Supplementary Information

Supplementary Methods

Lipid extraction and purification

The estuarine samples, between 70-160 g, were freeze dried, ground and Soxhlet extracted with dichloromethane/methanol (DCM/MeOH, 2:1, v/v) for 24 h. The total lipid extracts (TLEs) were concentrated using rotary evaporation and treated with activated (2N HCl) copper curls to remove elemental sulfur. Subsequently, the TLEs were separated into two fractions using Bond-Elut® column chromatography (Strata NH₂; 5 μm, 70 Å) by eluting with DCM/isopropanol (2:1 v/v; “neutral lipid fraction”) and an acetic acid solution (a 2% solution in diethyl ether; “acid fraction”). The neutral lipid fraction was further separated into two fractions using a column packed with 100% activated alumina by elution with hexane/DCM (9:1 v/v; “hydrocarbon fraction”) and DCM/MeOH (1:1 v/v; “polar fraction”). The acid fractions were derivatized with BF₃ in MeOH to convert acids into their corresponding methyl esters. Aliquots of the hydrocarbon and acid fractions were analyzed using gas chromatography/mass spectrometry (GC/MS), using the set-up as described elsewhere (van Dongen et al., 2008; Vonk et al., 2008).

Preparative capillary gas chromatography

Selected individual compounds were further isolated for radiocarbon analysis from the purified lipid extracts by preparative capillary gas chromatography (pcGC). The pcGC system was constructed around an Agilent 6890NGC system, equipped with a FID, coupled to a Gerstel GmbH (Mülheim an der Ruhr, Germany) Cold Injection System (CIS3) and Preparative Fraction Collector (PFC) (Eglinton et al., 1996; Mandalakis et al., 2003). The end results of pcGC isolation are displayed in Fig. S1a+b. The vial containing the sample was kept at 6°C during the whole pcGC procedure to limit the evaporation of solvent. A megabore fused silica capillary column (60m length, 0.53 mm i.d.) coated with 0.5 μm VF-5MS (cross-linked 5% phenyl methylpolysiloxane, Factor Four, Varian) was used with helium as the carrier gas and an inlet pressure of 68.9 kPa (10psi). Approximately 99% of the column flow was directed to the PFC, while the rest was diverted to the FID to monitor the separation. The fractions were injected at 50°C and
the oven was programmed to 130 °C at 20 °C min\(^{-1}\) and then to 300°C at 6 °C min\(^{-1}\) where it was kept isothermally for 16 min.

The PFC switch temperature and the transfer line temperature were kept constant at 320°C through all injections, with the number of injections ranging from 50 to 150. The trapping window started ca. 0.5 s before and ended ca. 0.5 s after the elution of the compound. The retention times were frequently checked, and the trapping windows were adjusted as necessary. The isolated compounds were rinsed from the glass trap capillaries five times with DCM. An aliquot (approximately 5%) was analyzed by GC/MS to evaluate the yield and purity (above 96%) of the isolated compounds (Fig. S1b) and to verify if the isolated amounts were sufficient for \(^{14}\)C analysis. In order to provide sufficient mass (>20 μg carbon) the harvested C\(_{27}\), C\(_{29}\) and C\(_{31}\) \(n\)-alkane homologues and the C\(_{24}\), C\(_{26}\) and C\(_{28}\) methylated \(n\)-alkanoic acid homologues were recombined after pcGC yielding a 'HMW \(n\)-alkane' and ‘HMW methylated \(n\)-alkanoic acid’ fraction, respectively. The pcGC protocol has been evaluated for low level C influence on molecular \(^{14}\)C results (Zencak et al., 2007).

**Radiocarbon analysis**

The isolated fractions and bulk samples were sent to the U.S. National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility of the Woods Hole Oceanographic Institution (WHOI, Woods Hole, USA) for \(\delta^{13}\)C and \(\Delta^{14}\)C analyses. The isolated compounds were transferred into precombusted quartz tubes, the DCM evaporated under a stream of nitrogen, and pre-combusted copper oxide was added. These tubes were then attached to a vacuum line, evacuated \((10^{-3} \text{ Torr})\) 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 introduced and purified on a vacuum line using a series of cold traps and quantified by manometry. About 10% of the carbon dioxide was kept for \(\delta^{13}\)C analysis by isotope ratio mass spectrometry and was reduced to graphite that was mounted on target wheels for \(^{14}\)C analysis by accelerator mass spectrometry. All of the \(\delta^{13}\)C, reported relatively to the Vienna Pee Dee Belemnite (VPDB) standard, and radiocarbon compositions of alkanoic acids, reported relative to NBS oxalic acid I as a fraction modern \((^{14}\text{C Fm-}\delta^{13}\text{C_{corr}})\) and \(\Delta^{14}\)C (Stuiver and Polach, 1997), were corrected for the addition of the derivative carbon using an isotopic mass balance.
Supplementary Text

Evaluation of a potential contribution of planktonic and/or petrogenic derived organic matter in the Western GRAR estuary sediments

Conceivably, a sizeable contribution to the OC from fresh planktonic-derived and thus radiocarbon-young carbon could explain the large discrepancies of the western estuaries. However, the molecular composition (Fig. 2a+b) and δ¹³C (Table 1) point to an overwhelmingly terrestrial origin of the sampled OM.

