville. Again, this stands in contrast with the sediments from Washington Margin [*Feng et al.*, 2013b], where shorter-chain FAs are younger than the C_{26} homologue, likely due to algal/bacterial inputs. We postulate that autotrophic algal/bacterial inputs are relatively small in this arctic watershed with low mean annual temperatures and that $C_{18,20,22}$ FAs have similar fossil OC sources as $C_{21,23}$ *n*-alkanes due to their similar ^{14}C contents. Yet unlike *n*-alkanes, shorter-chain (especially C_{18}) FAs are easy to degrade and hence seem unlikely to originate and survive transport from a fossil source (unless they were labile OC preserved in permafrost). Instead, the old age of C_{18} FA may reflect inputs of heterotrophic microbes that feed on fossil OC [*Petsch et al.*, 2001]. Furthermore, similar to C_{25} *n*-alkane, C_{24} FA was the most ^{14}C-enriched among the longer-chain homologues in the Colville and Yukon sediments and also exhibited higher Δ^{14}C values than the C_{25} *n*-alkane (Figures 2g–2i). As C_{24} and C_{26} homologues are the most abundant FAs in *Sphagnum* mosses [*Baas et al.*, 2000], the young age of C_{24} FA may also reflect OC inputs from contemporary mosses. The composite sample of $C_{26,28}$ FAs (Colville and Yukon) showed lower Δ^{14}C values, likely due to the ^{14}C dilution by C_{28} FA. By comparison, the Mackenzie sediments exhibited lower values ($-453‰$ to $-599‰$) for $C_{24,26,28}$ FAs but much

higher $\Delta^{14}C$ values (13‰ to −104‰) for the $C_{16,18}$ homologues (Figure 2j), indicating a greater proportion of marine algal/bacterially derived OC [*Drenzek et al.*, 2007].

In comparison with solvent-extractable FAs, b-FAs displayed decreasing $\Delta^{14}C$ values toward longer chain lengths (except Yenisey and Kolyma where only $C_{16,18}$ b-FAs were measured due to sample size limitations) such that short-chain ($C_{16,18}$) b-FAs were the most ^{14}C-enriched among all the lipid compounds investigated (Figures 2a–2i). Long-chain ($C_{24,26,28}$) b-FAs were more enriched in ^{14}C than FAs of the same chain lengths in Kalix, Indigirka, and Colville sediments, whereas C_{24} and $C_{26,28}$ b-FAs showed similar $\Delta^{14}C$ values to the corresponding FAs in Yukon and Ob', respectively. The younger or similar age of b-FAs relative to FAs is consistent with the lipid composition data [*Feng et al.*, 2015] and suggests that compared with FAs, b-FAs incorporate significant inputs of relatively fresh OC from at least two sources: (a) algal/bacterial OC, which may be significant for the shorter-chain homologues (especially in the four western Eurasian rivers); and (b) less decomposed terrestrial OC, which contributes to the younger age of long-chain b-FAs relative to solvent-extractable FAs emanating from the same rivers (Kalix, Indigirka, and Colville).

Similar to b-FAs, DAs showed decreasing $\Delta^{14}C$ values toward longer chain lengths (except in Kalix where $C_{24,26,28}$ DAs were not isolated due to the presence of unknown interfering compounds on the PCGC) such that the $\Delta^{14}C$ offset ranged 238–325‰ between short-chain (C_{16} or C_{18}) and long-chain ($C_{24,26,28}$) DAs in Indigirka, Kolyma, Colville, and Yukon (where both groups of homologues were measured). Unlike short-chain FAs that are ubiquitous in microbes as well as in plants, short-chain ($C_{16,18}$) DAs are exclusively derived from the cutin and suberin biopolymers of vascular plants [*Goñi and Hedges*, 1990a; *Otto and Simpson*, 2006] in the study area [see *Feng et al.*, 2015], while long-chain ($>C_{20}$) DAs predominantly occur in suberin [*Holloway*, 1983; *Otto and Simpson*, 2006]. As cutin appears to be more vulnerable to degradation than suberin [*Riederer et al.*, 1993; *Nierop et al.*, 2003], the younger age of short-chain DAs may correspond to a shorter residence time of cutin-derived OC in the watershed or a greater input of young OC from surface sources compared with suberin-derived long-chain DAs. Among the long-chain DAs, the $C_{20,22}$ homologues displayed significantly higher $\Delta^{14}C$ values than their $C_{24,26,28}$ counterparts (except in Ob'). While the former usually dominate (after $C_{18:1}$ DA) in plant tissues, and upper (Litter Fermentation Humus and organic) soil horizons [*Holloway*, 1983; *Graca and Santos*, 2006], the relative abundance of longer-chain ($>C_{24}$) DAs is found to increase in mineral soils [*Bull et al.*, 2000; *Naafs and van Bergen*, 2002; *Otto and Simpson*, 2006]. Hence, $C_{20,22}$ DA isotopic signatures may be more strongly influenced by recent inputs from surface layers, whereas $C_{24,26,28}$ DAs are dominated by inputs of pre-aged material from deeper, mineral soils. Contribution of aged DAs from Yedoma deposits is also possible. However, information on the distribution and abundances of hydrolyzable lipids (including DAs) in Yedoma is too sparse to attribute it as a source of pre-aged $C_{24,26,28}$ DAs. In addition to the dominant even-numbered DAs, we also isolated $C_{23,25,27}$ DAs (combined) from Ob' and Yenisey sediments (Figures 2b and 2c). Their similar $\Delta^{14}C$ values to $C_{20,22}$ DAs in Ob' and to $C_{24,26,28}$ DAs in Yenisey suggest that these relatively minor homologues have similar sources (from suberin) and transfer pathways in the watersheds.

Compared with b-FAs with the same chain length, DAs were more depleted in ^{14}C in almost all the Eurasian river samples (Figures 2a–2f; except for the similar $\Delta^{14}C$ values for $C_{24,26,28}$ DAs and b-FAs in Ob'), likely due to greater inputs of fresh OC to b-FAs as discussed above. By comparison, DAs in the Colville and Yukon sediments showed similar or slightly higher $\Delta^{14}C$ values than corresponding b-FAs (Figures 2g–2i), confirming a negligible input of autotrophic algal/bacterial OC to b-FAs, and implying similar terrestrial sources for b-FAs and DAs in these two North American river basins. Additionally, DAs exhibited varied radiocarbon contents relative to solvent-extractable FAs across the pan-Arctic, with younger ^{14}C ages particularly in Indigirka, Colville, and Yukon ($C_{18,22}$) sediments. This observation lends support to our previous conclusion that DAs are not oxidation products of FAs in these arctic sediments [*Feng et al.*, 2015], which would have led to similar or older ages of DAs than FAs.

