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Differential mobilization of terrestrial carbon pools in Eurasian Arctic river basins

Shorter title: Terrestrial carbon mobilization in the Arctic

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Abstract

Mobilization of Arctic permafrost carbon is expected to increase with warming-induced thawing. However, this effect is challenging to assess due to the diverse processes controlling the release of various organic carbon (OC) pools from heterogeneous Arctic landscapes. Here, by radiocarbon dating various terrestrial OC components in fluvially- and coastally-integrated estuarine sediments, we present a unique framework for deconvoluting the contrasting mobilization mechanisms of surface versus deep (permafrost) carbon pools across the climosequence of the Eurasian Arctic. Vascular-plant-derived lignin phenol ^{14}C contents reveal significant inputs of young carbon from surface sources whose delivery is dominantly controlled by river runoff. In contrast, plant wax lipids predominantly trace ancient (permafrost) OC that is preferentially mobilized from discontinuous permafrost regions where hydrological conduits penetrate deeper into soils and thermokarst erosion occurs more frequently. As river runoff has significantly increased across the Eurasian Arctic in recent decades, we estimate from an isotopic mixing model that, in tandem with an increased transfer of young surface carbon, the proportion of mobilized terrestrial OC accounted for by ancient carbon has increased by 3-6% between 1985–2004. These findings suggest that, while partly masked by surface-carbon export, climate-change-induced mobilization of old permafrost carbon is well under way in the Arctic.

Keywords: fluvial mobilization | compound-specific ^{14}C | hydrogeographic control

Introduction

Arctic permafrost, storing approximately half of the global reservoir of soil OC (1), is suggested to be highly sensitive to warming-induced perturbation and mobilization (2). While increased respiration of permafrost carbon has recently been documented with warming (3) and thawing (4) in Arctic soils, information on the large-scale mobilization of old carbon deposits via fluvial and coastal processes remains sparse (5, 6). As permafrost thaws, the active layer deepens and landscape structures collapse and erode, potentially releasing OC of older ages from deeper horizons into rivers and/or coastal oceans (2, 5, 7). Alteration in permafrost coverage also affects the availability of various hydrological conduits and thus mobilization pathways of OC associated with different permafrost depths and structures (6, 8). As important processes of carbon dispersal in the Arctic, fluvial transport and erosion are hence sensitive to climatic and hydrological changes (8-12). Furthermore, Arctic rivers provide an integrating perspective on carbon release from various OC pools associated with heterogeneous physiogeographic regimes in corresponding drainage basins (13). The central challenge to detecting climate-induced mobilization of permafrost is to distinguish the aged permafrost carbon among the diverse OC components carried in rivers (ranging from modern vegetation debris and plankton to ancient sedimentary rock) (5, 14, 15) and to separate the effect of warming from other hydrogeographic controls on carbon export from different pools.

Source-tracing organic molecules offer a unique perspective into the fate of specific carbon pools during fluvial and coastal transport (6, 16-19). As the second most abundant biopolymer and rigidifying tissue in terrestrial vascular plants, lignin represents both an excellent tracer and a quantitatively significant fraction of terrestrial OC (20). The radiocarbon age of lignin-derived phenols in sediments potentially provides an additional dimension of information on the source (recent surface OC versus old permafrost OC) and mobilization pathways of higher plant-derived carbon in the Arctic. Furthermore, Arctic soils contain significant carbon inputs from moss-dominated peat (21, 22), which represents 17% of permafrost carbon in the Northern Hemisphere (1). While this carbon pool does not contain lignin, it can be traced by hydroxy phenols (including *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone and *p*-hydroxybenzoic acid) that occur in higher abundances in mosses and peat than in vascular plants (23-25). Here, we examine the radiocarbon signature of lignin-derived and hydroxy phenols in estuarine surface sediments across the Eurasian

Arctic to compare the fate of various terrestrial OC pools transported over continental drainage basin scales and to exploit their ^{14}C signals as tracers for permafrost-carbon mobilization.

Using estuarine sediments as natural integrators of coastal and drainage basin processes, this study includes the estuaries of five Great Russian Arctic Rivers (GRARs: Ob, Yenisey, Lena, Indigirka and Kolyma), extended westward by the Kalix River draining Scandinavia north of the Arctic Circle (Fig. 1). The transect covers a continent-scale climate gradient from west to east (Fig. 2a and Table S1). The three eastern GRARs (Lena, Indigirka and Kolyma) are predominantly located in the continuous permafrost region with a drier and colder climate (26). This contrasts with the two western GRARs (Ob and Yenisey) and the Kalix River, which drain a wetter region rich in peatland and wetlands underlain by discontinuous permafrost (27, 28). These contrasting drainage basin characteristics allow us to investigate the hydroclimatic processes controlling the release and transport of Arctic carbon pools.

Results and Discussion

Contrasting ^{14}C characteristics of terrestrial OC components. We employed a recently modified method (29) to isolate lignin and hydroxy phenols from sedimentary matrices for compound-specific radiocarbon analysis. The radiocarbon content of OC components from estuarine surface sediments affords an average age of terrestrial OC released from the adjacent fluvial drainage basin and via coastal erosion processes. Individual lignin phenols exhibited relatively uniform $\Delta^{14}C$ values (–402 to –367 ‰) in the Indigirka and Kolyma sediments whereas much higher isotopic variability was observed in sediments from the Kalix and Ob (Fig. S1a), implying greater heterogeneity in lignin sources and/or more complex mobilization pathways in the western Eurasian Arctic watersheds. Nevertheless, there was no significant age offset between vanillyl and syringyl phenols in the same estuarine sediments (*t* test; $P > 0.05$; Fig. S1b). Concentration-weighted average $\Delta^{14}C$ values of lignin phenols ranged from –385 to +33 ‰ across the Eurasian Arctic transect, corresponding to conventional radiocarbon ages of 3,800 yr to modern (Fig. 2b). It is noteable that lignin phenols largely follow the trend of bulk OC radiocarbon ages (ranging from 570 to 7,500 yr; Fig. 2b), reflecting the role of lignin as a tracer of a major fraction of terrestrial OC during land-ocean transfer. The age offset between lignin phenols and bulk OC was however substantially higher in the three eastern GRARs (2,000 – 4,000 ^{14}C yr) than in the three western

rivers (< 700 yr; Fig. 2b). As these estuarine sediments have all been shown to be dominated by terrestrial OC with very minor contributions from rock-derived fossil carbon (26, 30), the larger age offsets in eastern GRARs likely reflect the larger contribution of old OC from erosion of the loess-like Yedoma ice complex that is prevalent in East Siberia (5, 13, 31).

Interestingly, the ^{14}C ages of lignin phenols were substantially younger than those of another suite of terrestrial OC tracer compounds, i.e., long-chain higher plant leaf wax lipids (32) [$C_{27,29,31}$ *n*-alkanes and $C_{24,26,28}$ *n*-alkanoic acids ranging from 5500 to 13600 ^{14}C yr in age (6)] previously measured in these sediment samples (Fig. 2b). The $\Delta^{14}C$ offset between lignin phenols and plant wax lipids increased from ~160-180 ‰ in the continuous permafrost region (Kolyma and Indigirka) to ~700 ‰ in the western watershed (Kalix) that has much lower permafrost coverage (Fig. 2a), corresponding to a ^{14}C age offset of up to 13,000 yr (Fig. 2b). The sharply contrasting ^{14}C characteristics suggest varied carbon sources and/or transfer mechanisms for these two groups of higher plant markers. In contrast to lignin, which is enriched in woody debris and coarse soil particles (33, 34), plant wax lipids are closely associated with fine-grained minerals and preferentially stabilized in deep mineral soils (34). Therefore, while plant wax lipids constitute a smaller component of the terrestrial OC (Table S2), their old ^{14}C ages reveal the mobilization of a pre-aged (deep permafrost soil) carbon pool. By comparison, lignin phenols appear to trace relatively recent OC inputs supplied from surface layers (organic and surface soil horizons).

