

Supplementary material for:

Abundant pre-industrial carbon detected in Canadian Arctic headwaters: implications for the permafrost carbon feedback

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Supplementary methods

Site geology

The study site is underlain by the Tertiary Beaufort Formation, which consists of unconsolidated chert, quartzitic sandstone and siltstone alluvial gravels. 1-m thick Quaternary Pleistocene tills overlay this formation, which is in turn overlain by the organic-rich topsoil. The study waters have a pH of 6.28 ± 0.05 (mean \pm standard error) and Ca^{2+} concentrations of $6.13 \pm 0.19 \text{ mg l}^{-1}$, with no evidence from the chemistry of the study waters indicating that there were significant contributions from carbonate weathering that would impact the ^{14}C values in the current study (Dean *et al* 2016).

Surface water discharge measurements

A discharge gauging station was constructed 960 m from the confluence of Siksik and Trail Valley Creeks (figure 1). Discharge data for Trail Valley Creek were available from a gauging station operated by Environment Canada located 750m upstream of its confluence with Siksik Creek (Dean *et al* 2016).

Aquatic DOC, CO₂ and CH₄ concentrations

DOC concentration samples ($n = 87$) were filtered to $0.45 \mu\text{m}$ in the field, and analyzed on a PPM LABTOC Analyser at the Centre for Ecology and Hydrology (CEH, Edinburgh, UK) (Dean *et al* 2016). CO_2 and CH_4 concentration samples ($n = 83$) were collected following the established headspace technique (Hope *et al* 1995), by equilibrating a 20 ml ambient headspace with a 40 ml water sample and shaking for 1 minute; the resultant headspace was injected into a pre-evacuated Exetainer® (Labco, UK) and analyzed on an HP5890 series II gas chromatograph (Hewlett-Packard) at CEH, Edinburgh (Dean *et al* 2016).

¹⁴C sample collection and sample processing

DO^{14}C samples were collected in acid washed 500 ml clear HDPE bottles after pre-rinsing with sample water, and filtered to $0.7 \mu\text{m}$ on pre-ashed GF/F filters within a week of sampling, then refrigerated and kept in dark conditions until analysis. GF/F filters were combusted at $\sim 500^\circ\text{C}$ for ~ 3 hours to avoid C contamination, but these filters are not available below $0.7 \mu\text{m}$

pore sizes. $^{14}\text{CO}_2$ samples were collected following Garnett *et al* (2016a); briefly, 3 L of sample water was equilibrated with a 1 L CO_2 -free headspace by shaking for 3 mins. The CO_2 in the headspace was then captured on a molecular sieve cartridge (MSC) where the sample is stable until analysis – multiple headspaces for a single sample (collected by equilibrating several separate 3 L water samples with separate 1 L headspaces) were loaded on a single MSC to ensure enough material for ^{14}C analysis (> 3 ml CO_2 , supplementary table S1). MSCs were heated (425°C) and the desorbed sample CO_2 recovered cryogenically. $^{14}\text{CH}_4$ was corrected for the minor atmospheric component of the headspace (see below), but $^{14}\text{CO}_2$ did not require a correction as a CO_2 -free headspace was used for equilibration (Garnett *et al* 2016a). DOC samples were processed to solids using rotary evaporation and acid fumigation, which were then combusted and the CO_2 produced was recovered cryogenically, following established methods. DO^{14}C samples were processed to stable solids within two months of collection, and processed to CO_2 and analyzed for ^{14}C within three months – this storage time should not have impacted the stable or radiogenic isotopic signatures of the samples (Gulliver *et al* 2010).

$^{14}\text{CH}_4$ samples were collected following Garnett *et al* (2016b), using the same headspace equilibration protocol as for $^{14}\text{CO}_2$, but the resultant headspaces were collected in 10 L foil gas bags (SKC Ltd, UK). $^{14}\text{CH}_4$ samples were transported to the Aurora Research Institute (Inuvik, NWT, Canada) in foil gas bags (SKC, UK), which were then scrubbed of CO_2 by pumping the sample through soda-lime; an EGM4 infrared gas analyzer (IRGA) was used to check the samples were CO_2 free. The sample was then combusted to CO_2 using platinum beads (Johnson Matthey Chemicals, UK) heated to $\sim 930^\circ\text{C}$, oxidizing the CH_4 to CO_2 (Garnett *et al* 2016b). The CO_2 produced was collected in-line onto a molecular sieve cartridge (MSC) for transport to the NERC Radiocarbon Facility, UK. The tubing system used to combust the CH_4 and collect the resulting CO_2 was repeatedly scrubbed with CO_2 -free ambient air via a soda-lime trap.

