Erosion of organic carbon in the Arctic as a geological carbon dioxide sink

Robert G. Hilton[1*], Valier Galy[2], Jérôme Gaillardet[3], Mathieu Dellinger[3], Charlotte Bryant[4], Matt O'Regan[5], Darren R. Gröcke[6], Helen Coxall[5], Julien Bouchez[3], & Damien Calmels[7]

[1]Department of Geography, Durham University, South Road, Durham, DH1 3LE, UK

[2]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, 266 Woods Hole Rd., Woods Hole, MA 02543-1050, USA

[3]Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France

[4]NERC Radiocarbon Facility, East Kilbride, Scotland, G75 OQF, UK

[5]Department of Geological Sciences, Stockholm University, Sweden

[6]Department of Earth Sciences, Durham University, South Road, Durham, DH1 3LE, UK

[7]Université Paris-Sud, Laboratoire GEOPS, UMR 8148 - CNRS, Orsay, F-91405, France

*To whom correspondence should be addressed. Email: r.g.hilton@durham.ac.uk. Phone: 0044 0191 33 41970

Soils of the northern high latitudes store carbon over millennial timescales (10^3 yrs) and contain approximately double the carbon stock of the atmosphere[1-3]. Warming and associated permafrost thaw can expose soil organic carbon and result in mineralisation and carbon dioxide (CO_2) release[4-6]. However, some of this soil organic carbon may be eroded and transferred to rivers[7-9]. If it escapes degradation during river transport and is buried in marine sediments, then it can contribute to a longer-term (>10^4 yrs), geological CO_2 sink[8-10]. Despite this recognition, the erosional flux and fate of particulate organic carbon (POC) in large rivers at high latitudes remains poorly constrained. Here, we quantify POC source in the Mackenzie River, the main sediment supplier to the Arctic Ocean[11,12] and assess its flux and fate. We combine measurements

of radiocarbon, stable carbon isotopes and element ratios to correct for rock-derived POC[10,13,14]. Our samples reveal that the eroded biospheric POC has resided in the basin for millennia, with a mean radiocarbon age of 5800±800 yr, much older than large tropical rivers[13,14]. Based on the measured biospheric POC content and variability in annual sediment yield[15], we calculate a biospheric POC flux of $2.2^{+1.3}_{-0.9}$ TgC yr^{-1} from the Mackenzie River, three times the CO_2 drawdown by silicate weathering[16]. Offshore we find evidence for efficient terrestrial organic carbon burial over the Holocene, suggesting that erosion of organic carbon-rich, high latitude soils may result in a significant geological CO_2 sink.

Photosynthesis and the production of organic carbon by the terrestrial biosphere ($OC_{biosphere}$) is a major pathway of atmospheric carbon dioxide (CO_2) drawdown. Over millennial timescales (10^3 yrs), some $OC_{biosphere}$ escapes oxidation and contributes to a transient CO_2 sink in soil[2,3,17]. Longer-term CO_2 drawdown (>10^4 yrs) can be achieved if $OC_{biosphere}$ is eroded, transferred by rivers and buried in sedimentary basins[9,10,18,19]. Burial of $OC_{biosphere}$ represents a major geological CO_2 sink (and O_2 source) alongside the chemical weathering of silicate minerals by carbonic acid, coupled to carbonate precipitation[16,19]. These fluxes negate CO_2 emissions from the solid Earth[20] and from oxidation of rock-derived OC[21], contributing to the long-term regulation of global climate[19,20]. Physical erosion is thought to play a significant role in this $OC_{biosphere}$ transfer because it controls the rate of biospheric particulate organic carbon ($POC_{biosphere}$) export by rivers[22] and influences sediment accumulation and the efficiency of OC burial[10,18,23].

In the northern high latitudes, large amounts of $OC_{biosphere}$ are stored in soil[1,2]. The upper three meters of soil in the region of northern circumpolar permafrost are estimated to contain 1035±150 PgC, approximately double the carbon dioxide (CO_2) content of the pre-industrial atmosphere[17]. Many of these soils accumulated during the retreat of large

continental ice sheets following the Last Glacial Maximum, with a peak expansion between 12,000 and 8,000 cal. yr BP[24] and the $OC_{biosphere}$ can be thousands of years old[8]. This vast carbon reservoir is located in a region sensitive to environmental change over glacial-interglacial timescales[24] and to warming over the coming century[3]. Much focus has been placed on its potential to become a CO_2 source[3-6,8]. However, geological CO_2 drawdown by $POC_{biosphere}$ erosion at high latitudes has remained poorly constrained[9].

Here we sample POC carried by the major rivers in the Mackenzie Basin and investigate its fate using an offshore sediment core extending over the Holocene (Extended Data Fig. 1). The Mackenzie River is the largest source of sediment to the Arctic Ocean[11,12,15] and erosion of mountainous topography in the basin results in a high sediment discharge, similar to the combined total of 16 Eurasian rivers draining to the Arctic[11,15]. We collected river depth profiles to characterise POC across the range of grain sizes carried by large rivers[13,14,25] at the main conduit for sediment export to the Arctic Ocean in the Mackenzie Delta, at key points on the Mackenzie River and from its major tributaries (Extended Data Fig. 1). To investigate temporal variability of POC composition, river depth profiles were collected shortly after ice-break up at high/rising stage (June 2011) and during falling stage (September 2010), while river surface and bank samples were collected in June 2009. To correct for rock-derived, 'petrogenic' POC (POC_{petro}), likely to be important in the Mackenzie Basin[7,25], we combine measurements of radiocarbon (^{14}C, reported as the 'fraction modern' F_{mod}), total OC content ($[OC_{total}]$, %), stable isotopes of OC ($\delta^{13}C_{org}$), nitrogen to OC ratio (N/OC_{total}) and aluminium to OC ratio (Al/OC_{total}), which allow us to assess the age and concentration of $POC_{biosphere}$ (Methods)[7,10,13,14,22]. Published surface samples from the Mackenzie River[4,7] (n=5) have ^{14}C-ages between 6,010 yr and 10,000 yr but the ^{14}C-depletion caused by POC_{petro} versus aged $POC_{biosphere}$ has not been assessed. We also examine the

