

Supporting Information

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SI Materials and Methods

Isolation of Lignin Phenols for ^{14}C Analysis. Details of the method are provided by Feng et al. (1). Briefly, the CuO oxidation products (in ethyl acetate) were blown carefully to $<100\ \mu\text{L}$ under N_2 , redissolved in water (pH 2), and loaded onto a Supelco Supelclean ENVI-18 solid-phase extraction (SPE) cartridge (preconditioned 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 $<0.5\ \text{mL}$, and further separated on a self-packed amino SPE cartridge (0.5 g, preconditioned with methanol, Supelclean LC-NH₂; Supelco) into phenolic aldehyde/ketone (eluting in methanol) and their corresponding acid (eluting with methanol and 12 M HCl, 95:5) fractions. Each fraction was blown carefully to $<100\ \mu\text{L}$ under N_2 and redissolved in methanol for separation on an Agilent 1200 HPLC system coupled to a diode array detector 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 \times 250 mm) with a Polar-RP SecurityGuard column (4 μm , 4.0 \times 3.0 mm) and a ZORBAX Eclipse XDB-C18 column (5 μm , 4.6 \times 150 mm) with a ZORBAX Eclipse C18 guard column (5 μm , 4.6 \times 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 are provided by Feng et al. (1)]. Five injections (in most cases, and 10 injections for phenols $>150\ \mu\text{g}$) were conducted for each sample to collect $\sim 20\text{--}300\ \mu\text{g}$ of each phenol (i.e., $\sim 10\text{--}150\ \mu\text{g}$ of carbon) 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 SiO₂ column using ethyl acetate to remove potential column bleed. A small aliquot of purified phenols was derivatized with N,O-bis-(trimethylsilyl) trifluoroacetamide

and pyridine to check compound purity by GC/MS, and was found to yield purities $>99\%$. Purified phenols were transferred into precombusted quartz tubes in ethyl acetate and blown dry carefully under a gentle stream of N_2 , with the addition of precombusted CuO afterward. The quartz tubes were evacuated on a vacuum line while immersed in an isopropanol/dry ice slush ($-78\ \text{°C}$), 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 s) 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, version 3; www.ncdc.noaa.gov/gHCN/). In total, 102 climatic stations were identified within the great Russian Arctic river (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, the 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 temperature during recent climate change (3). The value of the ASCT is given by the sum of mean T_m s for months with a T_m above 0 °C each year, and is thus related to the “thawing index” (4). The ASCT from 1985 to 2004 was calculated for each station separately and then averaged to represent the entire watershed.

1. Feng X, et al. (2013) ^{14}C and ^{13}C characteristics of higher plant biomarkers in Washington margin surface sediments. *Geochim Cosmochim Acta* 105:14–30.
2. Rinke A, et al. (2012) Arctic RCM simulations of temperature and precipitation derived indices relevant to future frozen ground conditions. *Global Planet Change* 80-81:136–148.

3. Hansen J, Sato M, Ruedy R (2012) Perception of climate change. *Proc Natl Acad Sci USA* 109(37):E2415–E2423.
4. Frauenfeld OW, Zhang T, McCreight JL (2007) Northern hemisphere freezing/thawing index variations over the twentieth century. *Int J Climatol* 27(1):47–63.