Finally, we isolated three homologues of ω-hydroxy FAs ($C_{16,20,22}$) from the Yukon sample for ^{14}C analysis. Measurements of these compounds yielded considerably higher $\Delta^{14}C$ values than the corresponding FAs ($C_{20,22}$; Figure 2i), ruling out diagenetic oxidation of FAs as a main source of ω-hydroxy FAs [*van Bergen et al.*, 1998] in this sediment. Moreover, ω-hydroxy FAs were more depleted in ^{14}C than b-FAs and DAs of the same chain lengths in Yukon, and the $\Delta^{14}C$ offset was particularly large for the C_{16} homologues (~80‰). This also,
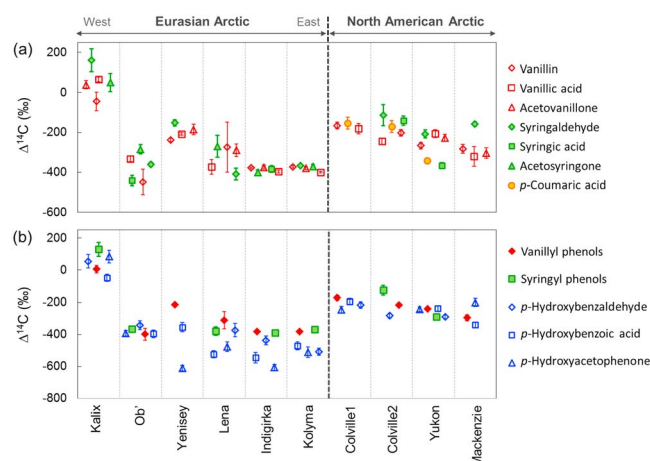
Figure 3. The Δ^{14}C values of (a) individual lignin phenols and (b) hydroxy phenols compared with the abundance-weighted average of vanillyl and syringyl phenols. All values are corrected for procedural blanks with the standard errors of analytical measurement propagated. Note that there is no significant difference in the average Δ^{14}C values between vanillyl and syringyl phenols from the same estuarine sediment (t test; $p > 0.05$) except Yenisey and Mackenzie, where only syringaldehyde was measured for syringyl phenols and hence the average Δ^{14}C values were not calculated. Data for six Eurasian arctic rivers are from *Feng et al.* [2013a].
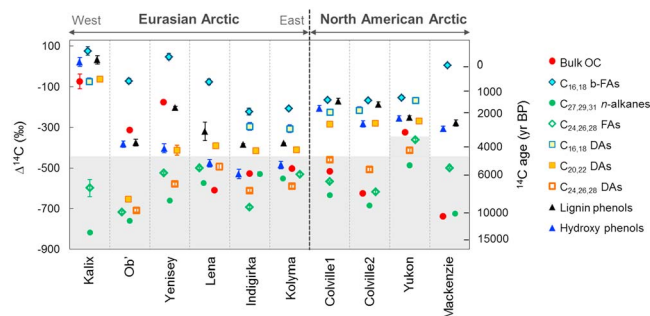
therefore, rules out the possibility of diagenetic oxidation of ω-hydroxy FAs to DAs [*Johns and Onder*, 1975; *van Bergen et al.*, 1998]. While DAs and ω-hydroxy FAs share similar biological sources and their degradability has not been reported to differ markedly in soils [*Riederer et al.*, 1993; *Otto and Simpson*, 2006], their relative abundance varies among plant tissues [*Goñi and Hedges*, 1990a]. ω-Hydroxy FAs are reported to dominate in the cutin- and suberin-derived C_{16} and C_{18} acids in roots relative to leaf tissues [*Otto and Simpson*, 2006]. Hence, C_{16} ω-hydroxy FA in the Yukon sediments may have received more pre-aged OC contributions from belowground sources compared with C_{16} DA or b-FA. Among the analyzed ω-hydroxy FAs, the C_{16} homologue had a more enriched Δ^{14}C value (-213‰) than its C_{20} and C_{22} counterparts (-272‰ and -303‰, respec-

tively). Similar to DAs, long-chain ($>C_{20}$) ω-hydroxy FAs are predominantly found in suberin, whereas C_{16} ω-hydroxy FA occurs in both cutin and suberin biopolymers [*Bernards*, 2002; *Otto and Simpson*, 2006]. The younger age of C_{16} ω-hydroxy FA in the bank sediment sample may therefore indicate a shorter residence time of cutin-derived compounds or a greater input of younger, surface-derived OC relative to C_{20} and C_{22} homologues.

3.3. Δ^{14}C Values of Individual Phenol Compounds

Individual lignin phenols displayed a variable range of Δ^{14}C values across the pan-arctic river sediments examined in this study (Figure 3a). Overall, among the Eurasian arctic rivers, the westernmost Kalix river exhibited the highest Δ^{14}C values and greatest variability among individual phenols (ranging from -45‰ to 161‰). The contemporary or postbomb ^{14}C signals suggest that lignin phenols have a short residence time (<50 years) in the Kalix watershed, which has the smallest basin area and highest runoff rate among the rivers investigated (Table 1). In contrast, lignin phenols from the far eastern rivers of Indigirka and Kolyma showed much lower and more coherent Δ^{14}C values, ranging from -402‰ to -367‰, indicative of much longer residence time in the drainage basins. There is a clear trend of increasing ^{14}C variability in lignin phenols across this east-to-west continent-wide set of estuarine sediments. Three lignin phenols (vanillin, vanillic acid, and p-coumaric acid) isolated from the Colville 1 sediment also exhibited very uniform Δ^{14}C values (-181‰ to -153‰). However, Δ^{14}C variability in the other arctic rivers ranged from 85‰ to 164‰, the latter being greater than that reported for the Washington margin sediments (~90‰) [*Feng et al.*, 2013b], and suggests a greater diversity in lignin sources in these arctic watersheds. Notably, there appears to be a relationship between the extent of permafrost coverage and the age heterogeneity of lignin sources.