hydrodynamic behaviour of POC, using the aluminium to silicon ratio (Al/Si) ratio as a proxy of sediment grain size[25].

We find that river POC is ^{14}C-depleted throughout the Mackenzie Basin (Extended Data Table 1). F_{mod} values range between 0.28 (^{14}C age = 10,106±42 yr) and 0.63 (^{14}C age = 3675±36 yr) in the suspended load (n=27) and F_{mod} = 0.12 (^{14}C age = 17,002±84 yr) to 0.16 (^{14}C age = 14,601±64 yr) in the river bed materials (n=4). To investigate the cause of this ^{14}C-depletion, we examine the N/OC_{total} ratio. Degradation of organic matter in soils can increase the relative N abundance[6,26], differentiating degraded $POC_{biosphere}$ (high N/OC_{total}) from young, fresh $POC_{biosphere}$ (low N/OC_{total}). Suspended load samples display a negative relationship between N/OC_{total} and F_{mod} (Fig. 1), similar to measurements from a peat core in the Mackenzie Basin[26] away from permafrost,. There, N/OC_{total} ratios increased with ^{14}C age (1,250 yr to 10,200 yr) and soil depth (0m to 3m). In contrast, river bed materials have lower F_{mod} values and a relatively restricted range of N/OC_{total} values and are distinct from suspended load (Fig. 1). A dominance of POC_{petro} in bed materials[10,14] with a N/OC_{total} ratio of ~0.07 can explain their composition.

Together, the F_{mod} and N/OC_{total} values suggest that POC in the Mackenzie River is a mixture of POC_{petro} and $POC_{biosphere}$, itself varying in ^{14}C age from 'modern' to ~8000 yrs (Fig. 1). The $\delta^{13}C_{org}$ values and Al/OC_{total} ratios support this inference (Extended Data Fig. 2). Using an end member mixing analysis[10,13] we quantify POC_{petro} content of sediments (Methods) and find that suspended load at the Mackenzie River Delta is dominated by $POC_{biosphere}$ (~70-90% of the total POC). Having corrected for POC_{petro}, we investigate the source of $POC_{biosphere}$ by estimating its average ^{14}C age. This varies from 3030±150 yr to 7900±400 yr (Extended Data Fig. 3) with an average ^{14}C age of $POC_{biosphere}$ = 5800±800 yr (±2SE) in suspended sediments of the Mackenzie River Delta. These values are older than estimates of $POC_{biosphere}$ age from the Amazon River (1120-2750 yr)[14] and Ganges River

(1600-2960 yr)[13]. The ages reflect mixing of young, fresh $POC_{biosphere}$ present in each of these large river basins, with an older $POC_{biosphere}$ in the Mackenzie Basin (Fig. 1), likely to be peats which expanded between 9,000 yr and 8,000 yr (^{14}C-age)[24]. $POC_{biosphere}$ can be eroded by slumping and landsliding on river banks, across deep soil profiles[4,7]. Sections of the landscape which have discontinuous permafrost and those undergoing permafrost degradation[27] may be important sources of aged $POC_{biosphere}$, in addition to river banks which are undercut during peak water discharge following ice-break up[15]. Our samples suggest that erosion and fluvial transfer of millennial-aged $POC_{biosphere}$ is extensive in the Mackenzie Basin.

Once in the river, $POC_{biosphere}$ is sorted with river depth, revealed by the Al/Si ratio (Fig. 2b) a proxy for grain size[25]. In bed materials with low Al/Si, POC_{petro} dominates (Fig. 1) and leads to low F_{mod} values (Fig. 2c). Just above the river bed, during the two sampling campaigns coarse suspended sediments (low Al/Si) hosted the youngest, least degraded $POC_{biosphere}$ (low N/C) leading to a significant contrast in ^{14}C age from the bed materials. Towards the river surface, older, more degraded $POC_{biosphere}$ appears to dominate, and is transported with fine sediment and clays (high Al/Si)[25]. The significant contribution of degraded, very old $POC_{biosphere}$ (>5000 yrs) contrasts with large tropical rivers where organic matter turnover in terrestrial ecosystems is more rapid (Fig. 2c)[13,14].