Hydroxy phenols displayed another distinct pattern in their $\Delta^{14}C$ values across the transect, with similar values to lignin phenols observed in two western rivers (–383 and +22 ‰ in Ob and Kalix, respectively) and values lower than lignin phenols but comparable to plant wax lipids in the three eastern GRARs (–529 to –477 ‰; Figs. 2b and S1b). Since wetlands dominated by *Sphagnum* mosses constitute a high proportion of the Ob and Kalix basins (Table S1) (27, 28), hydroxy phenols predominantly record OC inputs from contemporary wetlands in these watersheds and hence bear a similar age to the surface OC pool (represented by lignin phenols). In contrast, East Siberia has a very low wetland coverage (Fig. 2a and Table S1) but stores ancient peat deposits enriched in hydroxy phenols in permafrost soils (2, 13). Such old carbon may be released through cryoturbation, thermokarst and/or bank erosion processes (5, 35), contributing to the older ages of hydroxy phenols relative to lignin phenols in eastern GRARs. These observations suggest that

hydroxy phenols incorporate carbon released from both surface and deep OC pools across the transect.

Hydrogeographic controls on the mobilization of different OC pools. In accordance with the above interpretations, mobilization of each carbon pool is mediated by different physiogeographic and hydrological variables across the drainage basins (Figs. 2a and S2; Table S1). Among the investigated physiogeographic variables, runoff exerts a strong control on the $\Delta^{14}C$ values of lignin phenols across the Eurasian Arctic ($P < 0.01$; $R^2 = 0.92$; Figs. 3a) where younger lignin is transported by rivers with a higher mean annual runoff rate. This correlation is consistent with the efficient delivery of vascular plant debris during storm, flood and high-precipitation events (36-38), suggesting increased transfer of surface detrital carbon in high-runoff systems. It is noteable that at zero runoff rate (representing extreme base flow with minimum detrital input), regression analysis yields an end member $\Delta^{14}C$ value of –655 ‰ for lignin phenols, similar to that of plant wax lipids in the westernmost (Kalix) estuary. Assuming that surface detrital carbon has decadal turnover times in the high latitudes (39, 40), and hence a $\Delta^{14}C$ value of +100 to +200 ‰, while deep soil-derived lignin has a $\Delta^{14}C$ value of –655 ‰, we estimate from a binary mixing model (Table S3) that ~30-90 % of mobilized lignin across the Eurasian Arctic reflects modern carbon sources.

In contrast, the $\Delta^{14}C$ values of plant wax lipids are most strongly correlated with the watershed coverage of continuous permafrost ($P < 0.01$; $R^2 = 0.86$; Fig. 3b) but not with runoff ($P = 0.85$; Fig. S2), consistent with enhanced mobilization of deep, old permafrost carbon in discontinuous permafrost systems. This phenomenon may be associated with multiple processes. As continuous permafrost shifts to more discontinuous or sporadic permafrost regimes westward in the transect, more hydraulic conduits are accessible in the deep soil (Figs. 1b–c), leading carbon pools that are enriched in lipids relative to lignin. Moreover, thermokarst and thermal erosion processes potentially increase from perennially-frozen regions to warmer, seasonally-frozen zones (12, 41), enabling faster mobilization of deep OC from river banks and coastlines. While erosion may also play a part in releasing lignin-rich OC from surface layers, its effect seems to be dwarfed by surface runoff processes as neither temperature nor permafrost coverage is correlated with the lignin age (Fig. S2). Hence, transport of younger lignin is enhanced in the river with the

highest runoff rate (Kalix; Fig. 2a), leading to a larger age offset between lignin phenols and plant wax lipids towards the west end of the transect (Fig. 2b).

By comparison, corresponding $\Delta^{14}C$ values for hydroxy phenols were best correlated with the wetland coverage in the drainage basin ($P < 0.01$; $R^2 = 0.86$; Fig. 3c), and to a lesser degree, with the mean annual runoff rate ($P = 0.03$; $R^2 = 0.74$; Fig. 3d). This suggests that contemporary wetlands are the main source of modern hydroxy phenols across the Eurasian Arctic, whose delivery from surface litter and soil layers is, similar to lignin phenols, influenced by runoff processes. Moreover, in the $\Delta^{14}C$-runoff correlation plot (Fig. 3d), the hydroxy-phenol $\Delta^{14}C$ values of four eastern rivers all fall below the general trend line (black line) and have a much flatter slope against the runoff rate (blue line; $P < 0.05$; $R^2 = 0.81$). This suggests that surface runoff is less efficient in supplying modern hydroxy phenols in the watersheds with a low wetland coverage, where inputs of old hydroxy phenols from deeper soils are prominent.

Contribution of surface and deep permafrost carbon to bulk sedimentary OC. Our molecular radiocarbon data show that detrital carbon from recent vegetation and surface organic layers is a key component of the mobilized terrestrial carbon in the Eurasian Arctic that accumulates in estuarine sediments. To evaluate the magnitude of permafrost-carbon release, we need to first assess the contribution of surface and deep permafrost carbon pools to the bulk OC. Clearly, this is complicated due to inputs from other organic components [such as black carbon (42, 43) and planktonic carbon (5)], as underlined by the age difference of bulk OC relative to the terrestrial markers in Lena, Ob and Yenisey sediments (Fig. 2b). Assuming that hydroxy phenols incorporate the isotopic signal of terrestrial biospheric carbon derived from both surface and deep carbon sources while the $\Delta^{14}C$ values of lignin phenols and plant wax lipids represent the integrated radiocarbon signal of mobilized surface and deeper permafrost OC pools in each watershed, respectively, we estimate from a binary mixing model that 47-77 % of terrestrial biospheric carbon originates from deeper permafrost in the four eastern river basins (where modern wetland carbon contribution is small; Table S4). This estimate likely represents a lower limit as the surface OC end member (lignin) also incorporates a significant amount of pre-aged OC from surface soil horizons. Nonetheless, it implies that over half of the sedimentary OC in East Siberian estuaries originates from a previously stabilized or ancient soil pool, consistent with a recent estimate that 36-76 % of

sedimentary OC in the East Siberian Arctic Shelf is derived from erosion of Pleistocence Yedoma (5).

During the second half of the twentieth century, Eurasian Arctic river runoff increased at an average rate of approximately 0.60 – 0.74 mm/yr per year (44-46), likely increasing the delivery of surface-derived OC into estuaries. Based on the relationship between lignin phenol $\Delta^{14}C$ values and runoff ($\Delta^{14}C$ = 1.6018 × runoff – 655; Fig. 3a), the $\Delta^{14}C$ value of mobilized surface OC has increased by approximately 19 – 24 ‰ from 1985 to 2004, not considering the variation of bomb-derived ^{14}C in the atmosphere. This time window corresponds to the sediment-deposition time of 20 years, based on the surface sediment depth and sedimentation rate in the region (5). Assuming that the ^{14}C signals of exported OC have remained similar during this period and that the endmember $\Delta^{14}C$ value of deep permafrost OC has not altered, we estimate that the proportion of ancient OC in the total terrestrial carbon pool has increased by 3-6% in four eastern GRAR sediments (Table S4) over this period of time. When we assume that particulate organic carbon (POC) fluxes in these rivers (Table S1) are dominantly terrestrial in origin (26, 30), the 20-year increase is equivalent to approximately 1.4 Tg C transferred from old permafrost into estuarine sediments. While this number represents a rough estimate and is relatively small as compared to some other Arctic carbon fluxes (47), release of dissolved organic carbon (23, 47, 48) and water-column mineralization of POC (5, 49) associated with permafrost thawing may well exceed the size of this sediment OC budget in the context of a changing climate. Our estimate represents a conservative scenario as sedimentary $\Delta^{14}C$ values are postulated to further decrease with warming. Furthermore, particle transit time, albeit not well constrained, is likely to be longer than a few decades in these rivers, given the residence time of suspended sediments in large meandering rivers [~17 kyr in the Amazon River (50)] and woody debris in small mountainous rivers [~20 yr (51)]. The young terrestrial OC components mobilized into these sediments from 1985 to 2004 were hence likely derived from materials deposited in the surface layers before the 1980s and had an even larger increase in $\Delta^{14}C$ values due to the incorporation of bomb-derived ^{14}C into surface decadal OC pools (40). These calculations suggest that the magnitude of permafrost-carbon release, which may be masked or muted by other Arctic OC pools, is relevant on regional to continental scales.