No general trend in radiocarbon characteristics was observed between the aldehyde, ketone, and acid monomers of vanillyl and syringyl phenols. Moreover, with the exception of the Mackenzie, where syringal-dehyde displayed a higher Δ^{14}C value (-158‰) than vanillyl phenols (-283‰ to -320‰; Figure 3a), there was no significant offset in the abundance-weighted average Δ^{14}C values between vanillyl and syringyl phenols from the same estuarine sediment (Figure 3b; t test; $p > 0.05$). However, since only one syringyl phenol was measured for the Mackenzie sediment, we refrain from comparing Δ^{14}C values for these compounds against the average of vanillyl phenols. As for the less abundant cinnamyl phenols, p-coumaric acid was measured in Colville and Yukon sediments, exhibiting similar Δ^{14}C values to vanillyl and/or syringyl phenols

Figure 4. Comparison of the abundance-weighted average $\Delta^{14}C$ values of multiple markers with that of bulk organic carbon (OC) across the pan-Arctic. Markers in the shaded area had more depleted ^{14}C contents compared with those in the white part, suggesting incorporation of pre-aged OC from deeper soil horizons. In the Mackenzie sediment, the $\Delta^{14}C$ values of $C_{16,18}$ fatty acids (FAs) were used to replace $C_{16,18}$ bound FAs (b-FAs). In the North American arctic rivers, only $C_{27,29}$ n-alkanes and $C_{24,26}$ diacids (DAs) were measured. $C_{16,18}$ DAs were represented by C_{16} DA in Indigirka and C_{18} DA in Kalix and Colville, respectively. Only p-hydroxybenzaldehyde was measured for hydroxy phenols in Colville 2. See Table S1 in the supporting information for detailed $\Delta^{14}C$ values.

(Figure 3a). Hence, it appears that lignin phenols displayed no systematic age offsets in the same arctic sediments.

In contrast to the lignin-derived phenols, hydroxy phenols displayed a similar degree of $\Delta^{14}C$ variability in almost all arctic rivers (39–168‰). The Yenisey is the exception, which showed a particularly large offset between p-hydroxyacetophenone and p-hydroxybenzoic acid (256‰; Figure 3b). Occurring in higher abundances in mosses and peat than in vascular plants [*Lehto et al.*, 1985; *Zaccone et al.*, 2008; *Amon et al.*, 2012], hydroxy phenols exhibited similar $\Delta^{14}C$ values to lignin phenols in Kalix, Ob', and the North American arctic rivers, but lower values in four eastern GRARs. The latter is likely due to the incorporation of pre-aged OC from ancient peat deposits in these regions [*Feng et al.*, 2013a]. Similar to vanillyl and syringyl phenols, no pattern was observed for the $\Delta^{14}C$ values among the aldehyde, ketone, and acid forms of hydroxy phenols.

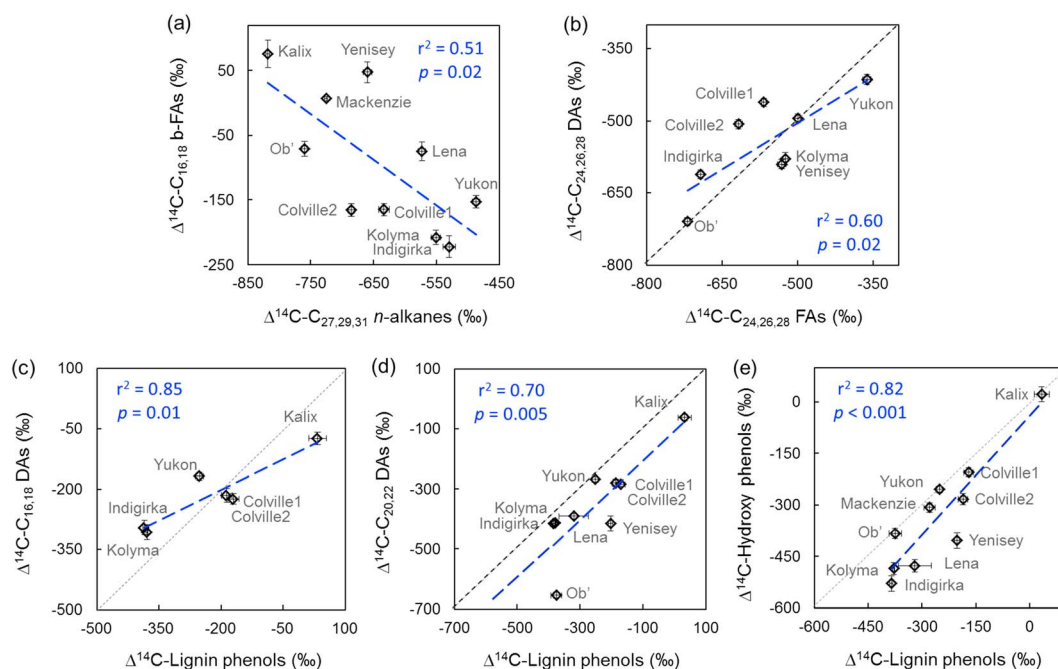### 3.4. Comparison of the ^{14}C Signatures of Various Terrestrial OC Tracers

The broad array of molecular marker compounds analyzed for ^{14}C content in this study allows us to develop a comprehensive picture of the ^{14}C characteristics of terrestrial OM delivered by rivers to arctic sediments. Among these, the abundance-weighted $\Delta^{14}C$ values of $C_{27,29,31}$ n-alkanes and $C_{24,26,28}$ FAs were selected to represent the ^{14}C content of plant wax lipids. $C_{16,18}$ DAs incorporate inputs from both cutin and suberin, whereas $C_{20,22}$ and $C_{24,26,28}$ DAs represent suberin-derived OC only. Since no systematic age offset was observed among the individual monomers for lignin from the same sediment, we calculated the abundance-weighted average $\Delta^{14}C$ values for all the lignin phenols. This approach was applied to hydroxy phenols from the same sample for the same reason. Comparisons of the ^{14}C composition between these groups of terrestrial markers, and with those of bulk OC and of short-chain ($C_{16,18}$) b-FAs (or FAs in Mackenzie) across the pan-Arctic, reveal several intriguing patterns (Figure 4).

First, $C_{16,18}$ b-FAs (or FAs in Mackenzie) were the youngest markers examined with positive (i.e., postbomb) $\Delta^{14}C$ values in Kalix, Yenisey, and Mackenzie samples. These signals were assumed to predominately originate from algal/bacterial sources as well as modern vegetation [*Pearson et al.*, 2001]. In sharp contrast, $C_{27,29,31}$ n-alkanes represented the oldest suite of compounds across the pan-Arctic (except in Indigirka and Kolyma), reflecting the recalcitrant nature of this group of terrestrial markers that derive from extensively pre-aged terrestrial OM. The $\Delta^{14}C$ offset between $C_{16,18}$ b-FAs and $C_{27,29,31}$ n-alkanes ranged from 334‰ (corresponding to ~4000 ^{14}C years) in the Yukon to 894‰ (~14,000 ^{14}C years) in the Kalix, highlighting marked contrast in ages and storage times of different carbon components delivered to arctic estuarine sediments. Interestingly, there is a significant negative correlation between the $\Delta^{14}C$ values of $C_{16,18}$ b-FAs and $C_{27,29,31}$ n-alkanes ($r^2 = 0.51$, $p = 0.02$; Figure 5a). As these two groups of compounds have varied origins, this discrepancy in ^{14}C characteristics may be controlled by contrasting mobilization mechanisms of their respective carbon sources (see discussion in section 3.5).