To assess how erosion in the Mackenzie River may lead to long-term CO_2 drawdown, we estimate $POC_{biosphere}$ discharge. River depth profiles collected at high and falling stage suggest that the $[OC_{total}]$ of the suspended sediment load did not vary systematically with sediment grain size (Extended Data Fig. 4). Future work should seek to assess temporal variability in POC content and composition. Our samples suggest that changes in grain size with water discharge (Fig. 2b) could be important in setting the variability of $POC_{biosphere}$ age carried by the river (Fig. 2c). The $[OC_{total}]$ values at the Delta were 1.6±0.5% (n=8, ±1σ),

which were similar to the mean measured in the Mackenzie Delta in June-July 1987 of 1.4±0.2 (n=10)[12]. While our sample set is modest in size, it helps us to better constrain the range of POC contents in suspended load of the Mackenzie River. In addition, our end member mixing analysis allows us to provide the first estimates of [$OC_{biosphere}$], which varies between 0.7±0.1% and 2.4±0.2%. To estimate $POC_{biosphere}$ discharge, we use the most complete dataset of annual sediment discharge to the Mackenzie Delta (1974-1994)[15], which ranged from 81 Tg yr^{-1} to 224 Tg yr^{-1}. A Monte Carlo approach is used to account for the modest sample size by using the full measured variability in both [$OC_{biosphere}$] and sediment discharge (Methods). We estimate $POC_{biosphere}$ discharge = $2.2^{+1.3}_{-0.9}$ TgC yr^{-1} which is sustainable over 10^3-10^4 years, depleting the soil carbon stock by ~0.006% yr^{-1} (Methods). We estimate the POC_{petro} discharge = $0.4^{+0.1}_{-0.1}$. These estimates do not account for ice covered conditions when <10% of the annual sediment discharge is conveyed[12]. Nevertheless, our estimate of $POC_{biosphere}$ discharge is greater than the combined POC discharge of ~1.9 TgC yr^{-1} by the major Eurasian Arctic Rivers (Ob, Yenisei, Lena, Indigirka and Koyma)[11,27] which cover ~$8.6x10^6$ km^2. Based on the available measurements, the Mackenzie River dominates the input of $POC_{biosphere}$ to the Arctic Ocean.

The mobilisation of millennial-aged $POC_{biosphere}$ from soils at high latitudes has been viewed as a short-term source to the atmosphere if decomposition releases greenhouse gases (CH_4 and CO_2)[2-6,8]. However, if $POC_{biosphere}$ escapes oxidation during river transport and is buried offshore, erosion acts as a long-term CO_2 sink[10,18,20]. Offshore, aged $POC_{biosphere}$ from the Mackenzie River (Fig. 1) can explain the ^{14}C depletion and $\delta^{13}C$ of bulk organic matter, and old ^{14}C ages of terrestrial plant wax compounds (up to 20,000 yr) in surface sediments of the Beaufort Sea[7,28,29]. We provide new evidence that terrestrial POC is buried efficiently offshore and accumulates in sediments over 10^4 years. Benthic foraminfera ^{14}C ages in a borehole located at the head of the Mackenzie Trough (MTW01) indicates that 21m of

sediment have accumulated since 9183^{+125}_{-156} cal. yr BP, suggesting a high sedimentation rate during the Holocene 2.7±0.1 m ka^{-1} (Extended Data Table 2, Methods). These marine sediments have [OC_{total}] values similar to those measured in the Mackenzie River in both the <63µm (1.5% to 1.7%) and >63µm (1.1% to 1.4%) size fractions (Fig. 3). Their N/OC_{total} and $\delta^{13}C_{org}$ values suggest that they are dominated by terrestrial POC with minor marine OC addition (Extended Data Fig. 5). We use the change in OC_{total}/Al ratios offshore to estimate OC burial efficiencies have been 65±27% or more over the Holocene at this site (Methods). Rapid sediment accumulation and low temperature are likely to promote high POC burial efficiency[18,23,28]. Also, the fluvial transport dynamics of $POC_{biosphere}$ may promote burial (Fig. 2c). The oldest, most-degraded $POC_{biosphere}$ is transported with clays[25], whose association with organic matter may enhance burial efficiency[18], while the youngest, least-degraded $POC_{biosphere}$ is carried near the river bed at the highest sediment concentrations. Our findings suggest that erosion and riverine transfer at high latitudes can lead to the long-term preservation of terrestrial POC in marine sediments (Fig. 3).

Erosion of high latitude soils and riverine export of $POC_{biosphere}$ may represent an important geological CO_2 sink. Our estimate of the modern day $POC_{biosphere}$ discharge of $2.2^{+1.3}_{-0.9}$ TgC yr^{-1} in the Mackenzie River may be refined by additional temporal sampling. However, it is three times the modern rates of CO_2 drawdown by weathering of silicate minerals by carbonic acid in the Mackenzie River[16], at ~0.7 TgC yr^{-1}. Preservation of POC offshore (Fig. 3) suggests that erosion of high latitude soils, riverine $POC_{biosphere}$ transport and export to the ocean acts as the largest geological CO_2 sink operating in the Mackenzie Basin. It is important to note that these longer-term fluxes are lower than estimates of greenhouse gas emissions from high latitude soils in permafrost zones due to projected warming over the coming century[3,5,6,30]. While theses fluxes remain uncertain, recent work[30] has proposed emissions of ~ 1–2 PgC yr^{-1} which equate to a yield of ~70 tC km^{-2} yr^{-1} over 17.8×10^8 km^2 of

soils in permafrost zones. This estimate of accelerated release of CO_2 due to anthropogenic warming[30] is more rapid than the natural geological drawdown fluxes, of which we estimate $POC_{biosphere} \sim 2–5$ tC km^{-2} yr^{-1} for the Mackenzie Basin (Methods). Over longer-time periods, we postulate that this geological CO_2 sink may be sensitive to climate conditions in the Arctic. The carbon transfer can operate when high latitudes host significant $POC_{biosphere}$ stocks in soil, and while rivers can erode and transfer sediments to the Arctic Ocean. Over the last 1Ma, the $POC_{biosphere}$ transfer was likely to have been enhanced during interglacials[24] (Fig. 3), whereas during glacial conditions, lower soil $POC_{biosphere}$ stocks and extensive ice-sheet coverage suggest that $POC_{biosphere}$ erosion may have been supressed. We propose that erosion of terrestrial $POC_{biosphere}$ by large rivers draining the Arctic could play an important role in long-term CO_2 drawdown[19,20], coupling the carbon cycle to climatic conditions at high latitudes.