The $^{14}\text{CH}_4$ values were corrected for the ambient atmospheric CH_4 component in the headspace (Dean *et al* 2017) using equation (S1):

$$(S1) \quad C_{i\text{corr}} = \frac{C_{i\text{meas}} - F_{\text{atmos}} \cdot C_{i\text{atmos}}}{1 - F_{\text{atmos}}}$$

where C_i represents the isotopic content (^{14}C in pmC, or $\delta^{13}\text{C}$ in ‰) of the corrected CH_4 sample corr , measured sample meas , and ambient atmosphere atmos . F_{atmos} is the fraction of atmospheric CH_4

in the sample CH₄ (headspace CH₄ concentration was measured after sampling using the Detecto Pak-Infrared gas analyzer, Heath Consultants, USA). Values for these parameters were taken from Dean *et al* (2017). The uncertainty introduced to the ¹⁴CH₄ values by this correction is estimated to be ± 0.56 pmC and ± 0.2 ‰ for ¹⁴C and δ¹³C, respectively (Dean *et al* 2017), and is incorporated into the results presented in this manuscript (table 1).

For all ¹⁴C samples, an aliquot of the recovered CO₂ was analyzed for δ¹³C using IRMS (Thermo Fisher Delta V), with results reported relative to the Vienna Pee Dee Belemnite standard. Calibration of the IRMS is performed routinely using a suite of international standards including NBS19, IAEA C1 and C5, and USGS 24. A further aliquot of CO₂ was graphitized using Fe-Zn reduction and the ¹⁴C content determined by Accelerator Mass Spectrometry (AMS) at the Scottish Universities Environmental Research Centre (Xu *et al* 2004). Following convention, all ¹⁴C results were normalized using the δ¹³C values and presented as percent modern carbon (pmC) and conventional ¹⁴C ages (in years B.P., where 0 B.P. = AD1950); additional ¹⁴C reporting details are provided in table 1 and supplementary table S1. Samples were prepared for ¹⁴C analysis at the NERC Radiocarbon Facility (East Kilbride, UK) with known age standards processed alongside samples using identical methods for quality assurance. Standards processed using the 0.7 μm pre-ashed GF/F filters showed an increased error range, which is reflected in the greater uncertainties in the reported radiocarbon values (table 1).

Statistical analyses

To analyze the difference in estimated C age between DOC and CO₂, and their temporal dynamics, we fitted a linear mixed-model (*lme* function, R version 3.3.2) with a natural log transformation of the C ages from the distribution analysis as the response, sampling date and C type (DOC or CO₂) as fixed effects, and sampling location as the random effect. The model did not include data from July due to a lack of DO¹⁴C measurements. We did not explicitly model differences between water types due to limited data points (see figure 1 for water type definitions).

Soil equilibrium age distribution estimates

We estimated the soil C stocks for the study site from the Northern Circumpolar Soil Carbon Database (Hugelius *et al* 2013; supplementary table S2). We then used literature values for net primary production (NPP) to estimate the input of OC to the soil profile per year (Shaver 2013). The values used (66.5 to 370.5 g C m⁻² yr⁻¹) encompass a wide range of values for Toolik Lake and similar areas (e.g., Ueyama *et al* 2013) that represent comparable settings to the present study site. We then calculated the expected median age of C exported from the soil under equilibrium conditions (i.e. soil C inputs = soil C outputs), using the equation:

$$(S2) \quad \textit{Expected median age} = \frac{\textit{Soil C content} \times \ln(2)}{\textit{NPP}}$$

Using NPP values means this approach includes all the ages of C exported from the soil (apart from autotrophic respiration), whereas in the observed samples in this study there will be some CO₂ age partitioning between that lost vertically through the soil and that which is transported laterally in the dissolved phase. This means that the expected ages calculated using equation S2 will underestimate the age of exported C; however, we consider these estimates only for context (see section 5).

Supplementary results and discussion:**Table S1.** Sample field concentrations and radiocarbon reporting publication codes (see table 1); dashes indicate that data are not available.