The overall suite of terrestrial markers examined in this study also spanned a wide spectrum of ^{14}C ages and may be grouped into two clusters based on their radiocarbon contents (see the shaded area in Figure 4). While three groups of DAs had positively correlated $\Delta^{14}C$ values with each other ($p < 0.05$), only $C_{24,26,28}$ DAs showed $\Delta^{14}C$ values positively correlated to those of $C_{24,26,28}$ FAs ($r^2 = 0.60$, $p = 0.02$; Figure 5b) and were among the oldest terrestrial markers together with $C_{27,29,31}$ n-alkanes and $C_{24,26,28}$ FAs. In contrast, $C_{16,18}$ and $C_{20,22}$ DAs exhibited much more enriched ^{14}C contents that were closer to lignin and hydroxy phenols across

Figure 5. Linear correlations between the abundance-weighted average $\Delta^{14}C$ values of various markers. Gray and blue dashed lines represent the 1:1 ratio and linear correlations, respectively. Note that the $\Delta^{14}C$ values of $C_{16,18}$ fatty acids (FAs) were used to replace $C_{16,18}$ bound FAs (b-FAs) in the Mackenzie sediment in Figure 5a. DAs: diacids.

the pan-Arctic (except in Ob') such that $C_{16,18}$ DAs and lignin phenols were the youngest exclusively terrestrial markers measured, representing the fast cycling component of terrestrial OC in the arctic land-ocean transfer. The $\Delta^{14}C$ offset between terrestrial markers was largest in Kalix (851‰ or 14,000 ^{14}C years) and smallest in Lena (253‰ or ~3700 ^{14}C years). Furthermore, $\Delta^{14}C$ values of lignin phenols, hydroxy phenols, and $C_{16,18}$ and $C_{20,22}$ DAs were positively correlated with each other despite some consistent offsets ($p < 0.05$; Figures 5c–5e), suggesting related carbon sources that are distinct from those supplying plant wax lipids and longer-chain DAs. As discussed previously, $C_{24,26,28}$ DAs may be dominated by inputs from mineral soils and hence exhibit a pre-aged ^{14}C signal similar to that of plant wax lipids [*Feng et al.*, 2013a]. On the other hand, $C_{20,22}$ and, in particular, $C_{16,18}$ DAs likely incorporate young carbon from surface layers that constitutes the main source of lignin in the Arctic [*Feng et al.*, 2013a]. Nonetheless, $C_{20,22}$ DAs showed older ages relative to the corresponding lignin phenols in Kalix, Ob', Yenisey, and Colville sediments (Figure 5d), reflecting some contribution from deeper soil layers, whereas hydroxy phenols exhibited significantly more depleted ^{14}C contents than lignin phenols in Yenisey and three eastern GRARs (Lena, Indigirka, and Kolyma; Figure 5e) where ancient peat deposits are abundant [*Feng et al.*, 2013a]. One Colville river sample (Colville 2) also yielded a lower hydroxy phenol $\Delta^{14}C$ value relative to lignin phenols (Figures 4 and 5e). However, as only one compound (*p*-hydroxybenzaldehyde) was measured for hydroxy phenols in this sample (Figure 3b), the comparison may be biased.

None of the investigated markers could solely account for the $\Delta^{14}C$ variations in bulk OC across the pan-Arctic (Figure 4). While lignin phenols largely track bulk OC in terms of ^{14}C contents in the western Eurasian arctic (Kalix, Ob', and Yenisey) and Yukon sediments, considerable age offsets (ranging from 2000 to 8000 ^{14}C years) exist between lignin and bulk OC in the other river systems (Figure 4). This is likely due to inputs of relict carbon from bitumen, shales, or coals from the Devonian Canol formation into Mackenzie [*Yunker et al.*, 2002; *Goñi et al.*, 2005; *Drenzek et al.*, 2007] and from Yedoma into eastern GRARs [*Schirrmeister et al.*, 2011; *Vonk et al.*, 2012, 2014] and Colville [*Schreiner et al.*, 2014]. Bulk OC in these river sediments hence had $\Delta^{14}C$ values closer to the older components of terrestrial markers (i.e., plant wax *n*-alkanes or FAs). In addition, none of the investigated biomarkers depict rock-derived OC, which is a universal and important component of sedimentary carbon [*Galy et al.*, 2015] and contributes to the old (essentially radiocarbon-dead) components of bulk OC. Hence, biomarkers analyzed here cannot fully explain the age or behavior of bulk OC. However, their
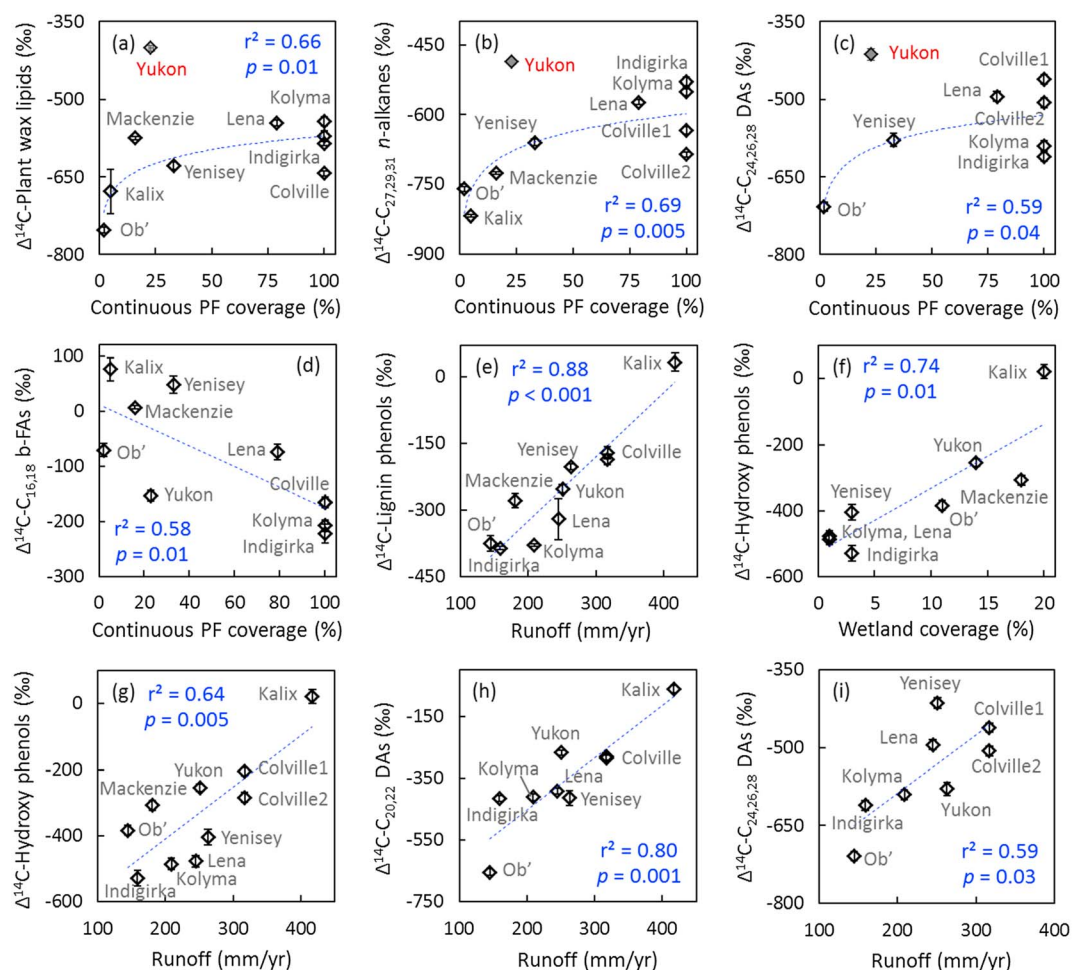
Figure 6. (a–c) Logarithmic and (d–h) linear correlations between the abundance-weighted average Δ^{14}C values of terrestrial markers and hydrogeographic variables of the arctic drainage basins. The Yukon data (in red) are outliers in Figures 6a–6c and are not included in the correlations. PF: permafrost; DAs: diacids; b-FAs: bound fatty acids. The Δ^{14}C values of plant wax lipids [including $C_{27,29,31}$ n-alkanes and $C_{24,26,28}$ fatty acids (FAs)] are calculated here to compare with findings from *Feng et al.* [2013a]. Note that the Δ^{14}C values of $C_{16,18}$ FAs were used to replace $C_{16,18}$ b-FAs in the Mackenzie sediment in Figure 6d and that the Colville River is not included in Figure 6f because the wetland coverage is not known.