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collected sediment and carbonate data from the offshore borehole. R.G.H., V.G., M.D., C.B. and D.G. processed the samples and carried out the geochemical analyses. R.G.H. wrote the manuscript with input from all co-authors.

Author Information: Data are found in the Extended Data Tables. Reprints and permissions information is available at www.nature.com/reprints. The authors declare they have no competing financial interests. Correspondence and requests for materials should be addressed to r.g.hilton@durham.ac.uk.

Figure Legends

Figure 1: Source of particulate organic carbon (POC) in the Mackenzie River Basin. Radiocarbon activity of POC (F_{mod}) versus the nitrogen to organic carbon ratio (N/OC_{total}) of sediments from the Mackenzie River (circles) at the delta (black), Tsiigehtchic (grey) and Norman Wells (white) and major tributaries the Liard (diamond), Peel (dark blue square) and Arctic Red (light blue square). River depth profiles collected in 2010 and 2011 suspended load (filled symbols), river bed materials (open symbols) and sieved bank samples (2009) are shown with analytical errors (2 s.d.) as grey lines if larger than points. The dashed line shows the compositions expected by mixing rock-derived, petrogenic POC (POC_{petro}) and biospheric POC ($POC_{biosphere}$). Solid green line is the trend from a peat core in western Canada[26].

Figure 2: Transport of particulate organic carbon (POC) in the Mackenzie River. a. River depth profile collection from the Mackenzie River Delta during falling stage, with Acoustic Doppler Current Profiler data to determine channel geometry, water velocity and water discharge ($m^3\ s^{-1}$). **b.** Aluminium to Silicon ratio (Al/Si, molar), a proxy for sediment grain size[25], with water depth normalised to maximum depth. Coarser materials are carried throughout the profile during high stage. **c.** Radiocarbon activity of POC (F_{mod}) versus Al/Si for the Mackenzie Basin (this study, symbols as Fig. 1), Amazon River[14], and Ganges

River[10,13]. River suspended load (filled) and river bed materials (open) are distinguished with analytical errors (2 s.d.) shown as grey lines if larger than points.

Figure 3: Fate of particulate organic carbon offshore. a. Organic carbon concentration ($[OC_{total}]$, %) of suspended sediments in the Mackenzie River Delta (n=8) where solid line and grey box show the mean ± standard error, whiskers show ± standard deviation and the circles indicate the minimum and maximum values. **b.** $[OC]_{total}$ in sediments <63µm and >63µm from core MTW01 in the Mackenzie Trough (Extended Data Fig. 1) for depths dated by the ^{14}C activity of mixed benthic foraminifera (Methods), where whiskers show analytical error if large than the point size.

Methods

River sample collection and preparation: River depth-profiles from September 2010 and June 2011 (Extended Data Table 1) were used to collect the full range of erosion products and POC in large river systems, taking advantage of the hydrodynamic sorting of particles[10,13,14,25]. At each sampling site (Fig. 1) channel depth, water velocity and instantaneous water discharge were measured by two or more transects with an Acoustic Doppler Current Profiler (ADCP Rio Grande 600 kHz) before each depth profile was collected at a single point (±10m) in the middle of the channel. On the boat, each sample (~7-8L) was evacuated into a clean bucket and stored in sterilised plastic bags and the procedure repeated depending upon the total water depth. Each bag was weighed to determine the sampled volume, then the entire sample was filtered within 24 hrs through pre-cleaned Teflon filter units through 90 mm diameter 0.2µm PES filters[13,25]. Suspended sediment was immediately rinsed from the filter using filtered river water into clean amber-glass vials and kept cool. River bed materials were collected at the base of the depth transects from the boat, using a metal bucket as a dredge, and decanted to a sterile bag. River bank deposits (June

2009) were collected from fresh deposits close to the channel (Extended Data Table 3) and sieved at 250 μm and 63 μm to investigate the sorting of POC[31]. All sediments were freeze dried upon return to laboratories within 2 weeks, weighed and homogenised in an agate grinder.

Offshore borehole sampling and benthic foraminifera sample preparation: Benthic foraminifera-containing marine sediment samples were obtained from the upper 22 m Holocene sequence of an 85.1 m MTW01 borehole[32] located at 69° 20' 53" N, 137° 59' 13" in 45 m water depth in the Mackenzie Trough (Extended Data Fig. 1). Drilled by the Geological Survey of Canada in 1984, the core is currently archived at the GSC-Atlantic core repository. To isolate foraminifera, sediment samples were disaggregated over a <38μm mesh sieve using deionized water. Based on down-hole microfossils counts, 4 samples were selected with sufficient specimens for radiocarbon dating.