Another possibility is that the ¹⁴C signals of the HMW n-alkanes are depleted because of a contribution from weathering of fossil/petroleum shale exposed in the drainage basins, such as observed in the Mackenzie estuary (Goñi et al., 2005). However, evaluation of the detailed molecular marker pattern in the GRAR sediments, including the absence of an unresolved complex mixture and αβ-hopanes, a distinct odd-over-even homolog abundance for n-alkanes (van Dongen et al., 2008) and low methylphenanthrene to phenanthrene ratios (Elmquist et al., 2008), suggest that a significant petroleum source is unlikely (see further details below).

The carbon preference index (CPI) of the n-alkanes in the Yenisey estuary sediment sample (6.5; van Dongen et al., 2008) is comparable to those typically observed for extant plants (Hedges and Prahl, 1993; Rieley et al., 1991) and those reported earlier for Russian Arctic sediments (Fahl and Stein, 1997; Fahl et al., 2003; Fernandes and Sicre, 2000). In contrast, the Ob estuary sediment sample showed a slightly lower n-alkane CPI value (3.2), comparable to n-alkane CPI values of 0.8-3.5 for other Ob estuary sediments (Fahl et al., 2003). Low n-alkane CPIs are also reported for the Mackenzie River estuary sediments (between 1.8 and 2.7; Drenzek et al., 2007), most likely reflecting a large petrogenic input. Although values as low as the Ob value are commonly observed in sediments and this value is still consistent with a predominantly higher plant origin (Brassell et al., 1978), this suggests a potential petrogenic input in the Ob estuary sediment.

Hopanes dominated by 17β(H),21β-hopanes, predominantly 17β(H),21β(H)-homohopane, are also present in the hydrocarbon fractions of the Ob and Yenisey estuary sediment samples, although in substantially lower amounts if compared to the HMW n-alkanes (Fig. S1). In contrast, the thermally more stable 17α(H),21β-hopanes, having a non-biogenic origin (Brassell, 1985), could not be detected. In addition, no unresolved complex mixture (UCM), typical of heavily biodegraded OM (Gough and Rowland, 1990) could be detected in the estuary sediments (Fig. S2 for Ob). The absence of both the thermally mature
hopanes and a UCM makes an input of OM with a thermally mature origin, such as natural oils seeps, weathering of petroleum source rocks or even petroleum contamination, unlikely. Furthermore, recent PAH analyses of these sediment samples indicate methylphenanthrenes to phenanthrene ratios of 1.02 and 0.71 for the Ob and Yenisey samples, respectively, again supporting a very low petrogenic input (Elmquist et al., 2008).

To summarize, although the CPI indicates a possible contribution of petrogenic origin for the Ob estuary sediment, evaluation of the detailed molecular marker composition of both western GRAR sediments suggests that a substantial contribution from weathering of fossil/petroleum shale exposed in the drainage basins is very unlikely.

Furthermore, the $\Delta^{14}$C of HMW $n$-alkanoic acids for the GRARs (Fig. 2d) is in the same general range as for the HMW $n$-alkanes, further supporting a negligible contribution of fossil shale weathering. The slightly more depleted $\Delta^{14}$C of $n$-alkanes than of $n$-alkanoic acid in Yenisey, Ob and Kalix likely reflects a higher reservoir age for the $n$-alkanes in the original soil/permafrost system prior to thaw release, consistent with a higher recalcitrance compared with their $n$-alkanoic acid counterparts (Cranwell, 1981).
Supplementary Figure S1. Total ion current gas chromatogram of the hydrocarbon fraction of the Ob estuary surface sediment (a) before and (b) after preparative capillary gas chromatography. The *n*-alkanes are represented by solid circles; internal standards as IS; and hopanes by plus symbols. Numbers indicate carbon chain length and ββ indicates stereochemistry of hopanes at C-17 and C-21 positions.
Supplementary Figure S2. Comparison between the $^{14}$C calendar ages of the recalcitrant transported carbon and the basal peat ages in the drainage basins of the GRARs. The basal peat ages were modified after MacDonald et al. (2006). The timing of peat land initiation based on 2° by 2° grids is shown below the figure. The grids map the oldest peat data within each grid cell.
Supplementary References


