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Key Points:
- Lowest δ^{13}C-DOC values reported to date in surface freshwaters
- δ^{13}C-DOC values likely a result of methane cycling
- Potential implications for the quality of DOC in Arctic catchments

Supporting Information:
- Supporting Information S1

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Origin and temporal variability of unusually low δ^{13}C-DOC values in two High Arctic catchments

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Abstract The stable carbon isotopic composition of dissolved organic matter (δ^{13}C-DOC) reveals information about its source and extent of biological processing. Here we report the lowest δ^{13}C-DOC values (−43.8‰) measured to date in surface waters. The streams were located in the High Arctic, a region currently experiencing rapid changes in climate and carbon cycling. Based on the widespread occurrence of methane cycling in permafrost regions and the detection of the *pmoA* gene, a proxy for aerobic methanotrophs, we conclude that the low δ^{13}C-DOC values are due to organic matter partially derived from methanotrophs consuming biologically produced, ^{13}C-depleted methane. These findings demonstrate the significant impact that biological activity has on the stream water chemistry exported from permafrost and glaciated environments in the Arctic. Given that the catchments studied here are representative of larger areas of the Arctic, occurrences of low δ^{13}C-DOC values may be more widespread than previously recognized, with implications for understanding C cycling in these environments.

1. Introduction

On a global scale, dissolved organic carbon (DOC) in rivers constitutes approximately 25% of the total carbon (inorganic and organic) flux to the world's oceans, making it one of the largest fluxes of carbon in the modern-day carbon cycle [*Sundquist and Visser*, 2003]. Despite the small size of the Arctic Ocean, it is estimated that this ocean basin receives approximately 15% of the global riverine DOC flux (34 Tg C yr^{-1}) [*Holmes et al.*, 2012]. The high proportion is due to the extensive carbon stocks stored in high-latitude soils and peatlands, which contain approximately 50% of the global belowground organic carbon [*Tarnocai et al.*, 2009]. There are concerns that the release of carbon from these reservoirs may be accelerated in a warming climate through the combined effects of permafrost thaw and coastal erosion [*Schuur et al.*, 2009; *Elberling et al.*, 2013]. Fluxes of DOC from terrestrial to marine systems are strongly controlled by hydrology with 20–70% of annual DOC exported during the spring freshet [*Raymond et al.*, 2007; *Guo et al.*, 2012]. Future projections of DOC fluxes are therefore highly dependent on accurate hydrological predictions and frequent sampling of DOC concentrations throughout the year.

The proportion of DOC which ultimately gets transferred to the atmosphere as opposed to being buried in ocean sediments depends on its lability, i.e., how easily it is able to be decomposed by microbes into CO_2 or CH_4. Traditionally, it was assumed that the DOC in Arctic rivers was refractory and would therefore have minimal biogeochemical impact once released into aquatic systems [*Amon*, 2004]. However, recent studies of DOC using optical (UV-visible absorbance and excitation-emission fluorescence scans) and chromatographic separation techniques to understand the chemical composition of DOC (e.g., size distribution and aromaticity) and incubation experiments to assess biodegradability [*Lafrenière and Sharp*, 2004; *Holmes et al.*, 2008; *Spencer et al.*, 2009; *Amon et al.*, 2012; *Mann et al.*, 2012; *Wickland et al.*, 2012] have demonstrated large seasonal variations in the source and lability of DOC. Spring freshet transports DOC derived from litter leachate, summer flow transports a deeper mineral source pool, and winter base flow transports water from even deeper flow paths [*Spencer et al.*, 2008; *Wickland et al.*, 2012]. Carbon-14 dating corroborates these broad source identifications: spring melt provides a dominant flux of young carbon from shallow soils with older carbon derived from deeper soil layers exported during winter base flow [*Raymond et al.*, 2007]. A similar effect is observed in glaciated catchments where the youngest carbon, from supraglacial sources, is exported at peak flow while

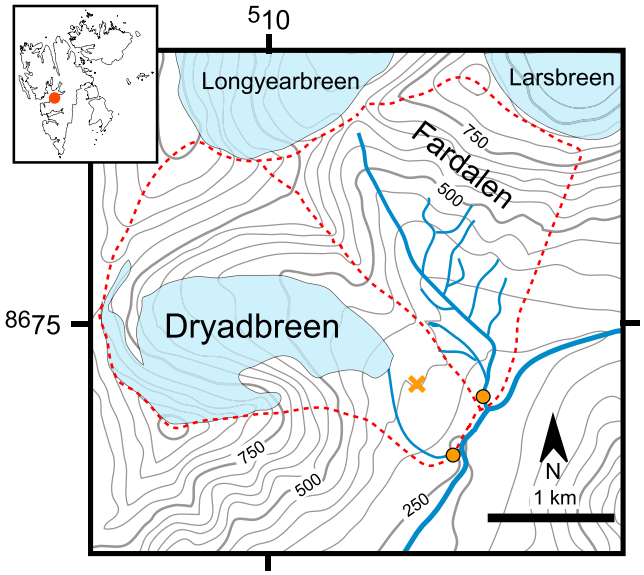

Figure 1. Topographic map of the two study catchments. The red dot in the inset shows the location of the study area (latitude, 78°08′N; longitude, 15°30′E) in relation to the rest of Svalbard. Dryadbreen is on the left and Fardalen on the right. The red dashed lines demarcate the catchment boundaries. Water samples from both catchments were collected immediately before the confluence with the main stream (orange circles). Sediment samples L, M, and O were collected at the water sampling locations, while sample A was collected on the sandur as indicated by the orange cross. The map is projected in universal transverse Mercator World Geodetic System (WGS 84) zone 33X with contours displayed at 50 m intervals.