Geochemical analyses: For the river suspended sediments and core samples for organic carbon analyses, inorganic carbon was removed using a HCl fumigation technique to avoid loss of a component of POC which is known to occur during a HCl leach[33]. An adapted method to ensure full removal of detrital dolomite was used[34]. In summary, samples were placed in an evacuated desiccator containing ~50 ml 12N HCl in an oven at between 60 and 65 °C for 60 to 72 hours. Sample were then transferred to another vacuum desiccator charged with indicating silica gel, pumped down again and dried to remove HCl fumes. River sediment samples were analysed for organic carbon concentration [OC_{total}] on acidified aliquots and nitrogen concentration ([N], %) on non-acidified aliquots by combustion at 1020°C in O_2 using a Costech elemental analyser (EA) in Durham. For river depth profile samples, acidified aliquots were prepared to graphite at the NERC Radiocarbon Facility of between 1-2 mg C for each sample and standard and ^{14}C was measured by Accelerator Mass Spectrometry at the Scottish Universities Environmental Research Centre and reported as

fraction modern (F_{mod}) by standard protocol[35]. Process standards (96H humin) and background materials (bituminous coal) were taken through all stages of sample preparation and ^{14}C analysis and were within 2σ uncertainty of expected values. Stable isotopes of POC ($\delta^{13}C_{org}$) were measured by dual-inlet isotope ratio mass spectrometer (IRMS) on an aliquot of the same CO_2. These measurements were consistent with $\delta^{13}C_{org}$ measurements made by EA-IRMS normalised based on measured values standards (n=7) spanning >30‰ and long-term analytical precision of 0.2‰. River bank samples from 2009 were analysed by similar procedures at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at Woods Hole Oceanographic Institution.

Mixed benthic foraminifera samples picked from the MTW01 core were analysed at NOSAMS for ^{14}C analyses. Samples were rinsed and no pre-treatments were used. The samples were directly hydrolyzed with strong acid, H_3PO_4, to convert the carbon in the sample to CO_2. Calibration of the ^{14}C dates was performed using CALIB (version 7.1)[36]. All ^{14}C dates were normalized to a $\delta^{13}C$ of -25‰ versus VPDB (http://intcal.qub.ac.uk/calib/). Foraminifera dates were calibrated using the MARINE13 dataset[37], with a reservoir age correction (ΔR) of 335±85 yrs (Extended Data Table 2). The ΔR value is based on a recent re-analysis of ages from 24 living molluscs collected before 1956 from the northwestern Canadian Arctic Archipelago[38]. This calibration set does not include specimens from the Beaufort Sea and as such provides only a best available estimate for ΔR in the Mackenzie Trough.

End member mixing model: The F_{mod}, N/OC_{total} (Fig. 1), $\delta^{13}C_{org}$ values and Al/OC_{total} values (Extended Data Fig. 2) are consistent with a mixing of POC_{petro} and $POC_{biosphere}$ dominating the bulk geochemical composition of river POC. Autochthonous sources are not significant based on those measured values, which is consistent with the turbid nature of the Mackenzie River (mean suspended sediment concentration of ~300-400 mg/L) meaning that

like other turbid river systems (e.g. the Ganges-Brahmaputra) light penetration is minimal. A mixture of POC_{petro} and $POC_{biosphere}$ can be described by governing equations[10,13,31]:

$$f_{biosphere} + f_{petro} = 1 \quad \text{(Equation 1)}$$

$$f_{biosphere} \times \theta_{biosphere} + f_{petro} \times \theta_{petro} = \theta_{sample} \quad \text{(Equation 2)}$$

where $f_{biosphere}$ and f_{petro} are the fractions of POC derived from biospheric and petrogenic sources, respectively. θ_{sample} is the measured composition (e.g. F_{mod}) of a river POC sample, and $\theta_{biosphere}$ and θ_{petro} are the compositions of biospheric and petrogenic sources. To quantify the f_{petro} in each sample we use the aluminium (Al) to OC_{total} concentration ratio in river sediments. At each locality, a linear trend between F_{mod} and Al/OC_{total} (Extended Data Fig. 2b) can be explained by a mixture of an Al-rich, OC-poor material (rock fragments containing POC_{petro}) with Al-poor, OC-rich material (soils and vegetation debris as $POC_{biosphere}$). Taking advantage of the fact that the POC_{petro} has F_{mod}~0, the intercept at F_{mod} = 0 gives an estimate of the Al/OC_{total} values and associated uncertainty of the sedimentary rock end member. To estimate the average concentration of OC_{petro} of bedrocks in each basin ($[OC_{petro}]$, %), we use the Al concentration of river bed materials as a proxy of for the Al concentration in the bedrocks[25] and the Al/OC_{total} value at $F_{mod} \sim 0$. Following previous work in large rivers, we then assume that the OC_{petro} is well mixed in the water column and has a relatively constant $[OC_{petro}]$ (refs 10,13,14). This method may overestimate f_{petro} if OC_{petro} has been more extensively oxidised in fine grained weathering products carried in the suspended load[21]. f_{petro} is quantified using $[OC_{petro}]$ and measured $[OC_{total}]$.

The mixing analysis returns a $[OC_{petro}] = 0.12 \pm 0.03\%$ ($\pm 2\sigma$) in the Liard River and Mackenzie River at Tsiigehtchic, higher values in the Peel River $[OC_{petro}] = 0.63 \pm 0.30\%$, with the Mackenzie River at the delta with an intermediate value $[OC_{petro}] = 0.29 \pm 0.05\%$. This is consistent with the known presence of POC_{petro}-bearing sedimentary rocks in the

Mackenzie River Basin and high OC_{total} contents of bedrocks in the upper Peel River Basin and Mackenzie mountains[39]. To quantify the average ^{14}C age of $POC_{biosphere}$ in each sample, Equations 1 and 2 can be solved for $\theta_{biosphere}$, using the f_{petro} and assumed unmeasurable above background ^{14}C content of POC_{petro} ($F_{mod} = 0$). The uncertainty mainly derives from that on f_{petro} and $[OC_{total}]$ and has been propagated through the calculations.