Site	Water type	Sampling date (2014)	CO ₂			DOC			CH ₄		
			Concentration (mg C l ⁻¹)	Radiocarbon publication code	Sample size (ml CO ₂)	Concentration (mg C l ⁻¹)	Radiocarbon publication code	Carbon content (% by weight)	Concentration (µg C l ⁻¹)	Radiocarbon publication code	Sample size (ml CO ₂)
S1	Stream	12/06	2.7	SUERC-54904	5.26	17.4	SUERC-55785	23.2	3.2	-	-
S3	Stream	12/06	3.4	SUERC-54905	5.69	23.8	SUERC-55786	21.4	22.0	-	-
S5	Stream	12/06	3.1	-	-	25.6	SUERC-55787	25.8	6.8	-	-
S7	Stream	12/06	2.9	SUERC-54906	5.24	26.4	SUERC-55790	30.6	0.2	-	-
L17	Polygon	12/06	6.9	SUERC-54909	6.38	36.6	SUERC-55791	25.5	4.9	-	-
L19	Polygon	12/06	2.5	SUERC-54910	5.54	34.1	SUERC-55792	19.6	16.2	-	-
S1	Stream	13/07	6.6	SUERC-55658	4.8	30.4	-	-	9.9	-	-
S3	Stream	13/07	7.5	SUERC-55659	4.2	36.6	-	-	129.0	SUERC-55674	3.5
S5	Stream	12/07	5.2	SUERC-55660	6.8	32.8	-	-	5.6	-	-
S7	Stream	12/07	6.3	SUERC-55663	5.4	43.6	-	-	8.3	-	-
L17	Polygon	12/07	9.1	SUERC-55664	8.3	45.1	-	-	8.0	-	-
L19	Polygon	12/07	4.3	SUERC-55665	4.4	40.5	-	-	1.3	-	-
S1	Stream	28/07	2.2	SUERC-55666	3.5	26.3	-	-	1.8	-	-
S3	Stream	28/07	2.6	SUERC-55667	3.8	28.1	-	-	14.2	-	-
S5	Stream	28/07	2.2	SUERC-55668	3.6	30.5	-	-	5.4	-	-
S7	Stream	28/07	4.0	SUERC-55669	6.6	29.4	-	-	0.0	-	-
L17	Polygon	25/07	13.8	SUERC-55670	11.9	46.9	-	-	16.2	SUERC-55675	1.3
L19	Polygon	26/07	4.7	SUERC-55673	4.0	35.2	-	-	0.5	-	-
S1	Stream	30/08	1.0	SUERC-57636	3.0	25.9	SUERC-59713	21.1	0.3	-	-
S3	Stream	30/08	1.0	SUERC-57639	3.4	25.5	SUERC-59715	18.2	2.3	-	-
S5	Stream	30/08	1.5	SUERC-57640	5.0	26.9	SUERC-59716	18.3	1.4	-	-
S7	Stream	30/08	1.9	SUERC-57641	9.3	30.3	SUERC-59719	26.1	0.0	-	-
L17	Polygon	29/08	-	SUERC-57634	6.1	31.6	SUERC-59711	14.2	-	-	-
L18	Polygon	29/08	-	SUERC-57633	7.3	30.0	SUERC-59710	14.2	-	-	-
L19	Polygon	29/08	5.7	SUERC-57635	5.5	31.9	SUERC-59712	17.0	11.9	-	-
L1	Lake	01/09	1.3	SUERC-57642	4.3	27.1	SUERC-59720	16.7	3.5	-	-
L2	Lake	01/09	2.8	SUERC-57643	7.2	24.6	SUERC-59721	15.2	3.5	-	-
L3	Lake	01/09	0.4	SUERC-57646	2.6	12.4	SUERC-59725	9.4	4.4	-	-
L5	Polygon	01/09	1.6	SUERC-57645	6.3	32.7	SUERC-59724	21.9	1.7	-	-
L6	Lake	01/09	1.9	SUERC-57644	7.3	25.6	SUERC-59722	21.1	0.0	-	-
L7	Lake	02/09	1.6	SUERC-57649	5.6	36.0	SUERC-59726	31.8	1.2	-	-
L9	Lake	02/09	0.6	SUERC-57650	4.2	14.4	SUERC-59729	15.0	7.8	-	-
S1	Stream	08/09	2.0	-	-	24.0	SUERC-59730	20.2	0.5	-	-
S3	Stream	08/09	2.2	SUERC-57651	5.6	25.9	SUERC-59731	17.3	3.8	-	-
S5	Stream	08/09	2.7	SUERC-57652	8.4	28.4	SUERC-59732	18.5	2.2	-	-
S7	Stream	08/09	5.9	SUERC-57653	6.8	30.2	SUERC-59733	28.5	81.8	-	-
L17	Polygon	08/09	-	SUERC-57654	19.0	-	SUERC-59734	16.0	-	-	-
L19	Polygon	08/09	-	SUERC-57655	6.6	-	SUERC-59735	15.1	-	-	-

Table S2. Parameters used in equation (S2) for estimating the expected age of C lost from the soils at the study site assuming soil C inputs and outputs are in equilibrium; values for different depths in the NCSCD were integrated to match the deepest average active layer depth in 2014.

	Active layer depth (m)	Soil organic C content (kg C m⁻²)
NCSCD	0.3-1.0	27.9
NCSCD	0.0-0.3	9.5
2014	0.6	11.2
Net Primary Production (g C m⁻² yr⁻²)		
Minimum	66.5	
Maximum	370.5	

NCSCD = Northern Circumpolar Soil Carbon Database (Hugelius *et al* 2013).