the oldest carbon, derived from overridden soils, is exported at the start of the melt season [*Bhatia et al.*, 2013]. Importantly, the DOC (of all ages) in Arctic regions has been shown to be more labile than previously thought, especially during freshet when DOC fluxes are highest, and is therefore able to potentially impact downstream ecosystems at all times of the year [*Holmes et al.*, 2008; *Spencer et al.*, 2008; *Mann et al.*, 2012; *Wickland et al.*, 2012]. However, in larger rivers, this labile DOC fraction may be utilized along the length of the river and thus never reach the ocean [*Vonk et al.*, 2013; *Spencer et al.*, 2015].

The stable carbon isotopic composition of DOC (δ^{13}C-DOC) also gives information on source provenance [*Wang et al.*, 1998]. Arctic rivers measured so far exhibit δ^{13}C-DOC values of around −27‰ reflecting carbon fixed by the Calvin-Benson-Bassham cycle (C3), likely via photosynthesis, with a limited range of seasonal variability [*Guo and Macdonald*, 2006; *Raymond et al.*, 2007]. Larger seasonal variability in δ^{13}C-DOC values has been observed in smaller temperate streams and can provide insights into the functioning of freshwater ecosystems and food web dynamics [*Schiff et al.*, 1990; *Ziegler and Brisco*, 2004]. δ^{13}C-DOC measurements can therefore, in the right conditions, also provide information on the couplings between biology and chemistry in freshwaters. In this study we report measurements of δ^{13}C-DOC from two High Arctic catchments and interpret these data in the context of the stream water chemistry [*Hindshaw et al.*, 2016] and the microbial community composition.

2. Description of Field Area

Svalbard is located in the Arctic Ocean. The archipelago has an Arctic climate with a mean annual air temperature of −5°C and mean annual precipitation of 180 mm (measured at Longyearbyen airport) [*Humlum et al.*, 2003]. Permafrost is continuous throughout the islands and can be up to 500 m thick [*Humlum et al.*, 2003]. The two studied catchments (Dryadbreen and Fardalen, Figure 1) are situated next to each other in the Paleogene sedimentary Central Basin of Svalbard. The sedimentary formations exposed in the catchments are from the Van Mijenfjorden group which is Paleocene to Eocene in age (66–33.9 Ma) and contain sandstones, siltstones, and shale [*Major et al.*, 2000].

Dryadbreen (Figures 1 and 2a) has been retreating since the end of the Little Ice Age (~1890) [*Ziaja*, 2001]. The thermal regime of the glacier is expected to be cold based with temperate patches, based on similar-sized glaciers in the same area [*Etzelmüller et al.*, 2000; *Etzelmüller and Hagen*, 2005]. Between 1936 and 2006 the area

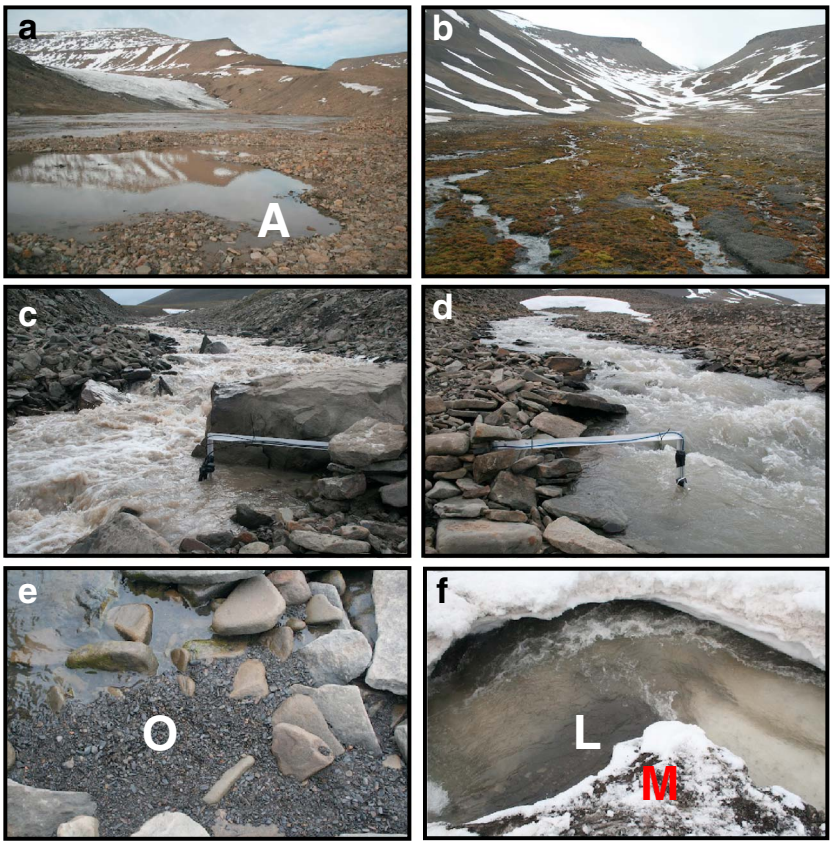

Figure 2. Photographs illustrating the nature of the two catchments: (a, c, and e) Dryadbreen and (b, d, and f) Fardalen. Figures 2a and 2b illustrate the upper reaches of each catchment in July. Dryadbreen is dominated by a sandur over which a braided stream flows and vegetation is negligible. Fardalen is patchily vegetated and the vegetation is predominantly mosses and lichens. Figures 2c and 2d illustrate the conditions at the water sampling locations (positions shown in Figure 1). The stream beds are dominated by large pieces of sandstone. The locations of the sediment samples used for microbial analyses are indicated by an "A" in Figure 2a, "O" in Figure 2e, and "L" and "M" in Figure 2f (see also Table 1).