To test if the mixing of $POC_{biosphere}$ and POC_{petro} can describe the composition of the suspended load samples, we predict the $\delta^{13}C_{org}$ measurements which were not used in the mixing analysis. The calculated f_{petro} values and end member values of -26.2±0.5‰ for $POC_{biosphere}$ and -28.6±0.5‰ for POC_{petro} were used, informed by measurements of bedrocks[39] and vegetation and soil in the basin[40]. The mixing model (equation 2) can robustly predict the $\delta^{13}C_{org}$ differences between the Peel and Liard rivers, and between suspended load and bed material $\delta^{13}C_{org}$ values (Extended Data Fig. 2c), supporting a mixing control on the variables.

Mackenzie River POC discharge: To quantify the discharge of POC we need to account for the variability in suspended sediment discharge and the variability in the $POC_{biosphere}$ and POC_{petro} content of sediments in the basin. We use the longest, most complete quantification of sediment flux by the Mackenzie River from 1974-1994[15], which has an average 127±40 Tg yr^{-1} (±1σ). Annual sediment yield varied from 81 Tg yr^{-1} to 224 Tg yr^{-1}. While the POC samples were not collected at the same time period, our measurements of $[OC_{total}]$ at the Delta, mean = 1.6±0.5% (n=8, ±1σ) and do not vary systematically between falling and high stage (Extended Data Fig. 4) and are consistent with available data from samples[12] collected in 1987 (1.4±0.2, n=10). While future work should aim to constrain the variability in POC composition further, these observations suggest that temporal variability may be less important than the potential variability in $[OC_{total}]$ with depth at a given time, where we find $[OC_{total}]$ values can range from 1.0% to 2.7%. We use our measured range of $[OC_{biosphere}]$ and

[OC_{petro}] values and the full range of annual sediment yields[15] to quantify $POC_{biosphere}$ and POC_{petro} discharge and associated uncertainty using a Monte Carlo approach. Over 100,000 simulations, we use a 'flat' probability for the range of values for both variables (i.e. equal probability of all measured values). This allows us to fully explore the range of estimates given the available measurements. Future work seeking to expand the number of [$OC_{biosphere}$] measurements to assess its flux-weighted mean and variability, while assessing temporal variability in more detail, will allow POC discharge estimates and their uncertainty to be refined. $POC_{biosphere}$ ($2.2^{+1.3}_{-0.9}$ TgC yr^{-1}) and POC_{petro} ($0.4^{+0.1}_{-0.1}$) discharges are reported as the median (50%) ± 1 s.d. Over the sediment source areas of the Mackenzie (Downstream of the Great Slave Lake[15]) of 774,200 km^2, these equate to yields of $POC_{biosphere} = 2.9^{+1.7}_{-1.1}$ tC km^{-2} yr^{-1} and $POC_{petro} = 0.6^{+0.2}_{-0.2}$ tC km^{-2} yr^{-1}. The total POC discharge is slightly higher than a previous estimate (2.1 TgC yr^{-1})[12] based on measurements of POC content made in 1987 because we: i) account for higher $POC_{biosphere}$ concentrations which may occur in water-logged $POC_{biosphere}$ near the river bed (Figs. 2c, Extended Data Fig. 4); and ii) account for the potential for very high annual sediment discharge[15]. Based on estimates of soil carbon stock in the Mackenzie Basin[2] of ~50x10^3 tC km^{-2} and the upstream sediment source area (downstream of the Great Slave Lake, 774,200 km^2), the present rate of $POC_{biosphere}$ export represents a depletion of the soil carbon stock by ~0.006% yr^{-1}, which is sustainable over 10^3-10^4 years.

OC burial efficiency in MTW01: To estimate the burial efficiency of terrestrial POC at the MTW01 site, we normalise the measured [OC_{total}] concentrations (Fig. 3) by Al concentration, an immobile inorganic element hosted by major mineral phases. The OC_{total}/Al normalization allows the effects of dilution to be distinguished from net OC gain (increased ratio) or OC loss (decreased ratio). The mean OC_{total}/Al of the MTW01 samples was 0.17±0.02 (g g^{-1}, n=4, ±2SE). This is lower than the mean OC_{total}/Al of the suspended load

samples from the Mackenzie River delta of 0.26±0.10 (g g^{-1}, n=8, ±2SE). The decrease in the ratio offshore may suggest a higher relative proportion of POC_{petro} (Extended Data Fig. 2b), however this is not consistent with the less negative $\delta^{13}C_{org}$ values (Extended Data Fig. 5). The decrease can therefore be interpreted in terms of OC loss, with the ratio of core to river samples (0.17±0.02 / 0.26±0.10). Assuming that all the change in OC_{total}/Al is driven by OC loss, and taking into account the measurement variability in these values, we estimate that 65±27% of the OC has been preserved. However, we note that the OC_{total}/Al ratios in the core are not statistically different from the river suspended load samples (one-way ANOVA, $P>0.1$) which suggest the OC burial efficiency could higher (i.e. 100%). In addition, if we use the OC_{total}/Al of finer river sediments carried near the channel surface which may be more easily conveyed offshore of 0.20±0.04 (g g^{-1}, n=4, ±2SE), we calculate burial efficiency = 85±20%. Future work should seek to better constrain these burial efficiencies with additional terrestrial and marine samples. Nevertheless, despite the remaining uncertainty, these high burial efficiencies[18] are consistent with the high sedimentation rate and low temperature setting. The long-term burial of POC delivered to sites deeper in the Beaufort Sea[28] still remains to be assessed, in order to provide a complete picture of source to sink carbon transfers.

