Differential mobilization of terrestrial carbon pools in Eurasian Arctic river basins

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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 vs. deep (permafrost) carbon pools across the clisequence 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 ther-mokarst erosion occurs more frequently. Because 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 and 2004. These findings suggest that although partly masked by surface carbon export, climate change-induced mobilization of old permafrost carbon is well under-way in the Arctic.

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samples (Fig. 2B). The Δ^14C 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 (Kalik), which has much lower permafrost coverage (Fig. 2A), corresponding to a Δ^14C age offset of up to 13,000 y (Fig. 2B). The sharply contrasting Δ^14C 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, although plant wax lipids constitute a smaller component of the terrestrial OC (Table S2), their old Δ^14C ages reveal the mobilization of a preaged (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 Δ^14C values across the transect, with similar values to lignin phenols observed in two western rivers (~383‰ and +22‰ in the Ob and Kalik, respectively) and values lower than lignin phenols but comparable to plant wax lipids in the three eastern GRARs (~529 to ~477‰; Fig. 2B and Fig. S1B). Because wetlands dominated by Sphagnum mosses constitute a high proportion of the Ob and Kalik basins (27, 28) (Table S1), 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

Results and Discussion

Contrasting Δ^14C Characteristics of Terrestrial OC Components. We used 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 Δ^14C values (~402 to ~367‰) in the Indigirka and Kolyma sediments, whereas much higher isotopic variability was observed in sediments from the Kalik 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 Δ^14C values of lignin phenols ranged from ~385 to +33‰ across the Eurasian Arctic transect, corresponding to conventional radiocarbon ages of 3,800 y to modern (Fig. 2B). It is notable that lignin phenols largely follow the trend of bulk OC radiocarbon ages (ranging from 570 to 7,500 y; 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 substantially higher in the three eastern GRARs (2,000–4,000 Δ^14C y) than in the three western rivers (<700 y; Fig. 2B), however. Because 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 Δ^14C ages of lignin phenols were substantially younger than those of another suite of terrestrial OC tracer compounds, long-chain higher plant leaf lipids (32) [C_{27,29,31} n-alkanes and C_{24,26,28} n-alkanoic acids ranging from 5,500 to 13,600 Δ^14C y in age (6)], previously measured in these sediment
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 (Fig. 2A, Fig. S2, and Table S1). Among the investigated physiogeographic variables, runoff exerts a strong control on the Δ14C values of lignin phenols across the Eurasian Arctic (P < 0.01, R2 = 0.92; Fig. 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 notable that at zero runoff rate (representing extreme base flow with minimum detrital input), regression analysis yields an end-member Δ14C 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 Δ14C value of +100 to +200‰, whereas deep soil-derived lignin has a Δ14C 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 Δ14C values of plant wax lipids are most strongly correlated with the watershed coverage of continuous permafrost (P < 0.01, R2 = 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 (Fig. 1B and C), leading to the release of older 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. Although erosion may also play a part in releasing lignin-rich OC from surface layers, its effect seems to be dwarfed by surface runoff processes because 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 toward the west end of the transect (Fig. 2B).

By comparison, corresponding Δ14C values for hydroxy phenols were best correlated with the wetland coverage in the drainage basin (P < 0.01, R2 = 0.86; Fig. 3C) and, to a lesser degree, with the mean annual runoff rate (P = 0.03, R2 = 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 Δ14C-runoff correlation plot (Fig. 3D), the hydroxy-phenol Δ14C 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, R2 = 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

Fig. 3. Hydrological and physiogeographic controls on the age of terrestrial markers in the integrating Eurasian Arctic estuaries: correlation of Δ14C\textsubscript{lignin phenols} with runoff rate (A), Δ14C\textsubscript{plant wax lipids} with continuous permafrost coverage (B), Δ14C\textsubscript{hydroxy phenols} with wetland coverage (C), and Δ14C\textsubscript{hydroxy phenols} with runoff rate (D). The blue dotted line in D represents linear correlation for the data of four eastern rivers (P < 0.05, R2 = 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.
the magnitude of permafrost carbon release, we first need to 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 [e.g., black carbon (42, 43) and planktonic carbon (5)], as underlined by the age difference of bulk OC relative to the terrestrial markers in the Lena, Ob, and Yenisey sediments (Fig. 2B). Assuming that hydroxy phenols incorporate the isotopic signal of terrestrial biogenic carbon derived from both surface and deep carbon sources, whereas the Δδ13C 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 biogenic carbon originates from deeper permafrost in the four eastern river basins (where the modern wetland carbon contribution is small; Table S4). This estimate likely represents a lower limit, because the surface OC end member (lignin) also incorporates a significant amount of preaged OC from surface soil horizons. Nonetheless, it implies that over half of the sedimentary OC in the 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 Pleistocene Yedoma (5).