of the glacier decreased from 2.59 to 0.91 km^2 leaving large terminal and lateral ice-cored moraines and a sandur in front of the glacier [*Ziaja and Pipała*, 2007]. The uppermost part of the catchment faces north-northeast, and the valley then curves around such that at lower elevations (<500 m) the catchment faces southeast. The catchment area is 4.8 km^2 and ranges in elevation from 250 to 1031 m above sea level (asl). The river in the sandur plain is braided, but the braids merge such that one stream drains the end moraine. This stream was sampled just before the confluence with the river in the main valley.

Fardalen (Figures 1 and 2b) is a nonglaciated catchment at the head of a valley of the same name. In contrast to Dryadbreen, the whole catchment has a southeasterly aspect which contributes to the absence of present-day glaciation. The valley is currently underlain by continuous permafrost and is likely to have been unglaciated for at least the last 10 kyr [*Svendsen and Mangerud*, 1997]. The catchment area is 3.4 km^2 and ranges in elevation from 250 to 1025 m asl. A first-order stream drains the catchment, and it was sampled just before the confluence with the river in the main valley.

The streams at the water sampling locations flowed over a mixture of larger sandstone blocks and smaller centimeter-sized pieces of shale (Figures 2c and 2d). No macrofauna was observed in either of the streams, but a few rocks in the slower parts of the stream draining Fardalen were observed to have algal biofilms.

3. Methods

3.1. Hydrology

Water stand was recorded every 10 min by a CS450 Campbell Scientific pressure transducer connected to a Campbell CR200X data logger. Water stand was converted to discharge using discharge measurements

obtained by salt tracing, which was performed using a point addition of 1–3 kg salt. The resulting change in conductivity ~70 m downstream was monitored by a Hobo U24 conductivity logger recording every second. The calibration of the conductivity meter and conversion to discharge was done following the procedure outlined in *Hudson and Fraser* [2005]. The amount of snow in May 2012 prevented installation of the loggers that early in the season; therefore, high-resolution hydrological data are only available for the period 25 July to 3 August 2012. At the start of May there was no surface water and no subsurface water was found by digging. Three weeks later, the landscape was still dominated by snow but both streams were flowing.

3.2. Water Chemistry

Samples were collected in the period June to August 2012 as part of a larger project investigating chemical weathering processes [*Hindshaw et al.*, 2016]. Each catchment was sampled at a single location near the confluence with the main valley river (Figures 1, 2c, and 2d). Additionally, a supraglacial stream water sample was collected on 1 August 2012 from the surface of Dryadbreen near the toe of the glacier. Samples for DOC analysis were filtered through 0.2 μm nylon filters into 25 mL brown glass vials using a syringe connected to a hand-held filter holder (Swinnex-47, Millipore, U.S.). The samples were acidified to pH ⩽3 with 85% H_3PO_4. The brown glass vials were cleaned before use by rinsing in 18.2 MΩ water and then heating at 550°C for 2 h.

DOC concentrations and δ^{13}C-DOC values were obtained using a method described by *Lang et al.* [2012]. In brief, organic compounds were oxidized to CO_2 using supersaturated potassium persulfate solution (100 mL H_2O + 4.0 g $K_2S_2O_8$ + 200 μL 85% H_3PO_4). The vials were then purged with high-purity helium to remove inorganic carbon and heated to 100°C for 1 h to convert any organic matter in the sample to CO_2. The carbon isotopic composition of the evolved CO_2 was then measured with a GasBench II coupled to a ConFlo IV interface and a Delta V Plus mass spectrometer (Thermo Fischer Scientific at ETH Zurich). Delta values are reported relative to Vienna Peedee belemnite (VPDB), and measurement error was ±0.6‰.

A filtered water sample was titrated with 3.3 mm HCl within an hour of collection, and alkalinity was calculated from the titration curve using the Gran method [*Stumm and Morgan*, 1996]. Dissolved inorganic carbon (DIC) was calculated using the measured pH and alkalinity of the water samples together with the K_1, K_2, and K_H values for 4°C [*Stumm and Morgan*, 1996]. Water samples for δ^{13}C-DIC analysis were filtered into a 1 L bottle using a polycarbonate vacuum filtration unit connected to a hand pump, and 6 mL of a 1M barium chloride/0.9M sodium hydroxide solution was immediately added. After at least 24 h, the solution was filtered and the precipitate washed 5–6 times with 18.2 MΩ water. The weight yield of dried barium precipitate (mixed barium sulfate and barium carbonate) was determined to ensure that the barium chloride had been in excess. $^{13}C/^{12}C$ ratios were determined on CO_2 produced by reaction with phosphoric acid in a Multiprep online to an IsoPrime dual-inlet mass spectrometer (GV Instruments at the Natural Environment Research Council (NERC) Isotope Geosciences Laboratory), with $^{13}C/^{12}C$ ratios calculated as δ^{13}C values versus VPDB (Vienna Peedee belemnite) by comparison with laboratory standards calibrated against National Bureau of Standards (NBS) 18 and 19. Analytical reproducibility was typically ≤0.1‰ (1 SD).