isotopic signatures can serve as end-member values (of surface and deep permafrost OC) to better constrain the behavior of bulk OC.

3.5. Hydrogeographic Controls on the [14]C Age

To assess environmental controls on the radiocarbon age of terrestrial OC transferred into these arctic sediments, we examined the fit of Δ^{14}C values of various markers against hydrogeographic variables of the drainage basins. Similar to prior observations on the Eurasian arctic rivers [*Feng et al.*, 2013a], continuous permafrost coverage in the watersheds provides the best control of the abundance-weighted average Δ^{14}C values of plant wax lipids (including $C_{27,29,31}$ n-alkanes and $C_{24,26,28}$ FAs) and $C_{27,29,31}$ n-alkanes across the pan-Arctic in a logarithmic model ($r^2 = 0.66$ and 0.69, respectively; $p < 0.05$; Figures 6a and 6b), but with Yukon as an outlier. Yukon has the youngest plant wax lipids of the investigated rivers and has a notably younger C_{24} FA than the longer-chain ($C_{26,28}$) counterparts (Figure 2i), possibly due to greater inputs of contemporary mosses (see discussion in section 3.1). However, even after removal of the C_{24} FA in the calculation of plant wax lipid Δ^{14}C values, Yukon remains an outlier in the logarithmic model fitting.

There may be several potential causes for the anomalous characteristics of the Yukon River sample. First, as the Yukon watershed has the highest coverage of discontinuous, sporadic, and isolated permafrost across the pan-Arctic (Table 1), such permafrost may have a similar (if not stronger) regulation on the mobilization

pathways and hence the ^{14}C content of wax lipids as continuous permafrost. This speculation is supported by the logarithmic correlation between the total permafrost (including continuous, discontinuous, sporadic, and isolated permafrost) coverage and Δ^{14}C values of both plant wax lipids and $C_{27,29,31}$ n-alkanes ($p < 0.05$; Figures S2a and S2b). Second, in contrast to the estuarine and shelf surface sediments of the Eurasian rivers and Mackenzie, the Yukon sample was collected from a fluvial deposit (~190 km) upstream of the river mouth that is considered to be the outflow point of the entire basin. This sample is thus devoid of influences of coastal erosion which can release old carbon from exposed deeper soil horizons [*Vonk et al.*, 2012]. Third, the fluvial deposit may be influenced by erosion of local river bank or soil material that is younger in age [see arctic topsoil Δ^{14}C values in *Guo et al.*, 2007, and *Vonk et al.*, 2012]. This influence may be reflected by the younger age of bulk OC in our Yukon sample compared with river POC and riverbed sediment collected at the Pilot Station of Yukon River in 2004 [*Guo et al.*, 2007]. While this different depositional location may have led to the younger ages of lipids in the Yukon sample, it does not seem to affect the age of lignin and hydroxy phenols (Figure 4), possibly due to the lower abundance of phenol compounds in mineral soils [*Wakeham et al.*, 2009; *Xu et al.*, 2009; *Tesi et al.*, 2014] that reduces the influence of coastal erosion on corresponding lignin phenol ages. Similar to the Yukon samples, Colville sediments were collected as fresh mud deposits on river ice during ice breakup close to (within 40 km of) the river mouth. In this instance the influence of local river bank erosion is likely to be negligible, and Δ^{14}C values of plant wax lipids and $C_{27,29,31}$ n-alkanes from both Colville samples fit the logarithmic model with continuous permafrost coverage (Figures 6a and 6b).

As another "old" component of terrestrial OC, $C_{24,26,28}$ DAs show a similar Δ^{14}C correlation with the continuous permafrost (with Yukon again as an outlier; $r^2 = 0.59$, $p = 0.04$; Figure 6c) and total permafrost coverage ($p < 0.05$; Figure S2c) in the pan-Arctic, indicating similar mobilization pathways to the plant wax lipids. These correlation patterns corroborate and expand our previous findings and suggest that the longer-chain terrestrial lipids incorporate significant inputs of pre-aged carbon from deeper soil horizons (and possibly also from Yedoma, although information is lacking on the distribution of long-chain DAs in Yedoma), whose mobilization is more dependent on (deep) flow paths that are related to nonlinear processes associated with permafrost distributions, such as local thaw, conduits of unfrozen ground in discontinuous permafrost, and frost cracks [e.g., *Gustafsson et al.*, 2011; *Feng et al.*, 2013].