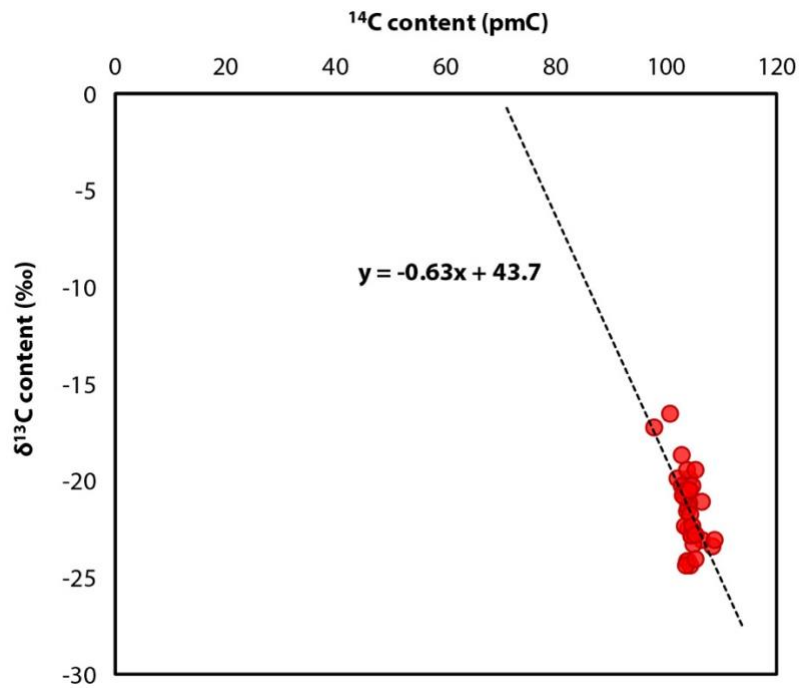


Figure S1. ^{14}C versus $\delta^{13}\text{C}$ for the CO_2 samples collected in this study. If carbonate weathering were contributing to the dissolved CO_2 measured in these samples, we would expect to see a linear regression that trended towards a ^{14}C content of 0 pmC at 0 ‰ $\delta^{13}\text{C}$. The linear regression between $\delta^{13}\text{C}$ and ^{14}C in this figure has an intercept at +43.7 ‰, demonstrating that there is unlikely to be input from carbonate weathering to the dissolved $^{14}\text{CO}_2$ measured in this study.

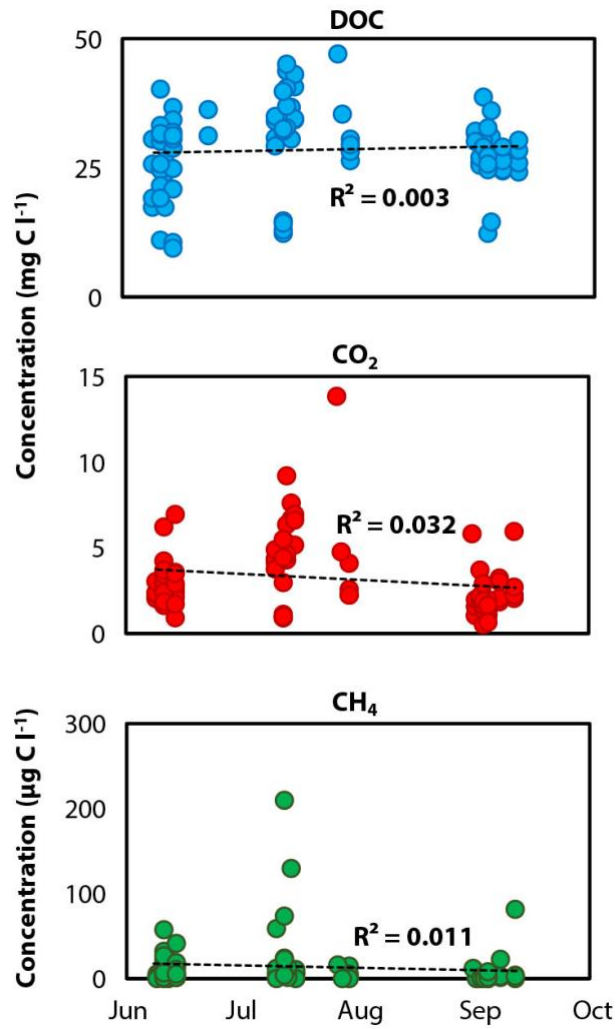


Figure S2. DOC, CO₂ and CH₄ concentrations during the sampling period (June to October 2014) at the sites sampled for ¹⁴C analyses. Linear trend lines are displayed as black dashed lines along with their respective R² values. Note the units are different for CH₄ concentration.

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