Implications for Arctic carbon cycling. Our results reveal marked age offsets between different terrestrial OC pools released from Arctic landscapes, which stands in contrast with some temperate and tropical systems where terrestrial OC components are retained on land for a similar period of time [such as the Columbia River (29)]. These findings highlight the linkage between carbon cycling and hydrological processes, which is particularly close in Arctic landscapes where surface and groundwater flows access different pools of carbon depending on the spatial distribution of permafrost. Surface runoff appears to control the release of a major component of terrestrial carbon while deep hydraulic conduits and bank/coastal erosion may mobilize very old permafrost carbon at depth. This observation reveals an important caveat in deriving OC budgets or reconstructing past carbon dynamics in the Arctic system based on bulk sedimentary OC properties as endmember values may vary substantially due to the release of significantly pre-aged soil carbon. Molecular-level ^{14}C measurements enable constraints to be placed on the relative contribution of surface and deep permafrost carbon pools to Arctic fluvial export. Unravelling such hydrogeographic controls on the differential delivery of Arctic carbon pools is key to unmasking warming effects on permafrost-carbon release. As such, our data suggest that export of old deep permafrost OC as a consequence of recent climate variations may be underestimated and masked by the synoptic increase in the transport of young surface OC associated with enhanced river runoff in the Arctic. The ability to differentiate and separately trace mobilized carbon pools across the Arctic will aid in refining both our understanding of the contemporary system and our ability to predict linkages between a warming climate and the mobilization of Arctic permafrost carbon.

Materials and Methods

Study area. The three eastern GRARs (Lena, Indigirka and Kolyma) drain into the Laptev Sea (Lena) and the East Siberian Sea (Indigirka and Kolyma; Fig. 1a). The climate in the drainage basin is semiarid to arid with average summer temperatures between +7 °C and +9 °C and winter temperatures below −40 °C. This contrasts with the two western GRARs (Ob and Yenisey) located in the west Siberian lowland and Kalix River that drains sub-Arctic Scandinavia into the Baltic Sea. The drainage basins have average summer temperatures comparable to northeastern Eurasia but much higher winter temperatures (around −20 °C) (28) and are wetter, with higher precipitation-to-evaporation ratios compared to eastern GRARs. All rivers have comparable drainage-area-

normalized fluxes of total organic carbon (TOC) and POC (Table S1) (27, 52). A more detailed description of the river drainage basins is provided elsewhere (26, 30). 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 (5, 26). 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 (26, 30).

Bulk analyses. Bulk sediments were kept frozen at −20 °C after collection and freeze-dried prior to analysis. A small aliquot was used for TOC and bulk $\delta^{13}C$ analyses at the UC Davis Stable Isotope Facility (http://stableisotopefacility.ucdavis.edu) and for bulk $\Delta^{14}C$ analysis at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution.

Isolation and ^{14}C analysis of individual compounds. As described previously (6), lipids were extracted from freeze-dried sediments (~30-70 g) using soxhlet extraction with dichloromethane/methanol (2:1; 24 h). Plant wax *n*-alkanes and *n*-alkanoic acids were isolated using preparative capillary gas chromatography (PCGC) and analyzed for ^{14}C content. The solvent-extracted residues were further hydrolyzed with 1 M KOH in methanol (100 °C, 3 h) to remove hydrolysable lipids. The dried residues were then subjected to alkaline CuO oxidation to release lignin and hydroxy phenols on a microwave system (MARS, CEM Corporation) (53). 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 each of 5-8 vessels containing sediments (3-10 g) with ~50 mg of TOC. Vessels containing all reagents but no sample were also included as procedural blanks along with each batch of sediments.

For compound-specific radiocarbon analysis, phenolic compounds were isolated using a high pressure liquid chromatography (HPLC)-based method (SI Methods and details in ref. 29). Briefly,

the CuO oxidation extracts were purified through two solid phase extraction (SPE) cartridges (Supelco Supelclean ENVI-18 and Supelclean LC-NH_2 SPEs) and separated through two HPLC-isolation steps consisting of a Phenomenex Synergi Polar-RP column and a ZORBAX Eclipse XDB-C18 column. Approximately 10-150 μg C of individual phenols were collected using a fraction collector, yielding purities > 99%. Procedural blanks were processed in the same manner for subsequent blank corrections.

Purified phenols 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) were sent to NOSAMS, graphitized, and measured on accelerator mass spectrometry (AMS). A second batch of CO_2 samples (~10-32 μg C) were directly measured without graphitization on the miniaturised radiocarbon dating system (MICADAS) at ETH Zürich using a gas feeding system (54). Radiocarbon contents are reported as $\Delta^{14}C$ (‰) and conventional ^{14}C age. Procedural blanks associated with the extraction-HPLC-combustion procedures yielded 2.5 ± 0.8 μg C with an F_m value of 0.21 ± 0.07 (n=5). All radiocarbon values are corrected for procedural blanks with the errors propagated. We did not observe significant difference between radiocarbon contents of the same sample measured at the two AMS facilities.

Binary mixing model. We employed a ^{14}C binary mixing model to assess the relative contributions of surface OC (Table S3) and permafrost OC (Table S4) to lignin or hydroxy phenols, respectively. The model is expressed in the following two equations:

$$f_S\,(\Delta^{14}C_S) + f_P\,(\Delta^{14}C_P) = \Delta^{14}C_{phenol} \quad [1]$$

$$f_S + f_P = 1 \quad [2]$$

where f is the percentage of surface or permafrost OC and the subscripts S and P refer to surface and permafrost, respectively.

Modeling and statistical analysis. A *T* test was used to compare the ^{14}C content of different phenols. Differences are considered to be significant at a level of $P < 0.05$. Linear regression analysis was used to assess the correlation between drainage basin characteristics and the ^{14}C content of terrestrial OC markers (Fig. S2). The main drainage basin parameters investigated as explanatory variables include basin area, runoff rate, mean annual summer cumulative temperature

(ASCT) and the coverage of forest, wetland and continuous permafrost in the watershed (Table S1). ASCT is calculated as the sum of mean monthly temperature for months with a mean temperature above 0°C within a year (details in SI Methods and Fig. S3) and is considered to have a major impact on permafrost thawing (55). POC flux and discharge are found to be correlated with continuous permafrost coverage ($P < 0.05$; $R^2 = 0.85$) and basin area ($P < 0.05$; $R^2 = 0.84$) respectively, and are hence not included as basin parameters in the ^{14}C correlation analyses. Correlation is 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.

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Author Contributions

X.F., T.I.E. and Ö.G. conceived the idea of using molecular ^{14}C analyses to deconvolute environmental effects on the release of terrestrial carbon pools across Eurasian Arctic. J.E.V., B.E.v.D., Ö.G., I.P.S. and O.V.D. collected samples. B.E.v.D. and J.E.V. prepared samples for bulk organic carbon analyses, stable isotope analysis and radiocarbon analyses (sediments). X.F. conducted compound-specific radiocarbon analysis of lignin and hydroxy phenols with assistance of

D.B.M. Radiocarbon analyses were facilitated by T.I.E. Z.W. and X.F. performed modeling and data analyses. X.F. wrote the paper, with input from all other authors.