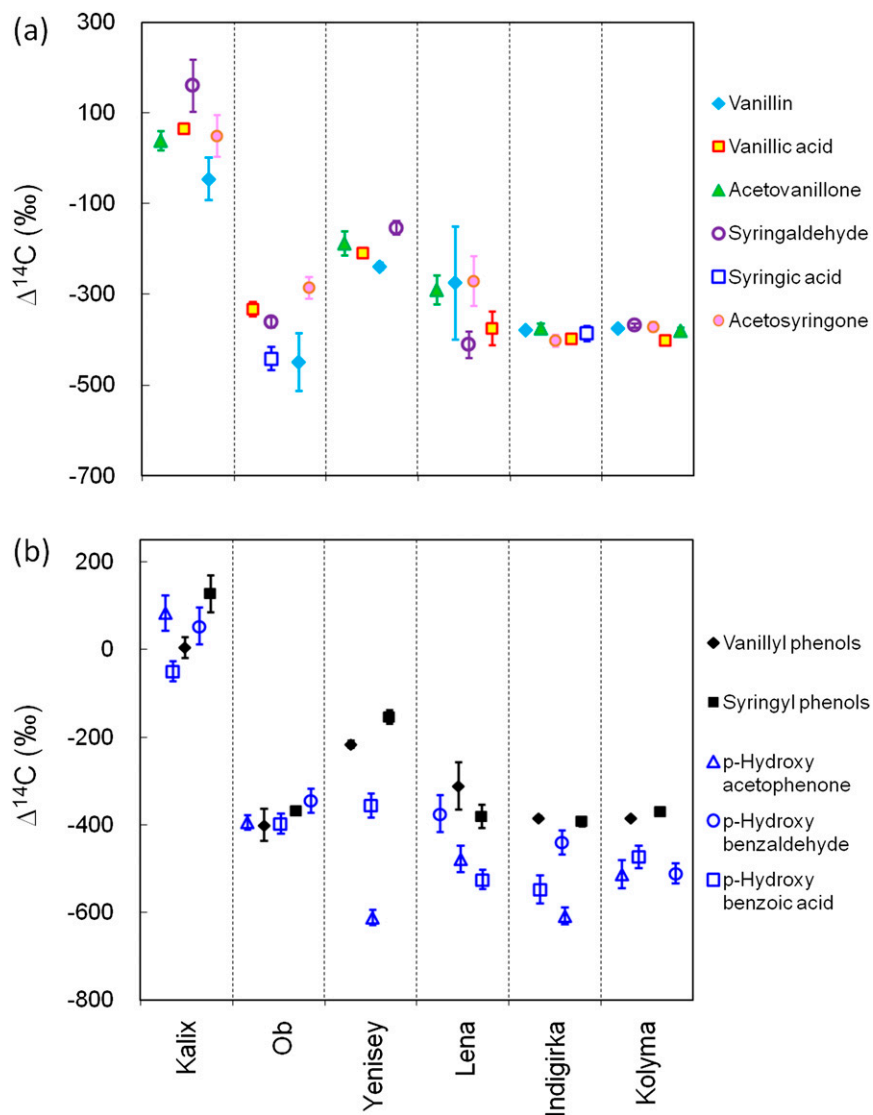


Fig. S1. $\Delta^{14}\text{C}$ values of individual lignin phenols (A) and individual hydroxy phenols (B) compared with the abundance-weighted average of vanillyl and syringyl phenols. All values are corrected for procedural blanks with the SEs of analytical measurement propagated. Note that there is no significant offset in the average $\Delta^{14}\text{C}$ values between vanillyl and syringyl phenols from the same estuarine sediment (t test, $P > 0.05$).