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Extended Data

Available by contacting the lead author (r.g.hilton@durham.ac.uk) or on the online version of the paper: doi:10.1038/nature14653.

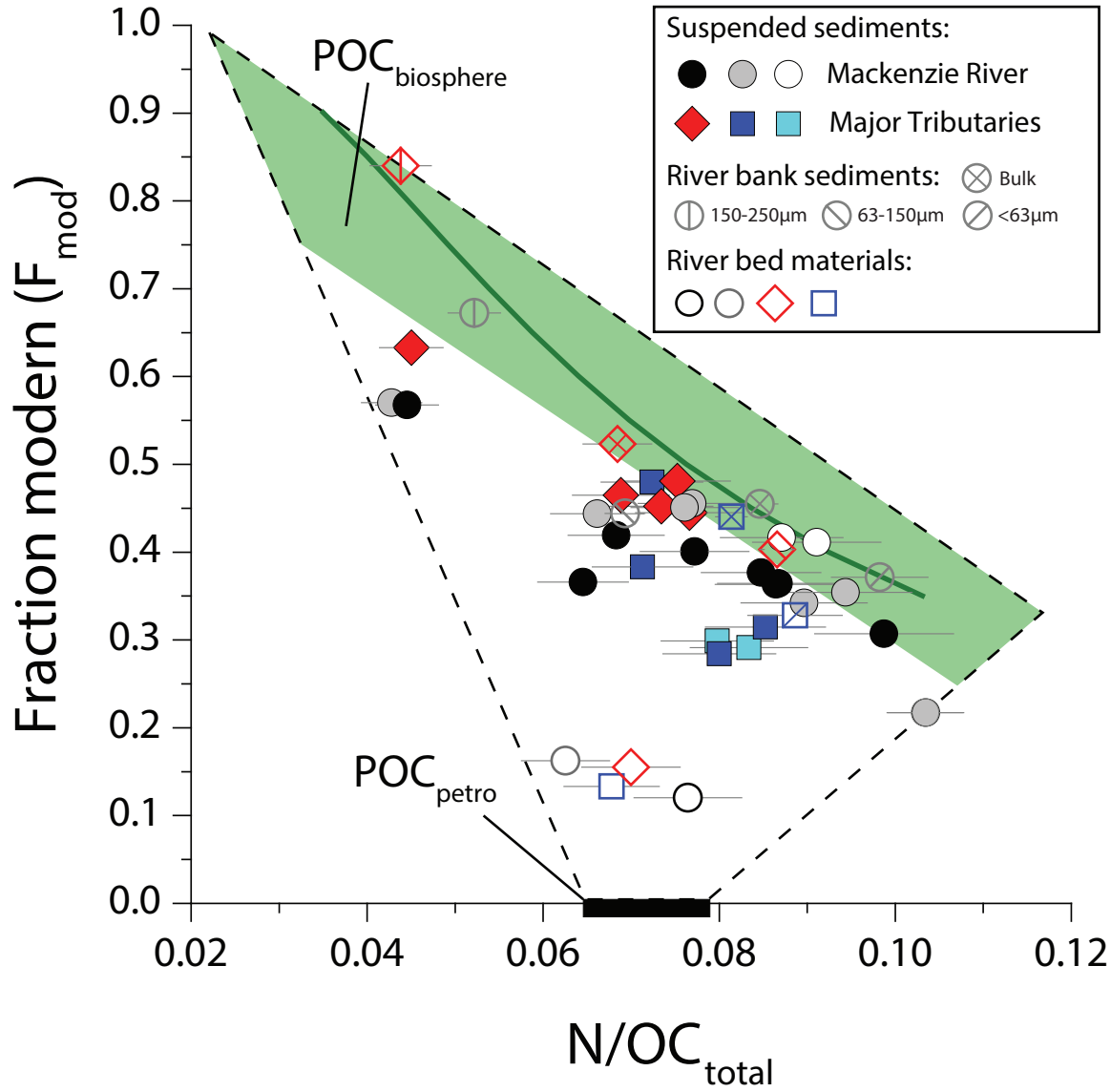
Suspended sediments:
Mackenzie River
Major Tributaries
River bank sediments:
Bulk
150-250µm
63-150µm
<63µm
River bed materials:
POC biosphere
POC petro
Fraction modern (F mod)
N/OC total
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.02
0.04
0.06
0.08
0.10
0.12