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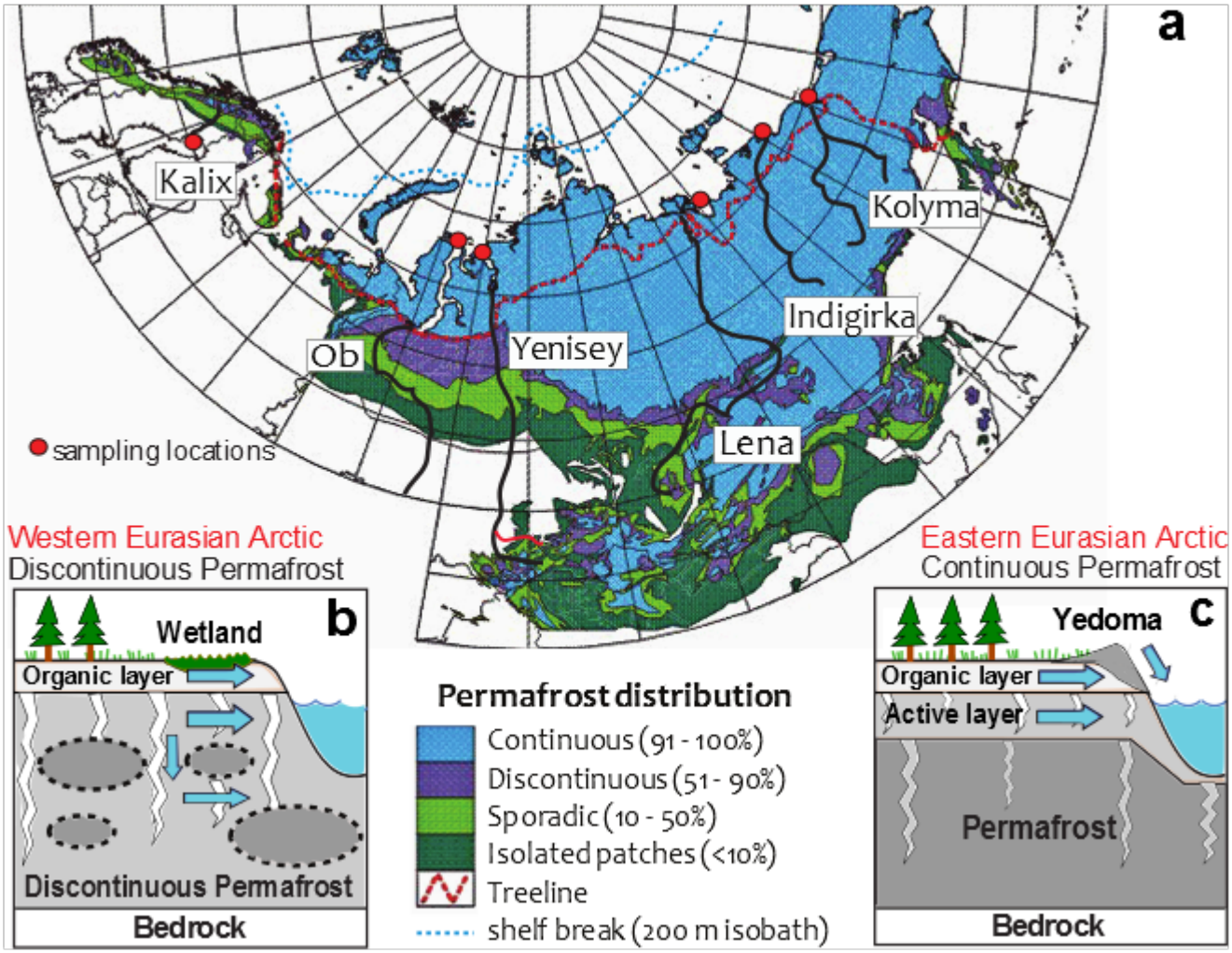
Figure Legends

Figure 1: The Eurasian Arctic transect and cartoon of hydrological mobilization of terrestrial carbon into rivers. (a) Map of the rivers (black lines) with permafrost distribution (modified from refs. 1 and 6) and sampling locations (red circles); (b) illustration of the western Eurasian Arctic characterized by extensive moss-dominated wetlands underlain by discontinuous permafrost and ubiquitous deep groundwater conduits; (c) illustration of eastern Eurasian Arctic characterized by a wide distribution of Yedoma ice complex, a thin seasonally thawing active layer and thick continuous permafrost below. Blue arrows indicate hydrological transport of carbon from different physiogeographic regimes.

Figure 2: Hydrogeographic characteristics of the Eurasian Arctic rivers (a) and contrasting radiocarbon contents (expressed as $\Delta^{14}C$ and conventional ^{14}C age) of terrestrial markers as compared with bulk organic carbon (OC) in the estuarine surface sediments (b). Runoff rate = discharge/basin area. Detailed hydrogeographic data are listed in Table S1 [compiled from refs. 6, 9, 27, 52 and "watersheds of the world" (http://archive.wri.org)]. The $\Delta^{14}C$ values of terrestrial markers represent concentration-weighted averages with the standard errors of analytical measurement propagated. Lignin phenols refer to vanillyl and syringyl phenols (detailed data in Fig. S1). Hydroxy phenols refer to *p*-hydroxybenzaldehyde, *p*-hydroxyacetophenone and *p*-hydroxybenzoic acid. Plant wax lipids constitute *n*-alkanes ($C_{27,29,31}$) and *n*-alkanoic acids ($C_{24,26,28}$) (6).

Figure 3: Hydrological and physiogeographic controls on the age of terrestrial markers in the integrating Eurasian Arctic estuaries: correlation of (a) $\Delta^{14}C_{\text{lignin phenols}}$ with runoff rate; (b) $\Delta^{14}C_{\text{plant wax lipids}}$ with continuous permafrost coverage; (c) $\Delta^{14}C_{\text{hydroxy phenols}}$ with wetland coverage; (d) $\Delta^{14}C_{\text{hydroxy phenols}}$ with runoff rate. The blue dotted line in (d) represents linear correlation for the data of four eastern rivers ($P < 0.05$; $R^2 = 0.81$). *Runoff rate = discharge/basin area. Contents of terrestrial markers are defined in Fig. 2. Further statistical analyses can be found in Fig. S2.