In contrast, the Δ^{14}C values of $C_{16,18}$ b-FAs (or $C_{16,18}$ FAs in Mackenzie) display a negative correlation with continuous permafrost coverage ($r^2 = 0.58$, $p = 0.01$; Figure 6d) such that $C_{16,18}$ b-FAs are considerably older (with Δ^{14}C values of -71‰ to -222‰) in the continuous-permafrost-dominated basins (Indigirka, Kolyma, and Colville). Presumably, this is caused by a slower decay and hence a longer residence time of short-chain FAs in these watersheds and/or a lower productivity and hence less inputs from contemporary algal/bacterial sources in the colder regions. It is worth mentioning that the Mackenzie sediment was collected in 1987 whereas all other samples were obtained in 2004–2007. The comtemporary geographic information provided in Table 1 is likely an underestimate of watershed permafrost coverage in the past decade (or two decades in the case of Mackenzie) as the Arctic is changing rapidly. We hence expect the Mackenzie data point to shift a bit horizontally to the right in Figures 6a, 6b, and 6d. But this is unlikely to change the significance of observed correlations and hence the above findings.

Also similar to Eurasian arctic rivers [*Feng et al.*, 2013a], mean annual runoff is strongly correlated with the abundance-weighted average Δ^{14}C values of lignin phenols across the pan-Arctic ($r^2 = 0.88$, $p < 0.001$; Figure 6e), whereas Δ^{14}C values of hydroxy phenols are correlated with both wetland coverage and runoff ($r^2 = 0.74$ and 0.64, respectively; $p < 0.05$; Figures 6f and 6g). Likewise, the Δ^{14}C values of $C_{20,22}$ DAs are linearly correlated only with runoff among all the hydrogeographic variables examined ($r^2 = 0.80$, $p = 0.001$; Figure 6h). Together, these relationships indicate that $C_{20,22}$ DAs, lignin, and hydroxy phenols mainly incorporate relatively young carbon supplied by runoff processes from surface layers (modern wetlands for hydroxy phenols in particular) in the Arctic. Sediment yield and POC export are both reported to increase with runoff on the long term globally [*Beusen et al.*, 2005; *Ludwig and Probst*, 1998; *Milliman and Syvitski*, 1992]. But it has rarely been shown how runoff affects the source or age of POC components. Our study shows that export of surface (young) biogenic OC increases with increasing runoff while deep (old) permafrost is not as sensitive in the Arctic.

Moreover, the Δ^{14}C values of $C_{24,26,28}$ DAs are also correlated with runoff ($r^2 = 0.59$, $p = 0.03$; Figure 6i), albeit within a narrower range of runoff values (due to the absence of the Kalix data). This suggests that other than

Table 2. Biomarker-Based Proxies of Organic Carbon (OC) Sources and Degradation Stages Used in This Paper [Based on *Feng et al.*, 2015] and the r^2 Values of Linear Correlation Tests Between the Abundance-Weighted Average $\Delta^{14}C$ Values of Multiple Markers and Proxies[a]

Proxies	Indications	r^2 Values Against the $\Delta^{14}C$ Value of					
		$C_{27,29,31}$ n-Alkanes	$C_{24,26,28}$ FAs	$C_{24,26,28}$ DAs	$C_{20,22}$ DAs	Lignin Phenols	Hydroxy Phenols
$C_{25}/(C_{25} + C_{29})$ n-alkanes	Increase with inputs of *Sphagnum* mosses relative to higher plants	0.66c	0.12	0.02	0.19	0.55b	0.66b
3,5Bd/V	Increase with peat inputs relative to higher plants	0.63c	0.13	0.00	0.19	0.50b	0.60b
S/V	Relative input of angiosperms; also decrease with degradation	0.02	0.56c	0.52c	0.18	0.08	0.05
C/V	Relative input of nonwoody tissues	0.03	0.09	0.08	0.20	0.24	0.25
$(Ad/Al)_p$	Increase with oxidation of hydroxy phenols; decrease with wetland coverage in our sample set	0.48b	0.05	0.18	0.38	0.44c	0.53c
$(Ad/Al)_v$	Increase with oxidation of vanillyl phenols	0.19	0.06	0.30	0.56c	0.20	0.37
$(Ad/Al)_s$	Increase with oxidation of syringyl phenols; but mainly increase with root input in our sample set	0.00	0.28	0.62b	0.37	0.16	0.39
ω-$C_{18}/\Sigma C_{18}$	Increase with root degradation; also increase with fresh root input (high values in fresh root tissues)	0.33	0.17	0.51b	0.01	0.02	0.00
HMW FAs/n-alkanes	Increase with FA preservation	0.01	0.36	0.71b	0.60b	0.31	0.51b

[a]$C_{25}/(C_{25} + C_{29})$ n-alkanes: ratio of $C_{25}/(C_{25} + C_{29})$ n-alkanes [*Vonk and Gustafsson*, 2009]; 3,5Bd/V: ratio of 3,5-dihydroxy benzoic acid (3,5Bd) to vanillyl (V) phenols; S/V: ratio of syringyl (S) to V phenols; C/V: ratio of cinnamyl (C) to V phenols; $(Ad/Al)_p$: ratio of p-hydroxybenzoic acid to p-hydroxybenzaldehyde; $(Ad/Al)_v$: ratio of vanillic acid to vanillin; $(Ad/Al)_s$: ratio of syringic acid to syringaldehyde [*Hedges and Mann*, 1979; *Amon et al.*, 2012; *Feng et al.*, 2015]; ω-C_{18}: ratio of C_{18} ω-hydroxy acid to the summation of all C_{18} hydroxy fatty acids (FAs) and diacids (DAs) [*Goñi and Hedges*, 1990b; *Otto and Simpson*, 2006; *Feng et al.*, 2010]; HMW FAs/n-alkanes: ratio of high-molecular-weight (HMW) FAs (C_{20}-C_{30}) to HMW n-alkanes (C_{20}-C_{34}) [*van Dongen et al.*, 2008a]; refer to Table S1 in the supporting information for detailed $\Delta^{14}C$ values.
[b]Denotes significance at $p < 0.05$. Values indicate significant positive correlations.
[c]Denotes significance at $p < 0.05$. Values indicate significant negative correlations.

deep OC sources (such as roots and subsoils) supplied via nonlinear processes, surface-derived OC pools (such as detrital material from tree barks) also transfer significant amounts of longer-chain DAs to river sediments by runoff processes. Another group of surface-derived markers ($C_{16,18}$ DAs) is not included in these correlation tests due to the limited number of data points (five rivers in total). Overall, however, the ^{14}C characteristics of various terrestrial biomarkers reveal that surface runoff and permafrost distribution exert a strong control on the release and delivery of different terrestrial OC pools into the arctic rivers, with the former governing surface land-derived young OC and the latter affecting aged OC from deep soil (and possibly Yedoma) sources.