Figure 1

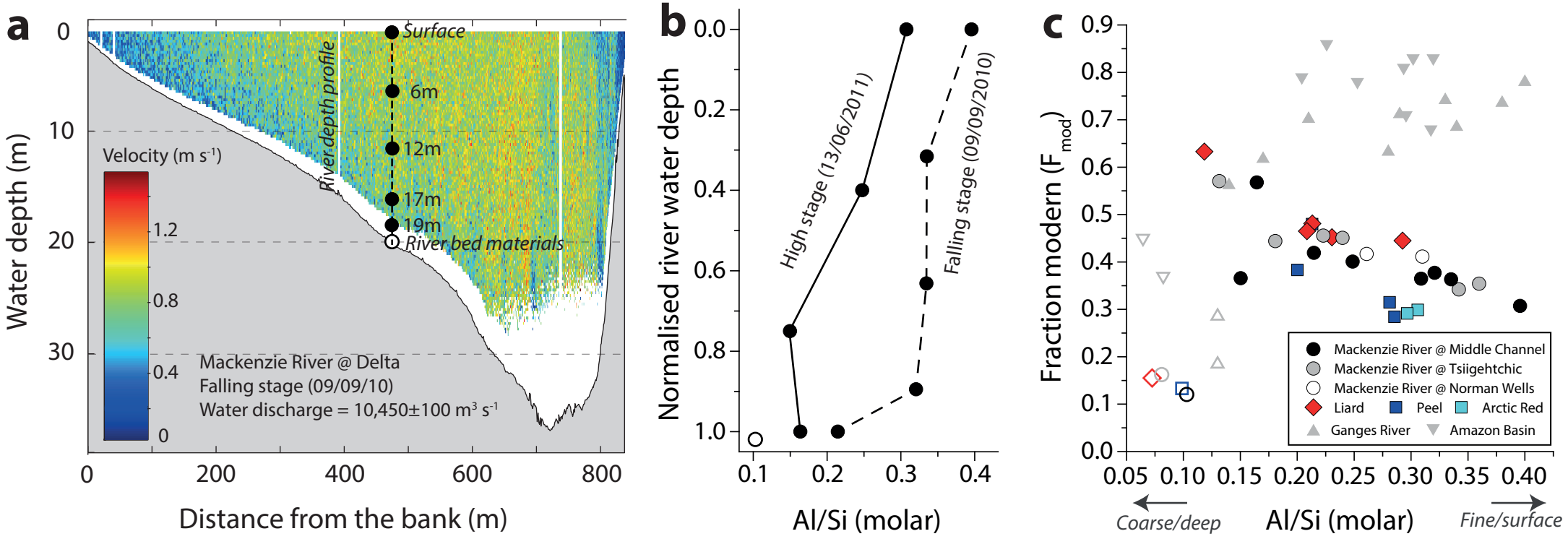
a
Water depth (m)
Distance from the bank (m)
Surface
6m
12m
17m
19m
River bed materials
River depth profile
Velocity (m s-1)
1.2
0.8
0.4
0
Mackenzie River @ Delta
Falling stage (09/09/10)
Water discharge = 10,450±100 m3 s-1
b
Normalised river water depth
Al/Si (molar)
High stage (13/06/2011)
Falling stage (09/09/2010)
c
Fraction modern (Fmod)
Al/Si (molar)
Coarse/deep
Fine/surface
Mackenzie River @ Middle Channel
Mackenzie River @ Tsiigehtchic
Mackenzie River @ Norman Wells
Liard
Peel
Arctic Red
Ganges River
Amazon Basin

Figure 2

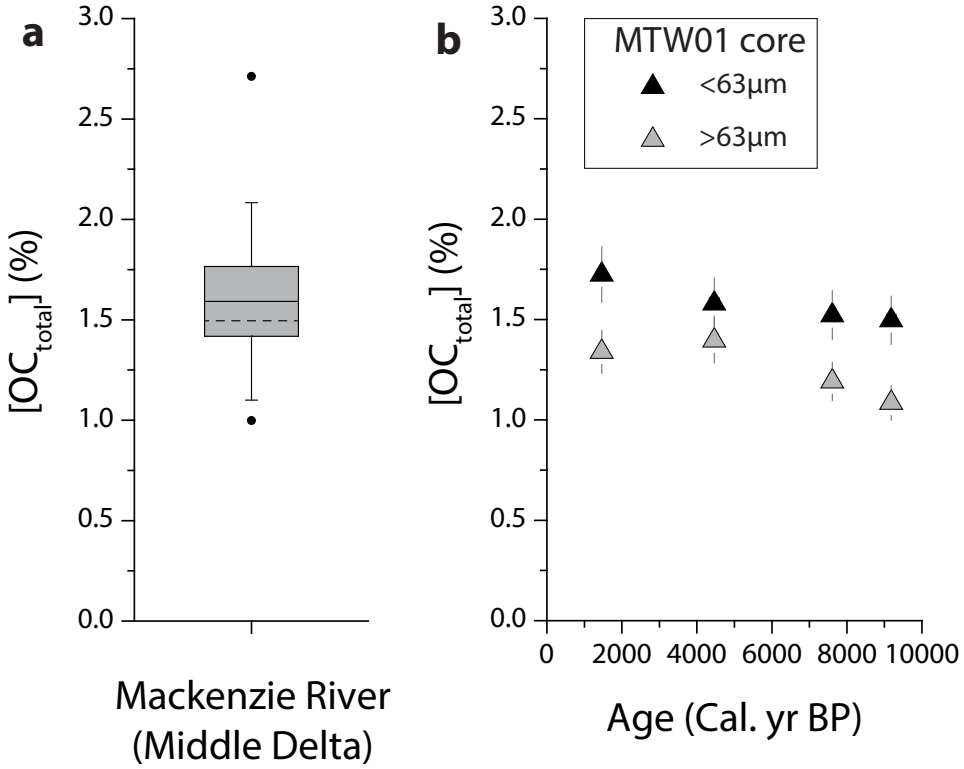
a
b
3.0
2.5
2.0
1.5
1.0
0.5
0.0
[OC$_{total}$] (%)
MTW01 core
<63µm
>63µm
0
2000
4000
6000
8000
10000
Mackenzie River
(Middle Delta)
Age (Cal. yr BP)

Figure 3