511 Figure 1



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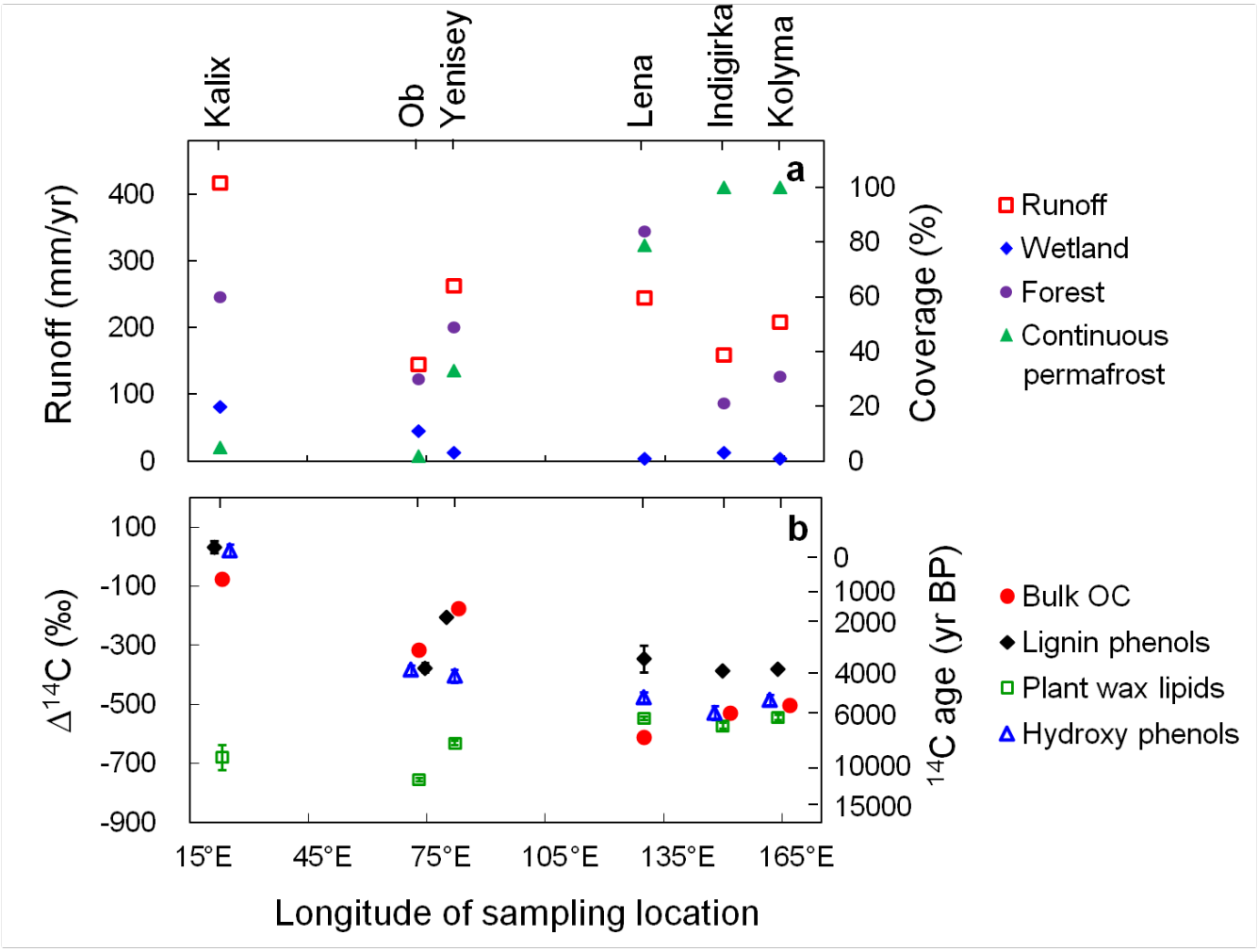
514 Figure 2



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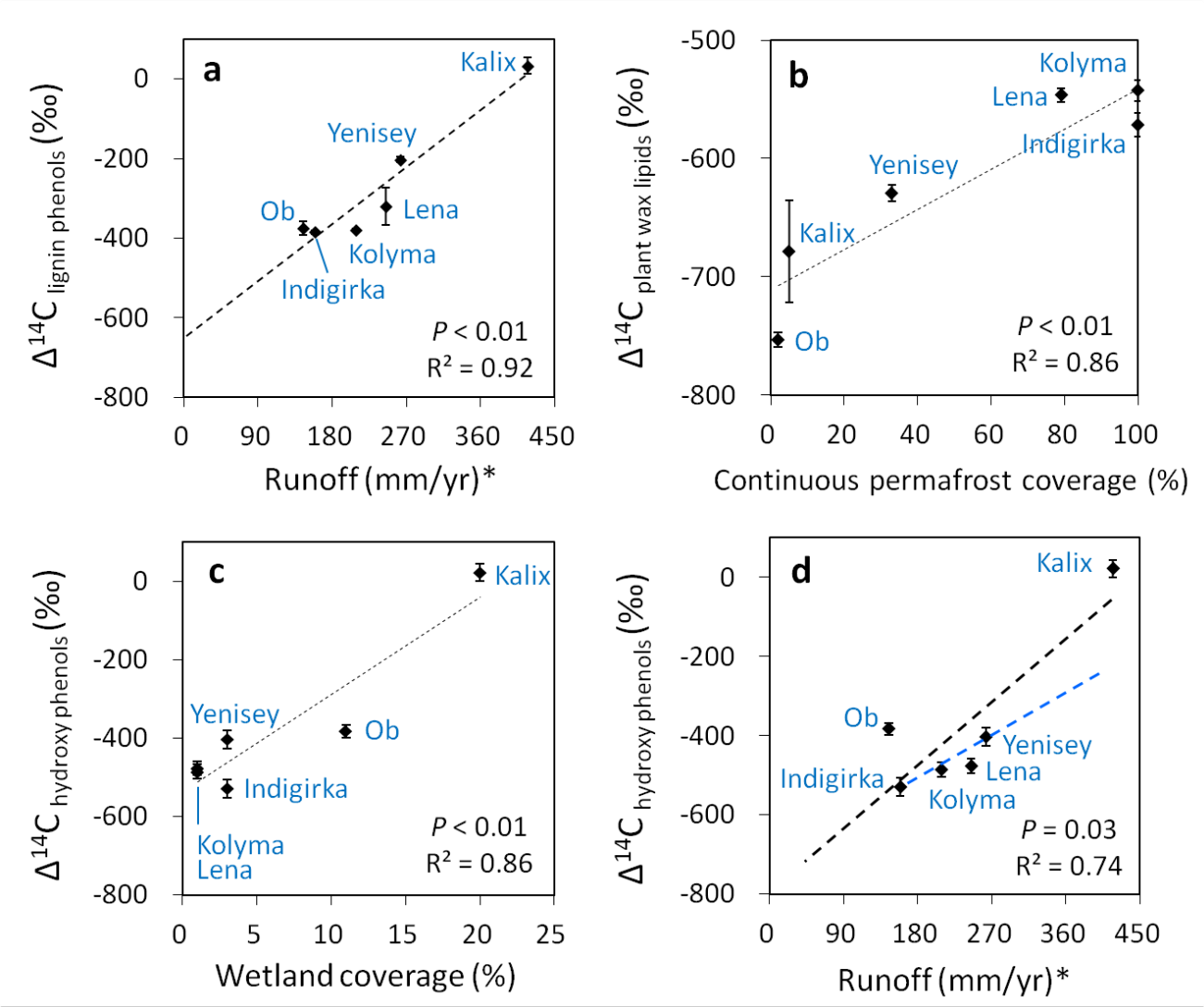
517 Figure 3