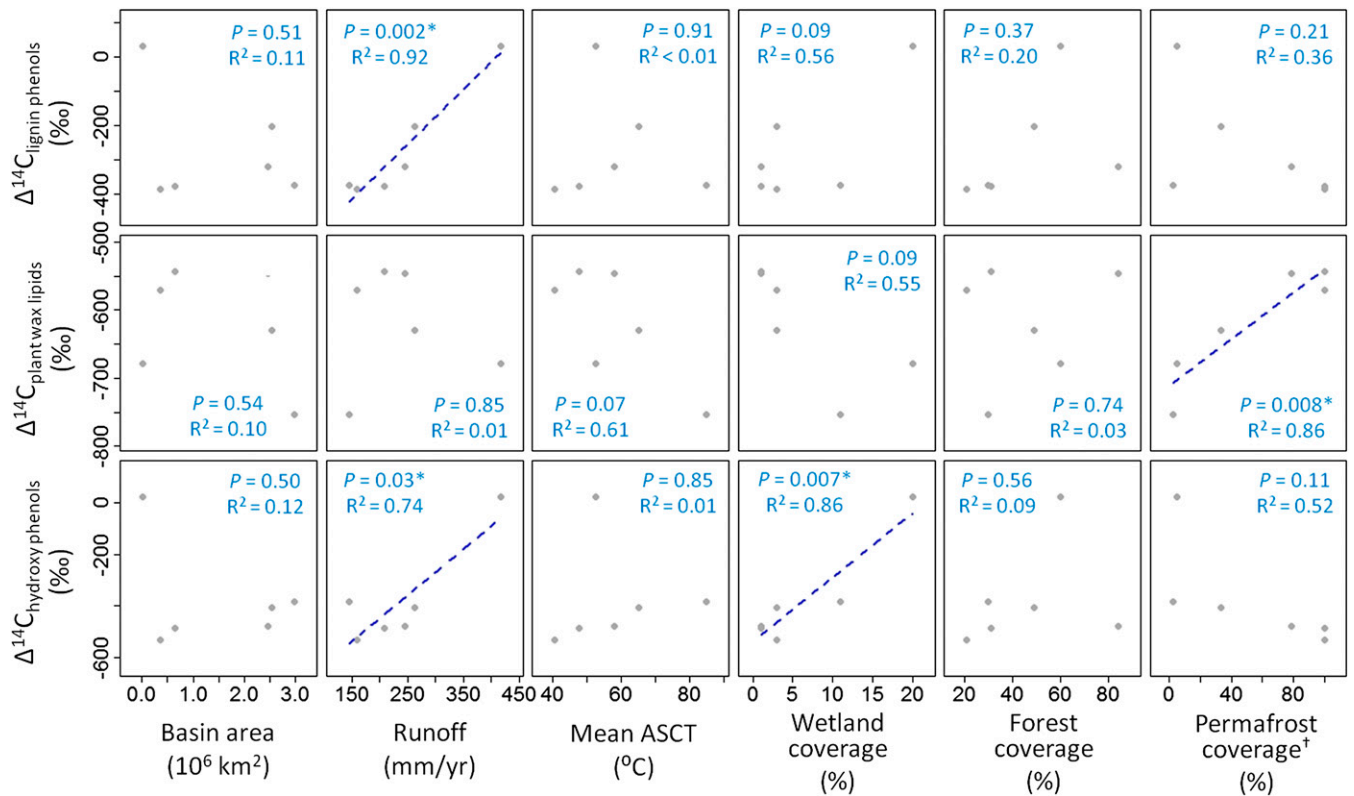


Fig. S2. Correlation between drainage basin characteristics and the $\Delta^{14}\text{C}$ values of terrestrial markers. Error bars represent the propagated SE of analytical measurement. *Linear correlation is considered to be significant at a level of $P < 0.05$, and the R^2 values are used to compare 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. The ASCT is given for months with a mean temperature above 0°C .