3.3. Particulate Organic Carbon

The suspended sediments (>0.2 μm, collected on nylon filter papers) were washed off the filter papers using deionized water and freeze dried. The sample was then reacted overnight with 1.5 M HCl to remove carbonates, washed free of acid, dried, and homogenized. The remaining sample (after removal of inorganic carbon) is assumed to represent particulate organic carbon (POC). $^{13}C/^{12}C$ ratios were determined by combustion to CO_2 in an EA-1120 elemental analyzer online to an isotope ratio mass spectrometry (Delta+XL, ThermoFinnigan at the NERC Isotope Geosciences Laboratory), with $^{13}C/^{12}C$ ratios calculated as δ^{13}C values versus VPDB by comparison with laboratory standards calibrated against NBS 19 and International Atomic Energy Agency CH-7. Analytical reproducibility was typically ≤0.2‰ (1 SD).

3.4. Microbial Sequencing

DNA was extracted from four surface sediment samples (Table 1): two from Fardalen collected in spring at the water sampling location (Figure 2f), L (river sediment) and M (sediment by the side of the river resting on snow) and two from Dryadbreen collected in summer, A (Figure 2a, sediment from a pool of water in the sandur, not connected to main river) and O (Figure 2e, sediment adjacent to the river at water sampling location). No microbial sequencing was conducted on water samples. Sediment samples were scooped directly into either sterile 300 mL PVC containers or sterile 50 mL Falcon™ centrifuge tubes. The samples were stored at ambient temperature (<4°C) until they were transported to the laboratory where they were desiccated by drying at 40°C (4 days). Desiccated samples were shipped internationally to the U.S. where they were

Table 1. Description of Sediment Samples Collected for Microbial Sequencing

Label	Catchment	Description	Photograph
A	Dryadbreen	Sediment from a pool of water in the sandur, not connected to main river	Figure 2a
O	Dryadbreen	Sediment adjacent to the river at the water sampling location	Figure 2e
L	Fardalen	Sediment in the river at the water sampling location	Figure 2f
M	Fardalen	Sediment by the side of the river resting on snow	Figure 2f

subjected to molecular analyses. DNA extraction, purification, quantification, and PCRs (polymerase chain reactions) for the amplification of bacterial and archaeal 16S rRNA genes were conducted as part of previous work [*Hindshaw et al.*, 2016], and the methods are described therein. Archaeal 16S rRNA gene amplicons were not recovered from any of the four sediment DNA extracts. DNA extracts were screened for the presence of genes encoding the alpha subunits of the particular methane monooxygenase (*pmoA*) and methyl coenzyme M reductase (*mcrA*) as proxies for methanotrophs and methanogens, respectively, since these two processes could conceivably impact on δ^{13}C-DOC values.

For amplification of *pmoA* from sediment DNA extracts, primers pmoA189F (5"-GGNGACTGGGACTTCTGG-3") and pmoA682R (5"-GAASGCNGAGAAGAASGC-3") were used in 35 cycles of PCR at an annealing temperature of 56°C [*Holmes et al.*, 1995] using reaction conditions as previously described [*Hamilton et al.*, 2013]. For amplification of *mcrA* from sediment DNA extracts, primers mcrF (5'-TAYGAYCARATGTGGYT-3') and mcrR (5'- ACRTTCATNGCRTARTT-3') were used in 35 cycles of PCR at an annealing temperature of 50°C [*Springer et al.*, 1995] using reaction conditions as previously described [*Hamilton et al.*, 2013]. All PCR reactions were run in triplicate with ~2 ng of DNA as template. Equal volumes of each replicate reaction were combined, purified, cloned, sequenced via the Sanger method, and analyzed as described previously [*Boyd et al.*, 2007].

The abundance of *pmoA* genes was determined via quantitative PCR using a BioRad CFX Connect PCR detection system (Hercules, CA) as previously described [*Boyd et al.*, 2011]. Briefly, qPCR reactions were performed in triplicate with 500 nM forward and reverse primer and the SsoAdvanced™ Universal SYBR®; Green Supermix (BioRad) according to the manufacturer's instructions. The following cycling conditions were used: an initial denaturing at 98°C for 30 s followed by 35 cycles of 98°C (30 s) and annealing and elongation at 56°C (60 s). Specificity of the qPCR assays was verified by melt curve analysis. Control reactions contained no template DNA. Plasmid standards for use in relating template copy number to threshold amplification signals were prepared as previously described [*Boyd et al.*, 2011].

4. Results

4.1. Hydrology

The discharge of both streams during the summer period are shown in Figure 3. Both streams exhibit diurnal cycles in discharge, and the range of discharge measured in both catchments was 0–0.5 $m^3\ s^{-1}$, but the median discharge over the period of data collection for Dryadbreen (0.40 $m^3\ s^{-1}$) was greater than for Fardalen (0.22 $m^3\ s^{-1}$). An increase in the amplitude of the diurnal discharge cycle was observed in both catchments during 31 July to 1 August. This event coincided with a period of sunny weather with little cloud cover, thus enhancing snow (and ice in Dryadbreen) melt.