During the second half of the 20th century, Eurasian Arctic river runoff increased at an average rate of ∼0.60–0.74 mmy (44–46), likely increasing the delivery of surface-derived OC to estuaries. Based on the relationship between lignin phenol Δδ13C values and runoff (Δδ13C = 1.6018 x runoff – 655; Fig. 3), the Δδ13C value of mobilized surface OC has increased by ∼19–24‰ from 1985 to 2004, not considering the variation of bomb-derived 14C in the atmosphere. This time window corresponds to the sediment-deposition time of 20 y, based on the surface sediment depth and sedimentation rate in the region (5). Assuming that the 14C signals of exported OC have remained similar during this period and that the end-member Δδ13C 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. When we assume that particulate organic carbon (POC) fluxes in these rivers (Table S1) are dominantly terrestrial in origin (26, 30), the 20-y increase is equivalent to ∼1.4 teragrams of carbon transferred from old permafrost into estuarine sediments. Although this number represents a rough estimate and is relatively small compared with some other Arctic carbon fluxes (47), release of dissolved OC (23, 47, 48) and water-column mineralization of POC (5, 49) associated with permafrost thawing may well exceed the size of this sedimentary OC budget in the context of a changing climate. Our estimate represents a conservative scenario because sedimentary Δδ13C values are postulated to decrease further 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 [∼17,000 y in the Amazon River (50)] and woody debris in small mountainous rivers [∼20 y (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 Δδ13C values due to the incorporation of bomb-derived 14C into surface decadal OC pools (40). These calculations suggest that the magnitude of permafrost carbon release, which may be masked or muted by other organic 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 to some temperate and tropical systems, where terrestrial OC components are retained on land for a similar period [e.g., 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, whereas deep hydraulic conduits and bank/coastal erosion may mobilize very old permafrost carbon of 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, because end-member values may vary substantially due to the release of significantly preaged soil carbon. Molecular-level 14C measurements enable constraints to be placed on the relative contribution of surface and deep permafrost carbon pools to Arctic fluvial export. Unraveling 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 −30 °C. This contrasts with the two western GRARs (Ob and Yenisey) located in the western Siberian Plain and the plans draining from 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) and are wetter, with higher precipitation-to-evaporation ratios compared with eastern GRARs. All rivers have comparable drainage area-normalized fluxes of total organic carbon (TOC) and POC (27, 52) (Table S1). 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 HIV Ivan Kireev) in 2004 and 2005 and from the Kalix in 2005 on the research vessel KBV005 from the Uméa Marine Research Center (Norbyn, Sweden). These sediments were mainly delivered by the annual spring freshet of the rivers and by coastal erosion during the past 20 y based on the sedimentation rate of 0.11–0.16 cm/y (5, 26). Previous molecular and isotopic investigations revealed a predominant 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 were freeze-dried before analysis. A small aliquot was used for TOC and bulk δ13C analyses at the University of California, Davis Stable Isotope Facility (http://stableisotopefacility.ucdavis.edu) and for bulk Δδ13C analysis at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility at Woods Hole Oceanographic Institution.

Isolation and 14C Analysis of Individual Compounds. As described previously (6), lipids were extracted from freeze-dried sediments (∼30–70 g) using Soxhlet extraction with dichloromethane–methanol (v:v 9:1) for 24 h. The lipid extracts and n-aliphatic acids and n-alkane acids were isolated using preparative capillary GC and analyzed for 14C 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, −5 g of CuO, 0.6 g of ferrous ammonium sulfate, and 0.3 g of Na2S2O4 (2 M) were added to eight 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 an HPLC-based method [Si Materials and Methods; details are provided in Feng et al. (20)] Briefly, the UO2 oxidation extracts were purified through two solid-phase extraction (SPE) cartridges (Supelco Supelclean ENV1-18 and Supelclean LC-NH2 SPEs) and separated through two HPLC isolation steps consisting of a Phenomenex Synergi Poly-RP column and a ZORBAX Eclipse XDB-C18 column. Approximately 10–150 μg of carbon of individual phenols was 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 CO2 was cryogenically purified and quantified. A batch of CO2 samples (23–150 μg of carbon) was sent to NOSAMS, graphitized, and measured on an accelerator mass spectrometer (AMS). A second batch of CO2 samples (10–32 μg carbon) was directly measured without graphitization on the miniaturized radiocarbon dating system at the Eidgenössische Technische Hochschule Zürich using a gasfeeding system (54). Radiocarbon contents are reported as Δ14C (‰) and conventional 14C age. Procedural blanks associated with the extraction/HPLC/combustion procedures yielded 2.5 ± 0.8 μg of carbon with a fraction modern (Fm) value of 0.21 ± 0.07 (n = 5). All radiocarbon values are corrected for procedural blanks with the errors propagated. We did not observe a significant difference between radiocarbon contents of the same sample measured at the two AMS facilities.

Binary Mixing Model. We used a 14C binary mixing model to assess the relative contributions of surface OC (Table 53) and permafrost OC (Table 54) to lignin or hydroxy phenol, respectively. The model is expressed in the following two equations:

\[ f_1(\Delta^{14}C_C) + f_2(\Delta^{14}C_P) = \Delta^{14}C_{\text{phenol}}. \]  
\[ f_1 + f_2 = 1. \]  

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 14C content of different phenols. Differences are considered to be significant at a confidence level of P < 0.05. Linear regression analysis was used to assess the correlation between drainage basin characteristics and the 14C content of terrestrial OC markers (Fig. 52). The main drainage basin parameters investigated as explanatory variables include basin area; runoff rate; mean annual summer temperature above 0 °C within a year (details are provided in 14). The ASCT; and the coverage of forest, wetland, and continuous permafrost in the watershed (Table S1). The ASCT is calculated as the sum of mean monthly temperature for months with a mean temperature of ≥ 0 °C within a year (details are provided in 14).

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