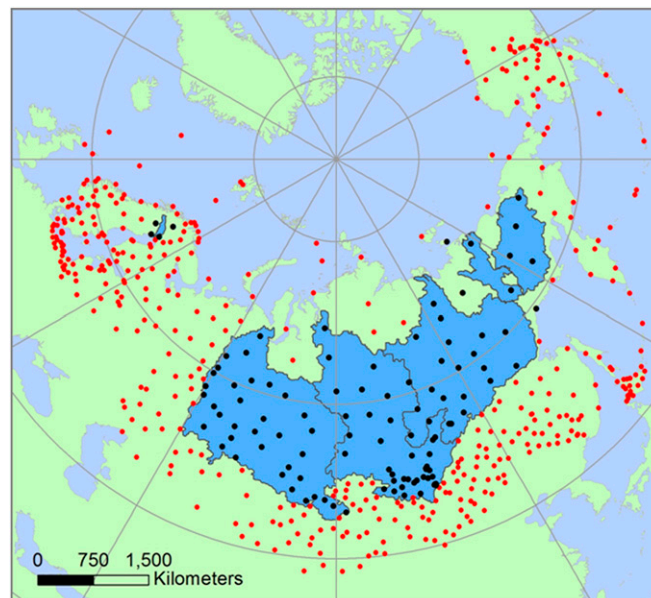


Fig. S3. Map of climatic stations recorded in the GHCN-M database for each drainage basin. The blue area represents the watersheds of great Russian Arctic rivers (GRARs) and the Kalix River; black and red points refer to the location of climatic stations included in the calculation of regional temperature data and for the interpolation method, respectively.

Table S1. Sample location, drainage basin characteristics, and bulk sediment properties of the great Russian Arctic rivers and Kalix River

Properties	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 /y ^{**}	10	427	673	588	54	136
Runoff, mm/y ^{**}	417	145	263	245	159	209
TOC/POC flux, t·km ⁻² ·y ^{-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, years B.P. ^{§§}	570 ± 250	3,000 ± 35	1,500 ± 30	7,500 ± 60	6,000 ± 50	5,600 ± 50

OC, organic carbon; POC, particulate organic carbon; TOC, total organic carbon.

*Combined surface sediments along a transect.

[†]According to the Arctic Monitoring and Assessment Programme (1).

[‡]ASCT was calculated as the sum of the mean T_m for months with a mean temperature above 0 °C within a year; temperature data were derived from the GHCN-M database.

[§]Data are from Ingri et al. (2) and “watersheds of the world” (<http://archive.wri.org>).

[¶]Given as % continuous; % (discontinuous + sporadic + isolated); % nonpermafrost (3, 4).

^{||}Data are from Ingri et al. (2), Gordeev et al. (5), Holmes et al. (6), and Rachold et al. (7).

^{**}Data are from Ingri et al. (2), Holmes et al. (4), and Stein and Macdonald (8).

^{††}Kalix data are from Ingri et al. (2); Great Russian Arctic River data are from Stein and Macdonald (8).

^{**}Mass ratio of OC to total nitrogen (9, 10).

^{§§}Measured in 2006; values are normalized for the year of measurement.

1. AMAP (1998) *AMAP Assessment Report: Arctic Pollution Issues* (Arctic Monitoring and Assessment Programme, Oslo).

2. Ingri J, Widerlund A, Land M (2005) Geochemistry of major elements in a pristine boreal river system; hydrological compartments and flow paths. *Aquat Geochem* 11(1):57–88.

3. Gustafsson Ö, van Dongen BE, Vonk JE, Dudarev OV, Semiletov IP (2011) Widespread release of old carbon across the Siberian Arctic echoed by its large rivers. *Biogeochemistry* 8: 1737–1743.

4. Holmes RM, et al. (2013) *Climatic Change and Global Warming of Inland Waters: Impacts and Mitigation for Ecosystems and Societies*, eds Goldman CR, Kumagai M, Robarts RD (Wiley, Chichester, UK), pp 3–26.

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9. van Dongen BE, Semiletov I, Weijers JWH, Gustafsson Ö (2008) Contrasting lipid biomarker composition of terrestrial organic matter exported from across the Eurasian Arctic by the five great Russian Arctic rivers. *Global Biogeochem Cycles* 22:GB1011, 10.1029/2007GB002974.

10. Vonk JE, van Dongen BE, Gustafsson Ö (2008) Lipid biomarker investigation of the origin and diagenetic state of sub-arctic terrestrial organic matter presently exported into the northern Bothnian Bay. *Mar Chem* 112(1–2):1–10.

11. McClelland JW, Dery SJ, Peterson BJ, Holmes RM, Wood EF (2006) A pan-arctic evaluation of changes in river discharge during the latter half of the 20th century. *Geophys Res Lett* 33: L06715, 10.1029/2006GL025753.