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Supporting Information

SI Methods

Isolation of lignin phenols for ^{14}C analysis. Details of the method are provided in ref. (1). Briefly, the CuO oxidation products (in ethyl acetate) were blown carefully to < 100 µL under N_2, re-dissolved in water (pH 2) and loaded onto a Supelclean ENVI-18 solid phase extraction (SPE) cartridge (Supelco, pre-conditioned with methanol and water). Lignin oxidation products were eluted with acetonitrile from the ENVI-18 SPE cartridge, blown under N_2 to a volume of < 0.5 mL and further separated on a self-packed amino SPE cartridge (0.5 g, Supelclean LC-NH_2, Supelco, preconditioned with methanol) into phenolic aldehyde/ketone (eluting in methanol) and their corresponding acid (eluting with methanol:12 M HCl, 95:5) fractions. Each fraction was blown carefully to < 100 µL under N_2 and re-dissolved in methanol for separation on an Agilent 1200 HPLC system coupled to a diode array detector (DAD) and a fraction collector. Individual phenols were collected through two HPLC-isolation steps consisting of a Phenomenex Synergi Polar-RP column (4 µm; 4.6 × 250 mm) with a Polar-RP SecurityGuard column (4 µm; 4.0 × 3.0 mm) and a ZORBAX Eclipse XDB-C18 column (5 µm; 4.6 × 150 mm) with a ZORBAX Eclipse C18 guard column (5 µm; 4.6 × 12.5 mm). The column temperature was maintained at 28 °C and a binary gradient of water/acetic acid (99.8:0.2) and methanol/acetonitrile (50:50) was used as mobile phases (flow rate of 0.8 mL/min; details in ref. 1). A total of 5 injections (in most cases; and 10 injections for phenols > 150 µg) were conducted for each sample to collect approximately 20-300 µg of each phenol (i.e., ~10 – 150 µg C) for ^{14}C measurement. After isolation, phenols were recovered from the aqueous mobile phase through extraction with ethyl acetate at pH 2 and eluted from a 5% deactivated SiO_2 column using ethyl acetate to remove potential column bleed. A small aliquot of purified phenols was derivatized with N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine to check compound purity by gas chromatography-mass spectrometry, and was found to yield purities > 99%. Purified phenols were transferred into pre-combusted quartz tubes in ethyl acetate and blown dry carefully under a gentle stream of N_2, with the addition of pre-combusted CuO afterwards. The quartz tubes were evacuated on a vacuum line while immersed in an isopropanol/dry ice slush (–78 °C), flame sealed, and combusted at 850 °C for 5 h. The resulting CO_2 was cryogenically purified and quantified by expansion into a calibrated volume. The procedural blanks were processed in the same manner.

Regional temperature data. Mean monthly temperatures (T_m) recorded at climatic stations in the six watersheds (Fig. S3) from 1955 to 2004 were obtained from the Global Historical Climatology Network Monthly (GHCN-M, v.3; http://www.ncdc.noaa.gov/ghcnm/). In total, 102 climatic stations were identified within the GRAR watersheds (Fig. S3). No climatic station within the Kalix drainage basin was found in the GHCN-M database. The five closest stations within 110 km from the watershed boundary were hence selected. Similarly, GHCN-M database recorded only two climate stations within the Indigirka watershed. To increase the reliability of the Indigirka climatic data, we selected another three stations within 250 km from the watershed boundary.

We used annual summer cumulative temperature (ASCT) as a key temperature variable because summer temperatures are considered to have a major impact on permafrost thawing (2) and experience more variations than mean annual temperture (MAT) during recent climate change (3). The value of ASCT is given by the sum of mean monthly temperatures (T_m) for months with a T_m above 0°C each year and is thus related to the "thawing index" (4). ASCT from 1985 to 2004 was calculated for each station separately and then averaged to represent the entire watershed.

SI Tables

Table S1: Sample location, drainage basin characteristics and bulk sediment properties of the Great Russian Arctic Rivers (GRARs) and Kalix River

	Kalix	**Ob**	**Yenisey**	**Lena**	**Indigirka**	**Kolyma**
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-71.02°N; 132.60°E*	72.06°N; 150.46°E	70.00°N; 163.70°E
Geological and physiographic regions†	Scandinavian mountains	West Siberian lowlands	West Siberian lowlands	Central Siberian plateau	East Siberian highlands	East Siberian highlands
Mean ASCT (1985 ‡– 2004; °C)	53.7	87.4	65.4	57.9	40.7	47.9
Forest coverage (%)§	60	30	49	84	21	31
Wetland coverage (%)§	20	11	3	1	3	1
Permafrost coverage¶	5/15/80	2/24/74	33/55/12	79/20/1	100/0/0	100/0/0
Basin area (10^6 km^2)‖	0.024	2.54-2.99	2.44-2.59	2.40-2.49	0.34-0.36	0.65-0.66
Discharge (km^3/yr)**	10	427	673	588	54	136
Runoff (mm/yr)**	417	145	263	245	159	209
TOC/POC flux (t km^{-2} yr^{-1})††	1.4/0.099	1.1/0.14	1.8/0.066	1.9/0.49	1.2/0.47	1.5/0.48
OC (%)	4.5	0.9	1.9	0.5	1.5	1.7
OC/N‡‡	10.9 ± 0.3	10.0 ± 0.1	10.5 ± 0.1	12.3 ± 0.8	14.7 ± 0.2	15.9 ± 1.2
δ^{13}C-TOC (‰)	–27.1	–27.4	–26.5	–25.0	–26.6	–26.7
Δ^{14}C-TOC (‰)§§	–74 ± 37	–314 ± 3	–175 ± 3	–609 ± 3	–527 ± 3	–502 ± 2
^{14}C age of TOC (yr BP)§§	570 ± 250	3000 ± 35	1500 ± 30	7500 ± 60	6000 ± 50	5600 ± 50

* Combined surface sediments along a transect;
† According to ref. (5);

‡ ASCT: annual summer cumulative temperature, calculated as the sum of mean monthly temperature for months with a mean temperature above 0°C within a year, temperature data derived from the Global Historical Climatology Network Monthly (GHCN-M) database.
§ Data from ref. (6) and "Watersheds of the world" (http://archive.wri.org);
¶ Given as % continuous; % (discontinuous+sporadic+isolated); % non-permafrost (7, 8);
‖ Data from refs. (6, 9-11);
** Data from refs. (6, 8, 12);
†† Kalix data from ref. (6), GRAR data from ref. (12);
‡‡ Mass ratio of OC to total nitrogen (13, 14);
§§ Measured in 2006; values normalized for the year of measurement; BP: before present.

Table S2: Abundance of terrestrial OC markers in the estuarine surface sediments (mg/g OC) of the Great Russian Arctic Rivers (GRARs) and Kalix River

	Kalix	Ob	Yenisey	Lena	Indigirka	Kolyma
Lignin phenols*	**14.35**	**13.36**	**11.15**	**11.41**	**21.37**	**22.78**
vanillin	4.06	3.11	2.94	3.64	4.58	5.17
acetovanillone	2.04	1.80	1.76	2.30	3.68	3.38
vanillic acid	2.34	2.35	2.38	2.78	3.62	3.69
syringaldehyde	1.73	2.51	1.75	1.13	3.90	4.20
acetosyringone	0.75	1.06	0.58	0.32	1.55	1.75
syringic acid	1.42	1.45	0.87	0.67	2.16	2.60
p-coumaric acid	1.60	0.56	0.52	0.40	0.78	0.93
ferulic acid	0.41	0.52	0.34	0.18	1.11	1.05
Hydroxy phenols*	**6.73**	**4.13**	**2.90**	**3.67**	**4.37**	**4.80**
p-hydroxybenzaldehyde	2.92	1.02	0.75	0.99	0.90	0.93
p-hydroxyacetophenone	1.32	0.75	0.43	0.50	0.44	0.81
p-hydroxybenzoic acid	2.49	2.36	1.72	2.18	3.03	3.06
Plant wax lipids†	**0.44**	**0.91**	**0.62**	**0.44**	**1.22**	**1.17**
$C_{27,29,31}$ *n*-alkanes†	0.16	0.76	0.48	0.28	0.91	0.65
$C_{24,26,28}$ *n*-alkanoic acids†	0.28	0.15	0.14	0.16	0.31	0.52

* Lignin and hydroxy phenols were measured on GC/MS as trimethylsilyl derivatives of CuO oxidation products;

† Plant wax lipids refer to the summary of $C_{27,29,31}$ *n*-alkanes and $C_{24,26,28}$ *n*-alkanoic acids measured previously (13, 14).