3.6. Influence of OM Sources and Degradation Stages on the ^{14}C Contents

We further explored the influence of OM sources and degradation stages on the radiocarbon characteristics of terrestrial markers using a range of biomarker-based proxies that were previously discussed [*Feng et al.*, 2015] (Table 2). Among them, the *Sphagnum*-input proxy, i.e., ratio of $C_{25}/(C_{25} + C_{29})$ n-alkanes [*Vonk and Gustafsson*, 2009] and the peat-input proxy [3,5-dihydroxy benzoic acid/vanillyl phenols (3,5Bd/V)] are positively correlated [*Feng et al.*, 2015]. Moreover, both show negative correlations with the $\Delta^{14}C$ values of $C_{27,29,31}$ n-alkanes ($r^2 = 0.66$ and 0.63, respectively; $p < 0.01$; Table 2), suggesting increasing plant wax n-alkane ages with increasing inputs of *Sphagnum*- or peat-derived OM. On the other hand, $C_{27,29,31}$ n-alkane ages decrease with increasing acid-to-aldehyde (Ad/Al) ratios of hydroxy phenols {p-hydroxybenzoic acid/p-hydroxybenzaldehyde $[(Ad/Al)_p]$; $r^2 = 0.48$; $p = 0.03$}. Given that the $(Ad/Al)_p$ ratio is negatively correlated with the wetland coverage in the drainage basins [*Feng et al.*, 2015], its positive correlation with $\Delta^{14}C$ values of $C_{27,29,31}$ n-alkanes may be controlled

by the mobilization of aged n-alkanes from moss-dominated wetlands as well. The correlations of $C_{27,29,31}$ n-alkane ages with these proxies stand in contrast with those of lignin and hydroxy phenols, which become younger with increasing ratios of $C_{25}/(C_{25} + C_{29})$ n-alkanes and 3,5Bd/V, and a decreasing $(Ad/Al)_p$ ratio ($p < 0.05$). This contrasting behavior underscores the distinct OC sources for plant wax n-alkanes and phenol compounds in these watersheds. While OM in contemporary wetlands is a major source of young lignin and hydroxy phenols in the Kalix basin, OC derived from *Sphagnum* and peat instead comprises as source for old $C_{27,29,31}$ n-alkanes, presumably emanating from pre-aged OC in deeper peat/soils horizons rather than from contemporary surface wetlands as plant wax n-alkanes are more enriched in mineral-associated subsoils [*Xu et al.*, 2009].

The $\Delta^{14}C$ values of lignin phenols show no correlation with their molecular composition [i.e., syringyl-to-vanillyl (S/V) and cinnamyl-to-vanillyl (C/V) ratios] or the Ad/Al ratios of vanillyl [$(Ad/Al)_v$] or syringyl phenols [$(Ad/Al)_s$; Table 2]. This implies no direct relationship between the biological sources or oxidation state of lignin and its age, consistent with previous observations at the Washington Margin [*Feng et al.*, 2013b] and Mekong River [*Martin et al.*, 2013]. The ^{14}C age of hydroxy phenols, however, decreases as the ratio of high-molecular-weight (HMW) FAs (C_{20}-C_{30}) to HMW n-alkanes (C_{20}-C_{34}; HMW FAs/n-alkanes) increases ($r^2 = 0.51$; $p = 0.02$). The latter ratio reflects increased OM preservation toward the eastern Eurasian Arctic, presumably due to inhibited microbial degradation of FAs resulting from shorter thawed-out summer seasons [*van Dongen et al.*, 2008a]. $\Delta^{14}C$ values of $C_{20,22}$ and $C_{24,26,28}$ DAs are also positively correlated with the HMW FAs/n-alkanes degradation proxy ratio ($r^2 = 0.71$ and 0.60, respectively; $p = 0.01$), suggesting younger ("fresher") hydroxy phenols and long-chain DAs with increased OM preservation.

Interestingly, while $C_{20,22}$ DAs exhibit older ages with an increasing oxidation state of vanillyl phenols [i.e., an increasing $(Ad/Al)_v$ ratio; $r^2 = 0.56$; $p = 0.02$], $C_{24,26,28}$ DAs display younger ages with an increasing $(Ad/Al)_s$ ratio ($r^2 = 0.62$; $p = 0.02$). As demonstrated previously [*Feng et al.*, 2015], the $(Ad/Al)_s$ ratio increases with root inputs and is more of a source rather than a degradation indicator in our sample set. Hence, the positive correlation between $\Delta^{14}C$ values of $C_{24,26,28}$ DAs and $(Ad/Al)_s$ ratios is consistent with fresh roots comprising a major source for longer-chain DAs. In line with this explanation, $C_{24,26,28}$ DAs are also more enriched in ^{14}C with an increasing ratio of C_{18} ω-hydroxy acid to the sum of all C_{18} hydroxy FAs and DAs (ω-$C_{18}/\Sigma C_{18}$; $r^2 = 0.51$; $p < 0.05$), which exhibits high values in fresh root tissues [*Otto and Simpson*, 2006; *Feng et al.*, 2010].

Lastly, both $C_{24,26,28}$ DAs and $C_{24,26,28}$ FAs become increasingly ^{14}C depleted with increasing S/V ratios ($r^2 = 0.52$ and 0.56, respectively; $p < 0.05$). It is very unlikely that angiosperm-derived OM (high in S/V ratios) contribute to the old age of these markers as angiosperms appeared much later than gymnosperms during the course of species evolution. Syringyl phenols are reported to degrade faster than vanillyl phenols in both aquatic and terrestrial environments, leading to lower S/V ratios with increasing degradation [*Hedges et al.*, 1988; *Opsahl and Benner*, 1995; *Otto et al.*, 2005]. The negative correlation of $\Delta^{14}C$ values of $C_{24,26,28}$ DAs and $C_{24,26,28}$ FAs with S/V ratios hence reflects a disconnection between the age of longer-chain DAs and FAs and lignin degradation. As longer-chain lipids (including plant wax lipids and DAs) are found to become older emanating from nonpermafrost-dominated landscapes (Figure 6), we posit that a higher proportion of angiosperm is distributed in nonpermafrost-dominated watersheds, contributing to the aging of longer-chain DAs and FAs as well as the higher S/V ratios.