4.2. Carbon Concentrations and Isotopic Compositions

DOC concentrations range from 132 to 2071 μmol C/L in Dryadbreen and from 113 to 1191 μmol C/L in Fardalen (Figure 3 and Table S1 in the supporting information). DIC concentrations tended to be lower than DOC concentrations and ranged from 280 to 948 μmol C/L in Dryadbreen and from 135 to 393 μmol C/L in Fardalen (Figure 3 and Table S1). There was no significant difference in DOC concentrations between the two streams as tested by a Student's *t* test. Average DOC concentrations in each catchment (740 and 678 μmol C/L in Dryadbreen and Fardalen, respectively) were similar to that observed in other streams draining permafrost-dominated catchments [*MacLean et al.*, 1999].

The δ^{13}C-DOC values were relatively constant in both streams at −43.8 to −38.7‰, with the exception of two outliers (Figure 3 and Table S1). More positive δ^{13}C-DOC values were recorded on 1 August in Fardalen (−28.1‰) and on 2 August in Dryadbreen (−27.6‰). These two more positive values correspond to the lowest DOC concentrations measured and approach the average δ^{13}C value measured in POC and the δ^{13}C-DOC

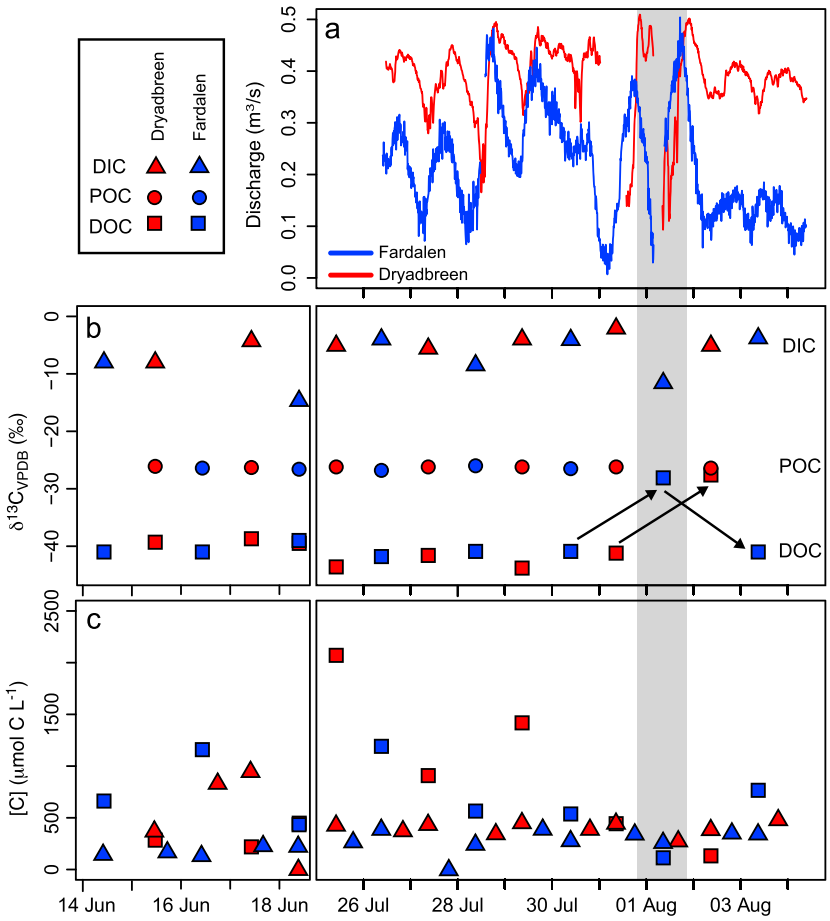

Figure 3. (a) Hydrological data collected from Dryadbreen (red) and Fardalen (blue). The grey band highlights the diurnal cycle of 31 July to 1 August which was greater in amplitude than previously recorded diurnal cycles. Gaps in the data indicate periods when the logger malfunctioned. (b) δ^{13}C values of DOC (squares), POC (circles) and DIC (triangles) in Dryadbreen (red) and Fardalen (blue). The arrows highlight the higher δ^{13}C-DOC values observed during and immediately after the high-amplitude diurnal cycle. (c) Concentrations of DOC (squares) and DIC (triangles) in Dryadbreen (red) and Fardalen (blue).

value of −27.2‰ measured in supraglacial water (Figure 4). As far as we are aware, the δ^{13}C-DOC value of −43.8‰ is the lowest ever reported for surface freshwaters. The carbon isotopic composition of dissolved inorganic carbon (δ^{13}C-DIC) spanned a range of 12.6‰ (Figure 3 and Table S1). The lowest values in each catchment were measured in spring (−8.0‰ (Dryadbreen) and −14.7‰ (Fardalen)) and the highest values in summer (−2.1‰ (Dryadbreen) and −3.8‰ (Fardalen)). The carbon isotopic composition of DIC in these catchments is likely to be mainly controlled by a mixture of DIC derived from the weathering of carbonates and the oxidation of soil organic matter.

The δ^{13}C values and concentrations of POC showed neither temporal nor spatial variation, and the average values were −26.3±0.2‰ (1 SD) and 2200±500 mmol C/kg (1 SD), respectively (Figure 3 and Table S1). The δ^{13}C values reflect carbon fixed by the Calvin-Benson-Bassham cycle (C3) which may be of plant [*Kendall and Doctor*, 2003] or microbial origin [*Havig et al.*, 2011].