12. Peterson BJ, et al. (2002) Increasing river discharge to the Arctic Ocean. *Science* 298(5601):2171–2173.

Table S2. Abundance of terrestrial OC markers in the estuarine surface sediments (milligrams per gram of OC) of the great Russian Arctic rivers and Kalix River

Compounds	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</p>	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</p>	2.92	1.02	0.75	0.99	0.90	0.93
<p>-Hydroxyacetophenone</p>	1.32	0.75	0.43	0.50	0.44	0.81
<p>-Hydroxybenzoic acid</p>	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} <i>n</i> -alkanes [†]	0.16	0.76	0.48	0.28	0.91	0.65
C _{24,26,28} <i>n</i> -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 (1, 2).

- van Dongen BE, Semiletov I, Weijers JWH, Gustafsson Ö (2008) Contrasting lipid biomarker composition of terrestrial organic matter exported from across the Eurasian Arctic by the five great Russian Arctic rivers. *Global Biogeochem Cycles* 22:GB1011, 10.1029/2007GB002974.
- Vonk JE, van Dongen BE, Gustafsson Ö (2008) Lipid biomarker investigation of the origin and diagenetic state of sub-arctic terrestrial organic matter presently exported into the northern Bothnian Bay. *Mar Chem* 112(1–2):1–10.

Table S3. Average $\Delta^{14}\text{C}$ values of lignin phenols in estuarine surface sediments of the great Russian Arctic rivers and Kalix River and contributions of modern surface OC to lignin estimated from the ^{14}C binary mixing model

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

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

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

Table S4. Average $\Delta^{14}\text{C}$ values of terrestrial OC pools (represented by different groups of markers) and contributions of surface vs. deep permafrost OC to terrestrial biospheric OC in surface sediments of the great Russian Arctic rivers and Kalix River in 2004 and 1985

Content	Kalix	Ob	Yenisey	Lena	Indigirka	Kolyma
Average $\Delta^{14}\text{C}$ value of terrestrial biospheric OC (represented by hydroxy phenols)*	+22 ± 22	-383 ± 15	-404 ± 23	-477 ± 18	-529 ± 23	-486 ± 18
<i>Current budget (2004)</i>						
Average $\Delta^{14}\text{C}$ 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
<i>Budget of the past (1985)</i>						
Average $\Delta^{14}\text{C}$ 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 are provided in Fig. S1.

[†]Original values of long-chain *n*-alkanes and *n*-alkanoic acids are taken from Gustafsson et al. (1).

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

[§]Based on the linear relationship between lignin phenol $\Delta^{14}\text{C}$ values and runoff ($\Delta^{14}\text{C} = 1.6018 \times \text{runoff} - 655$; Fig. 3A) and the runoff increasing rate of ~0.60 (Indigirka) to 0.74 mm/y [the other great Russian Arctic rivers (GRARs)] from 1964 to 2000 in Eurasian Arctic rivers (2, 3). Lignin phenol $\Delta^{14}\text{C}$ values are estimated to be lower by 19‰ [$0.60 \text{ mm/y} \times 20 \text{ y} \times 1.6018\text{‰}/(\text{mm/y})$ for Indigirka] to 24‰ [$0.74 \text{ mm/y} \times 20 \text{ y} \times 1.6018\text{‰}/(\text{mm/y})$ for the other big GRARs] in 1985 compared with those measured in 2004 (not considering the dilution of bomb ^{14}C in the atmosphere). The $\Delta^{14}\text{C}$ values of plant wax lipid and hydroxy phenols are assumed to remain the same as in 2004.

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

- Gustafsson Ö, van Dongen BE, Vonk JE, Dudarev OV, Semiletov IP (2011) Widespread release of old carbon across the Siberian Arctic echoed by its large rivers. *Biogeosciences* 8: 1737–1743.
- McClelland JW, Dery SJ, Peterson BJ, Holmes RM, Wood EF (2006) A pan-arctic evaluation of changes in river discharge during the latter half of the 20th century. *Geophys Res Lett* 33: L06715, 10.1029/2006GL025753.
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