4. Summary and Implications

Although the present study describes observations on a limited suite of samples, the measurements reported encompass the major arctic river systems and presently represent the most comprehensive multimolecular ^{14}C investigation of terrestrial materials exported from these or any other fluvial systems. The resulting findings have shed new light on terrestrial carbon sources and mobilization pathways in arctic river basins. Key findings are as follows:

First, by expanding compound-specific radiocarbon analysis to suberin- and/or cutin-derived biomarkers (DAs and hydroxy FAs), we found that DAs of different chain lengths could differentiate terrestrial OC derived from surface layers versus deeper soil horizons (or possibly ancient Yedoma deposits) in arctic watersheds. Specifically, ^{14}C contents of shorter-chain ($C_{16,18}$ and $C_{20,22}$) DAs mirrored those of lignin or hydroxy phenols across the pan-Arctic, suggesting the incorporation of more recent carbon from surface layers, whereas longer-chain
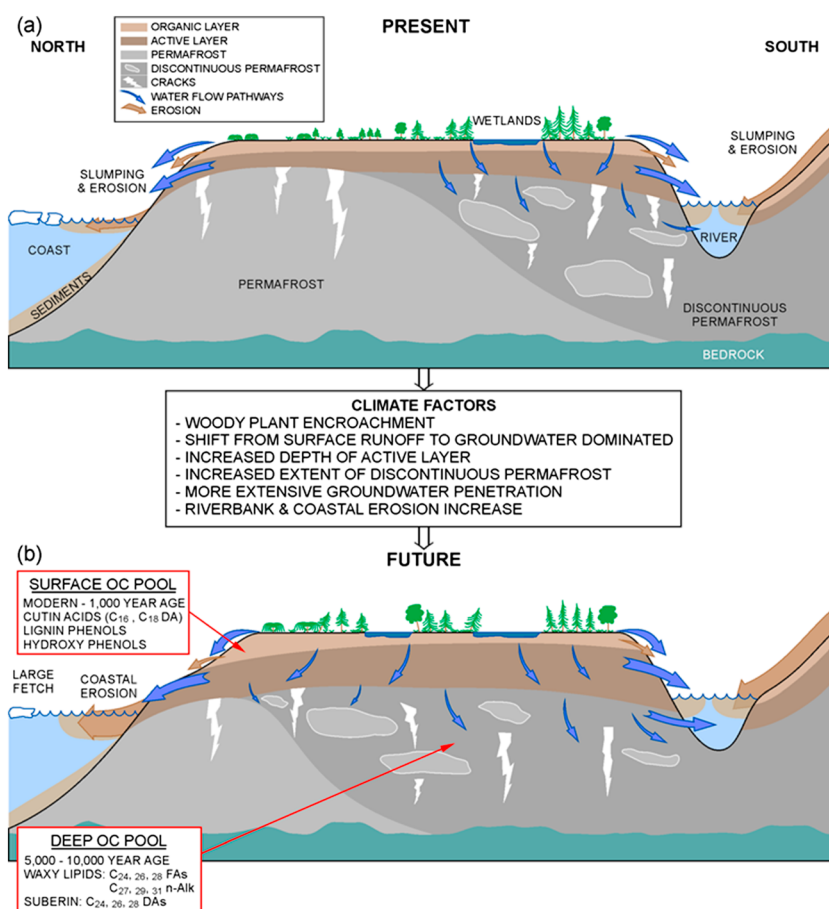
Figure 7. Conceptual scheme of the distribution and mobilization of terrestrial organic carbon (OC) pools in the arctic watersheds (a) at present and (b) in the future. The age of surface and deep OC pools are estimated based on the ^{14}C age of biomarkers analyzed in this study. The surface and deep OC pools are enriched in (and represented by) different biomarkers listed in the red boxes. DA: diacid; FAs: fatty acids; n-Alk: *n*-alkanes.

($C_{24,26,28}$) DAs exhibited much older ^{14}C ages, implying supply from deeper mineral soils or possibly ICD/Yedoma. As DAs are less susceptible to petrogenic influences relative to solvent-extractable *n*-alkanes, their radiocarbon characteristics render them valuable tracers of mobilization of different arctic OC pools. Moreover, the similarity and positive correlation of Δ^{14}C values between $C_{24,26,28}$ DAs and $C_{24,26,28}$ FAs showed across the pan-Arctic further constrains the ages of "old" components of mobilized arctic terrestrial OC pools.

A second contribution of this pan-arctic study is the examination of this broad suite of molecular radiocarbon data in the context of environmental/hydrogeographic controls. A picture has emerged that reveals at least two distinct terrestrial OC pools that are mobilized by different pathways into the Arctic Ocean (Figure 7). While relatively "young" OC (traced by $C_{16,18}$ DAs, lignin, and hydroxy phenols) is mainly supplied by runoff processes from surface layers (including litter, organic horizon, and potentially surface active layers), pre-aged carbon derived from deeper soil horizons (traced by $C_{24,26,28}$ DAs and plant wax lipids) is mobilized by nonlinear processes associated with the permafrost distribution. The radiocarbon signature of these terrestrial components is further influenced by the fresh OC inputs from plants (roots) and degradation processes.

With the predicted warming of the arctic region, it is interesting to speculate how mobilization pathways and associated carbon fluxes may change in the future, and how these changes might manifest themselves, or be detected using the molecular isotopic tracers described in this study. The arctic landmass is anticipated to experience intensified woody encroachment [*Tape et al.*, 2006] and increased river runoff [*Peterson et al.*, 2002; *Pohl et al.*, 2007], which may lead to enhanced production and mobilization of the young, surface OC pool. Meanwhile, deepening of the active layer, increased extent of discontinuous relative to continuous permafrost coverage, and enhanced riverbank and coastal erosion associated with

permafrost degradation [*Romanovsky et al.*, 2007], together with intensified groundwater flow [*Frey and McClelland*, 2009], may conspire to increase the transfer of old, deep OC pools into rivers and the ocean. Hence, while POC export is expected to increase with elevated runoff overall, mixed ^{14}C signals will most likely be tied in with an intensified mobilization of terrestrial OC in the future Arctic. The fate of previously "cryo-locked" carbon upon its entry into the aquatic environment [*Vonk and Gustafsson*, 2013] will further complicate estimates and prediction of the consequences of permafrost carbon release in the face of the climate-induced change [*Schuur et al.*, 2015]. The broad spectrum of radiocarbon contents of different terrestrial OC pools provides a powerful means to attribute source and fate, and (multi)molecular radiocarbon may prove essential for deconvoluting inputs and distinguishing the fate of these various OC pools. The suite of ^{14}C data on terrestrial markers presented here from nine pan-arctic rivers may serve as a benchmark against which to gauge future change. Future investigations on the age as well as distribution of the multitracers in the source materials (litter, soils, Yedoma, etc.) will benefit improved quantification of OC budgets across the arctic watersheds.

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