4.3. Microbial Sequencing

The bacterial community composition of these samples was described in *Hindshaw et al.* [2016], and no archaeal sequences were detected (data not shown).

Briefly, cluster analysis of the phylogenetic composition of the communities indicated that the taxonomic compositions of samples A and L were similar. These samples were sediments collected underwater, from a pool of water on the sandur adjacent (but not connected to) the Dryadbreen river and from the Fardalen river. Both samples were dominated by sequences affiliated with the phylum proteobacteria (A = 49% and

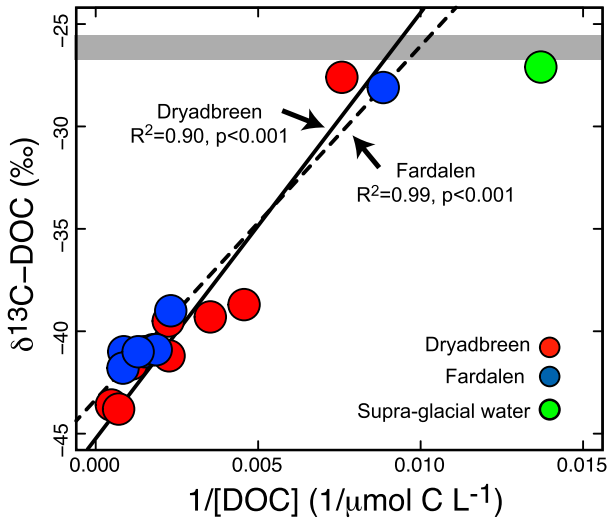

Figure 4. Plot of δ^{13}C-DOC versus the inverse of DOC concentration in μmol C/L. The grey band indicates the average bulk δ^{13}C-POC value of −26‰ (Table S1). The regression lines indicate that the variation in δ^{13}C-DOC values can be explained by two-component mixing between a "terrestrial" DOC source with δ^{13}C-DOC values close to POC and a source with δ^{13}C-DOC values of −45 to −43‰. This latter source is consistent with DOC originating from the active layer of the permafrost where methane cycling occurs. The relationship between 1/DOC and δ^{13}C-DOC remains statistically significant in each catchment even when the high δ^{13}C-DOC point is not included (Dryadbreen $R^2 = 0.83$, $p < 0.01$ and Fardalen $R^2 = 0.65$, $p < 0.05$).

$L = 65\%$). Samples O and M were both sediments adjacent to the Dryadbreen and Fardalen rivers, respectively. Both locations were damp at the time of sampling. These samples contained fewer sequences affiliated with proteobacteria ($M = 25\%$ and $O = 30\%$) but more that were affiliated with Firmicutes ($M = 15\%$ and $O = 31\%$). Physiological inferences based on phylogenetic affiliation of sequences indicate that heterotrophic bacteria were dominant in the bacterial communities with 70 and 52% of the bacterial communities present in A and L, respectively, inferred to use heterotrophic metabolisms. *mcrA* amplicons (marker for methanogens) were not detected in any of the four environments, and *pmoA* amplicons (marker for aerobic methanotrophs) were obtained in sample O (Dryadbreen sediments) only.

5. Discussion

The majority of studies reporting δ^{13}C-DOC values from glaciated and permafrost-dominated catchments show negligible deviation from the δ^{13}C values expected from carbon fixed by the Calvin-Benson-Bassham cycle (C3), i.e., values of around −27‰ (Figure 5). The values of approximately −40‰ for δ^{13}C-DOC which we report are very unusual: there are only a few reported values less than −32‰ (lower limit of C3-derived δ^{13}C), and these are from small (less than 10 km^2), temperate catchments (Figure 5).

5.1. What Is the Origin of the Very Low δ^{13}C-DOC Values?

Low δ^{13}C-DOC values (<−40‰) are not uncommon in the low molecular weight fraction of groundwater and pore waters and have been linked to the presence of kerogen and microbial cycling of this DOC fraction [*Murphy et al.*, 1989a, 1989b; *Wassenaar et al.*, 1989, 1990]. In surface waters, however, low δ^{13}C-DOC values of bulk DOC are much rarer. *Schiff et al.* [1990] report a single value of −40.2‰ from a beaver pond in Ontario under high flow conditions and stated that this indicated internal DOC cycling.

DOC in streams has two primary sources: aquatic organisms (autotrophs) and terrestrial sources (soil and plants). Assuming complete organic C utilization, there is little fractionation in δ^{13}C up the food chain and the C isotopic composition of the stream biomass (and therefore the DOC produced) is determined by the autotrophic organisms [*McGoldrick et al.*, 2008]. Given that DOC derived from terrestrial sources will have a similar isotopic composition to that measured in the POC fraction (−26‰, Table S1), the low δ^{13}C-DOC values must arise from aquatic organisms. There are two groups of autotrophic organisms to consider: photoautotrophs and chemoautotrophs.