Table S3: Average $\Delta^{14}C$ values of lignin phenols in estuarine surface sediments of the Great Russian Arctic Rivers (GRARs) and Kalix River and contributions of modern surface OC to lignin estimated from the ^{14}C binary mixing model

	Kalix	**Ob**	**Yenisey**	**Lena**	**Indigirka**	**Kolyma**
Average $\Delta^{14}C$ of lignin phenols (‰)*	+33 ± 21	–375 ±17	–203 ± 7	–320 ± 46	–385 ± 4	–379 ± 3
Percentage of modern surface OC in lignin (%)						
When $\Delta^{14}C_S$ = +100 ‰, $\Delta^{14}C_P$ = –655 ‰†	91 ± 3	37 ± 2	60 ± 1	44 ± 6	36 ± 1	37 ± 1
When $\Delta^{14}C_S$ = +200 ‰, $\Delta^{14}C_P$ = –655 ‰†	80 ± 3	33 ± 2	53 ± 1	39 ± 6	32 ± 1	32 ± 1

* Abundance-weighted average values with errors propagated, original values in Fig. S1;

† $\Delta^{14}C_S$ and $\Delta^{14}C_P$ refer to the $\Delta^{14}C$ value of surface and permafrost OC, respectively; the $\Delta^{14}C_P$ value is estimated from the regression relationship between lignin phenol $\Delta^{14}C$ values and runoff rate (Fig. 3a).

Table S4: Average $\Delta^{14}C$ values of terrestrial OC pools (represented by different groups of markers) and contributions of surface versus deep permafrost OC to terrestrial biospheric OC in surface sediments of the Great Russian Arctic Rivers (GRARs) and Kalix River in 2004 and 1985

	Kalix	**Ob**	**Yenisey**	**Lena**	**Indigirka**	**Kolyma**
Average $\Delta^{14}C$ value of terrestrial biospheric OC (represented by hydroxy phenols)*	+22 ± 22	–383 ±15	–404 ± 23	–477 ± 18	–529 ± 23	–486 ± 18
Current budget (2004)						
Average $\Delta^{14}C$ value of terrestrial OC pools (‰)						
Surface-dominated OC (represented by lignin phenols)*	+33 ± 21	–375 ±17	–203 ± 7	–320 ± 46	–385 ± 4	–379 ± 3
Deep-permafrost-dominated OC (represented by plant wax lipids)†	–679 ± 43	–753 ± 6	–630 ± 7	–546 ± 6	–571 ± 10	–543 ± 9
Contribution of OC pools (%)‡						
Surface OC	98 ± 2	98 ± 2	53 ± 5	31 ± 8	23 ± 13	35 ± 11
Deep permafrost OC	2 ± 2	2 ± 2	47 ± 5	69 ± 8	77 ± 13	65 ± 11
Budget of the past (1985)						
Average $\Delta^{14}C$ value of terrestrial OC pools (‰)						
Surface-dominated OC (represented by lignin phenols)§	+9 ± 21	–399 ±17	–227 ± 7	–344 ± 46	–404 ± 4	–403 ± 3
Deep-permafrost-dominated OC (represented by plant wax lipids)§	–679 ± 43	–753 ± 6	–630 ± 7	–546 ± 6	–571 ± 10	–543 ± 9
Contribution of OC pools (%)‡						
Surface OC	nc¶	nc¶	56 ± 5	34 ± 8	25 ± 13	41 ± 11
Deep permafrost OC	nc¶	nc¶	44 ± 5	66 ± 8	75 ± 13	59 ± 11

* Abundance-weighted average values with errors propagated, original values in Fig. S1;

† Original values of long-chain *n*-alkanes and *n*-alkanoic acids from ref. (7);

‡ Estimated from the ^{14}C binary mixing model (Eq. 1), where the $\Delta^{14}C$ value of terrestrial biospheric OC is represented by that of hydroxyl phenols (derived from both surface OC and deep permafrost) while surface and deep permafrost end member values ($\Delta^{14}C_S$ and $\Delta^{14}C_P$) equal those of lignin phenols and plant wax lipids in each basin, respectively. Hence, $f_{surface} = (\Delta^{14}C_{hydroxy\ phenols} - \Delta^{14}C_{plant\ wax\ lipids})/(\Delta^{14}C_{lignin\ phenols} - \Delta^{14}C_{plant\ wax\ lipids})$.

§ Based on the linear relationship between lignin phenol $\Delta^{14}C$ values and runoff ($\Delta^{14}C = 1.6018 \times runoff - 655$; Fig. 3a) and the runoff increasing rate of approximately 0.60 (Indigirka) to 0.74 mm/yr per year (the other GRARs) from 1964-2000 in Eurasian Arctic rivers (15, 16), lignin phenol $\Delta^{14}C$ values are estimated to be lower by 19‰ (0.60 mm/yr per year × 20 years × 1.6018 ‰/(mm/yr) for Indigirka) to 24‰ (0.74 mm/yr per year × 20 years × 1.6018 ‰/(mm/yr) for the other big GRARs) in 1985 as compared with those measured in 2004 (not considering the dilution of bomb ^{14}C in the atmosphere). The $\Delta^{14}C$ values of plant wax lipid and hydroxy phenols are assumed to remain the same as in 2004.

¶ Past OC contribution in Kalix and Ob is not calculated (nc) because the estimated $\Delta^{14}C$ values of surface OC (lignin phenols) are lower than those of terrestrial biospheric OC (hydroxy phenols).

SI Figures

Figure S1: The $\Delta^{14}C$ values of (a) individual lignin phenols and (b) individual hydroxy phenols as 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 offset in the average $\Delta^{14}C$ values between vanillyl and syringyl phenols from the same estuarine sediment (*t* test; $P > 0.05$).