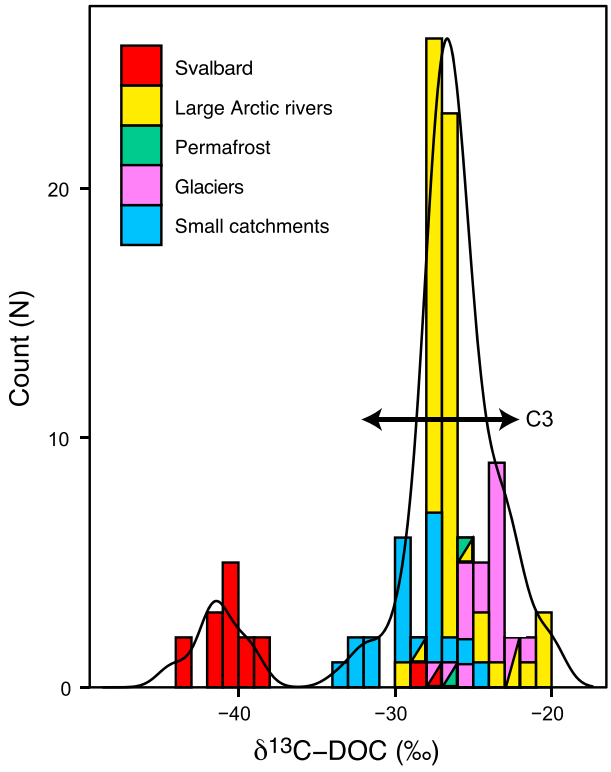

Figure 5. Histogram of δ^{13}C-DOC data from Svalbard (this study) together with literature data from glaciated, permafrost-dominated, and small (<10 km^2), temperate catchments. Bin size is 1‰, and the density function for all the data is shown overlaid with a bandwidth of 1.5. The double-headed arrow marked "C3" indicates the range of δ^{13}C values found in C3 terrestrial plants and soil organic matter [*Finlay and Kendall*, 2008]. Large Arctic rivers [*Raymond et al.*, 2007; *Guo et al.*, 2007]: compilation of data from the Yukon, Mackenzie, Lena, Ob, and Yenisey. Permafrost [*Vonk et al.*, 2013]: small tributaries of the Kolyma river draining the Yedoma. Glaciers [*Hood et al.*, 2009; *Bhatia et al.*, 2013; *Spencer et al.*, 2014a, 2014b]: rivers draining glaciated catchments. Small catchments [*Palmer et al.*, 2001; *Schiff et al.*, 1990; *Ziegler and Brisco*, 2004]: catchments smaller than 10 km^2.

5.1.1. Photoautotophy

Several studies have shown that the C isotopic composition of the periphyton (algae and cyanobacteria) can be as low as −40‰ [e.g., *Singer et al.*, 2005; *Ziegler and Brisco*, 2004; *Finlay and Kendall*, 2008; *Ishikawa et al.*, 2012]. Conditions leading to low δ^{13}C values in periphyton include slow growth rates [*Finlay and Kendall*, 2008], light limitation and cold temperatures [*MacLeod and Barton*, 1998; *Ishikawa et al.*, 2012], and a nutrient supply that is in excess of demand [*McGoldrick et al.*, 2008]. These conditions are likely to prevail in the streams sampled here which are cold (0.1–5.3°C) and snow covered for approximately 8 months of the year. However, the high suspended sediment load (Figure 2), particularly in the glacial stream, is likely to severely impact on photosynthesis [*Bilotta and Brazier*, 2008] and this is confirmed by the absence of cyanobacteria and the low abundance of algae (less than 3%) in all the sediment samples analyzed. The low abundance of photosynthetic microbes has been observed in streams draining other glaciers [*Hamilton et al.*, 2013; *Sheik et al.*, 2015]. We therefore find it unlikely that photoautotrophs are responsible for the low δ^{13}C-DOC values.

5.1.2. Chemoautotrophy

The majority of chemoautotrophic bacteria use the Calvin-Benson-Bassham cycle [*Havig et al.*, 2011; *Boyd et al.*, 2014], which would ultimately result in DOC with typical C3 plant δ^{13}C values (−32 to −22‰) [*Finlay and Kendall*, 2008]. However, methanotrophs can oxidize isotopically light methane, resulting in δ^{13}C-DOC values less than −32‰. Biogenic methane typically has δ^{13}C values of between −60 and −110‰ [*Whiticar*, 1999], and methanotrophs that utilize this biogenic methane will have isotope compositions a few permil lighter than the source methane [*Conway et al.*, 1994; *Summons et al.*, 1998; *Whiticar*, 1999]. Therefore, any heterotrophs that consume this methane-based food source are expected to also be ^{13}C depleted, typically less than −40‰, as will any associated DOC [*Kohzu et al.*, 2004, and references therein]. The initial methane can be produced by two potential pathways (methanogenesis) which both require anaerobic conditions

to be favorable: the hydrogenotrophic ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) and the acetoclastic pathway ($CH_3COOH \rightarrow CH_4 + CO_2$). The occurrence of methanogenesis and methanotrophy (by archaea) requires anoxic conditions, while methanotrophy (by bacteria) occurs under oxic conditions. In permafrost, an oxic/anoxic interface is located in the active layer (the seasonally thawed top layer of soil above permafrost) with the lower saturated and anaerobic layer overlain by an unsaturated, aerobic layer. Methane cycling is therefore expected to occur in these catchments.