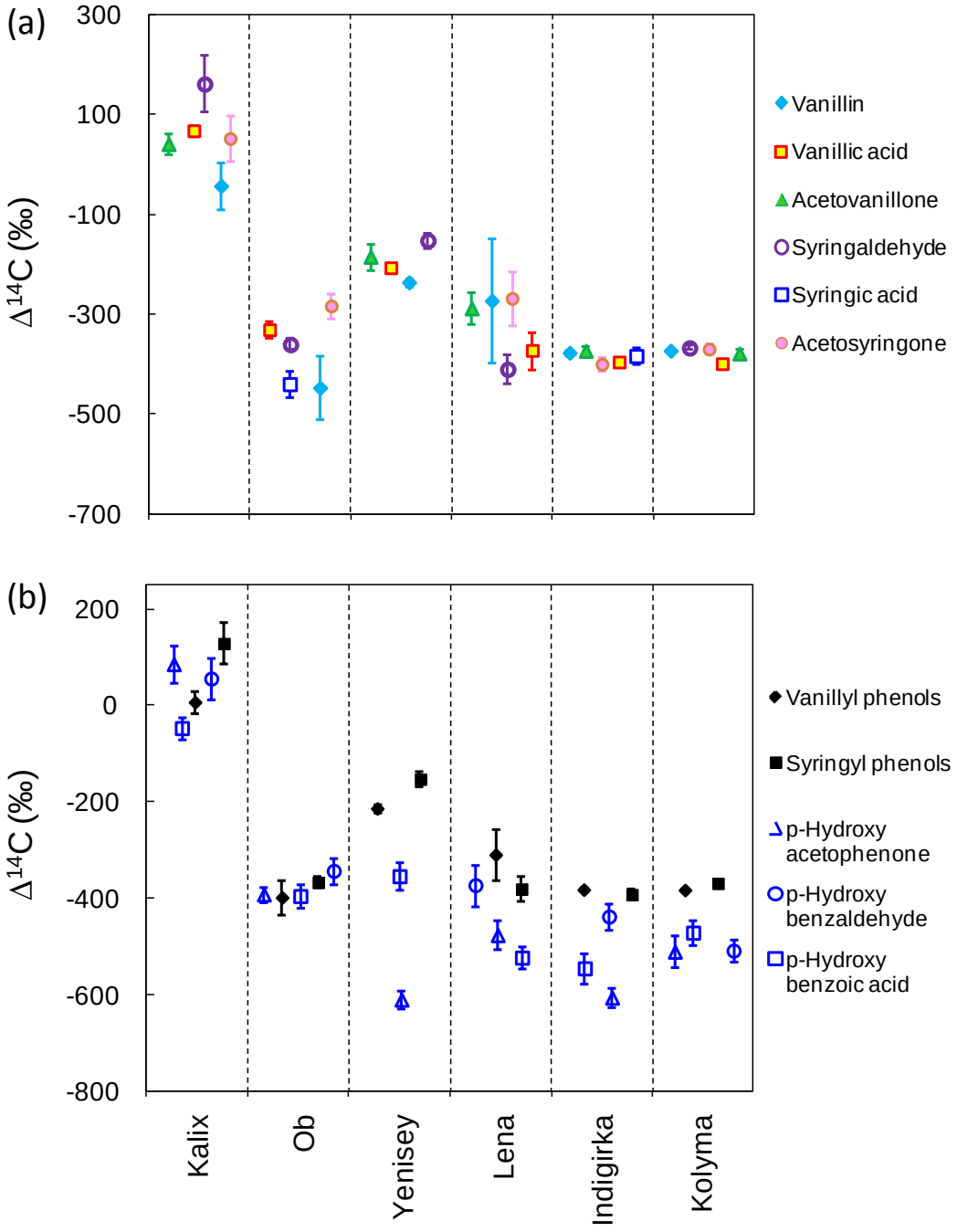


Figure S2: Correlation between drainage basin characteristics and the $\Delta^{14}C$ values of terrestrial markers. Error bars represent propagated standard error of analytical measurement. *Linear correlation is considered to be significant at a level of $P < 0.05$ and the R^2 values are used to compare the explanatory power of the variables. †Continuous permafrost coverage. Note that runoff, continuous permafrost and wetland coverage best explain the ^{14}C age of lignin phenols, plant wax lipids and hydroxy phenols across the Eurasian Arctic, respectively. ASCT: annual summer cumulative temperature (for months with a mean temperautre above 0°C).

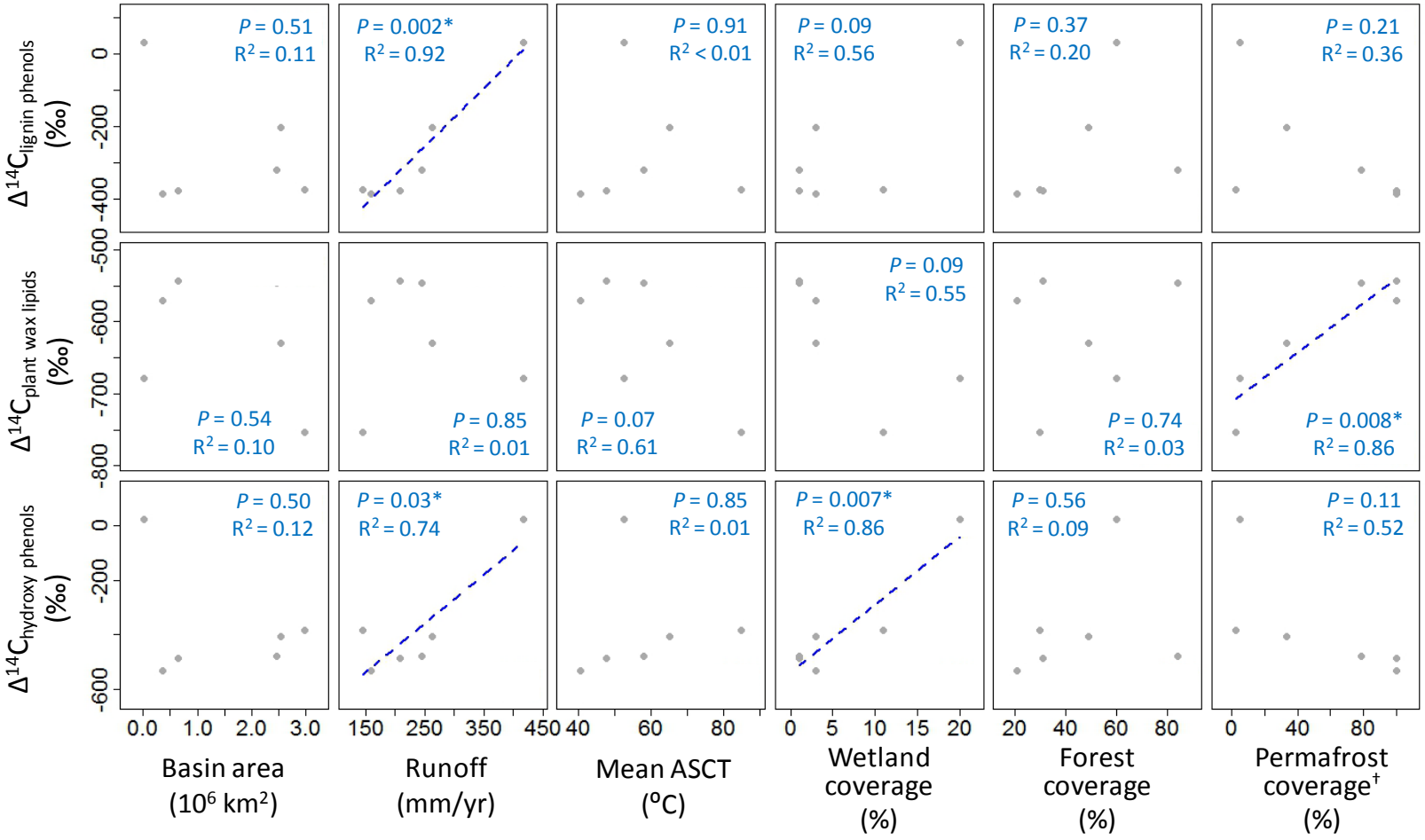
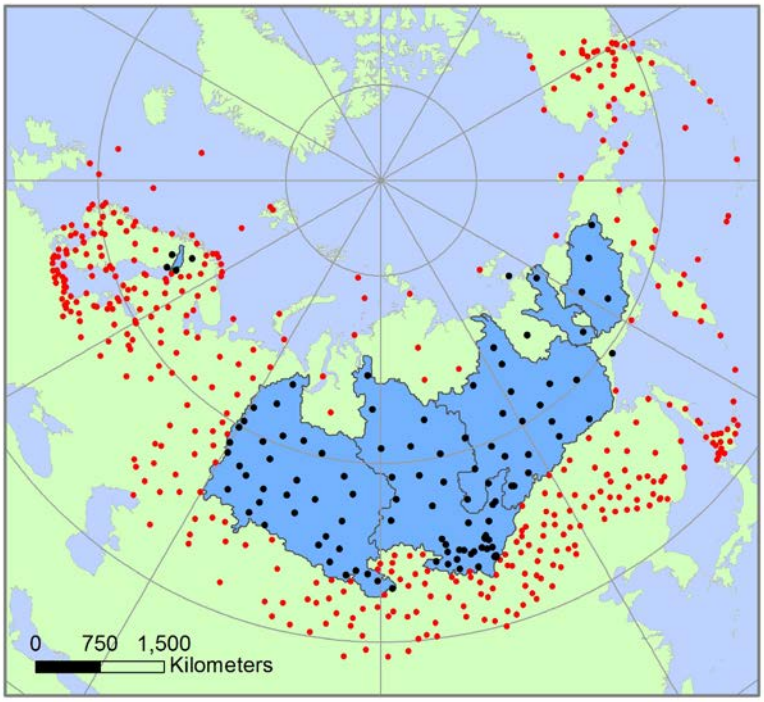


Figure S3: Map of climatic stations recorded in the GHCN-M database for each drainage basin. Blue area represents the watersheds of GRARs and Kalix River; black and red points refer to the location of climatic stations included in the calculation of regional temperature data and for the interpolation method, respectively.



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