Microbial sequencing is increasingly being used to gain insight into biogeochemical cycling [e.g., *Skidmore et al.*, 2005; *Boyd et al.*, 2014]. The widespread occurrence of methane cycling in northern latitude systems is supported by the detection of methanogens and methanotrophs both in unglaciated permafrost areas [e.g., *Høj et al.*, 2006; *Barbier et al.*, 2012; *Gray et al.*, 2014] and in subglacial environments [*Boyd et al.*, 2010; *Hamilton et al.*, 2013; *Dieser et al.*, 2014]. In this study, neither archaeal 16S rRNA amplicons nor *mcrA* (alpha subunit of the methyl coenzyme M reductase), a gene required for methanogenesis [*Luton et al.*, 2002], were detected in any of the four sediment samples, suggesting the apparent absence of methanogens. The lack of detection is perhaps not surprising given that methanogens are strict anaerobes and the sampling sites likely contained oxygen (Figure 2). An oxic environment at the sampling locations is supported by the bacterial community composition [*Hindshaw et al.*, 2016]. In Arctic soils, methanogens reside below or deep in the active layer where methane accumulates and is released upon thaw [*Mackelprang et al.*, 2011; *Tveit et al.*, 2013]. It is therefore most likely that the source of the biogenic methane is upstream of the sampling area, in portions of the subsurface that were not sampled as part of the current study.

DOC production from methane is facilitated by methanotrophs, and the distribution of the alpha subunit of the particulate methane monooxygenase gene *pmoA*, which is an enzyme found in all aerobic methanotrophs [*McDonald and Murrell*, 1997], supports the presence of methanotrophs in site O, in the sediments adjacent to the river in the glaciated catchment (Figure 2e and Table 1). The abundance of *pmoA* genes in site O was 3.1×10^6 templates gdm^{-1}. Assuming one *pmoA* gene and one 16S rRNA gene per bacterial chromosome, this corresponds to 1 in ~25 genomes present in O sediments encoding for the capacity to oxidize CH_4. Sequencing and subsequent translation of *pmoA* genes from site O revealed the presence of three phylotypes that were distantly related to PmoA from *Crenothrix polyspora* (58–69% sequence identities). Interestingly, the PmoA phylotypes that were recovered here exhibit close affiliation to (94–96% sequence identities) to PmoA sequences recovered from Arctic tundra [*Pacheco-Oliver et al.*, 2002] suggesting that these methanotrophs might play a global role in methane cycling. While several bacterial 16S rRNA gene sequences were recovered that exhibited affiliation to known methanotrophs, they were in low abundance (<0.2% of total reads) and were not related to *Cleothrix* which may reflect primer bias in either the 16S rRNA or *pmoA* gene primers. The genus of methanotroph detected was *Methylobacter*, a gamma proteobacteria and a type I methanotroph, which has been detected at other sites in Svalbard [*Graef et al.*, 2011; *Tveit et al.*, 2013]. However, it is increasingly being speculated that species from the methylotrophic order *Methylophilales* may also be able to oxidize methane [*Trotsenko and Murrell*, 2008; *Conrad*, 2009; *Martineau et al.*, 2010]. If members of this order are included, then the abundance of methanotrophs increases to 0.7% (L) and 0.0% (M) of total reads in the unglaciated catchment and 0.2% (O) to 1.3 % (A) in the glaciated catchment.

While evidence for methanotrophy in the molecular data is limited from the four locally collected sediment samples, methanotrophic bacteria are widespread in Arctic permafrost systems [e.g., *Mackelprang et al.*, 2011] and have been postulated to contribute to lotic food webs (and by extension, DOC) in other ecosystems, including oxic environments such as flowing streams [*Kohzu et al.*, 2004; *Trimmer et al.*, 2009; *Shelley et al.*, 2014]. It is therefore most likely that methanotrophic bacteria are the source of low δ^{13}C-DOC values. The lack of *mcrA* genes from the four local sediments and the absence of *pmoA* genes from all but one sediment sample does not preclude transport of ^{13}C-depleted DOC from upstream environments where microbial CH_4 cycling may be taking place. Because this study was designed to focus on river chemistry, a full suite of riverine and subsurface samples were not collected and analyzed for DNA. Verifying or ruling out a methanotrophic source of DOC will require further detailed fieldwork including direct measurements of the carbon and hydrogen isotopic composition of any methane detected and further work characterizing the structure and activity of the microbial community.

5.2. Temporal Variation of δ^{13}C-DOC

There is little temporal variation in δ^{13}C-DOC values with the exception of the values measured on 1 August in Fardalen (−28.1‰) and 2 August in Dryadbreen (−27.6‰) which occur after the diurnal cycle of 31 July.

This diurnal cycle had a markedly greater amplitude in discharge in both catchments compared to previously recorded diurnal cycles (Figure 3) and was likely caused by a period of cloud-free, sunny weather. The significant correlation between δ^{13}C-DOC and the inverse of DOC concentration in both catchments (Figure 4) is consistent with the mixing of two end-members. The high δ^{13}C-DOC end-member is very likely to be terrestrial material with a composition similar to that measured in POC (δ^{13}C = -26‰) and in the supraglacial stream (δ^{13}C-DOC = -27.1‰). In both catchments the terrestrial source is likely to be derived from snow (and ice) melt containing DOC derived from wind-blown dust, surface primary productivity on the surface of the snow (chemosynthesis or photosynthesis via the Calvin-Benson-Bassham cycle) [e.g., *Telling et al.*, 2012; *Hamilton et al.*, 2013; *Cameron et al.*, 2015] and material transported from the sides of the valley by avalanches. In the unglaciated catchment there will also likely be a DOC contribution from the soil. Coincident with the higher δ^{13}C-DOC value in Fardalen, a decrease in the δ^{13}C-DIC value from around −4‰ to −11.6‰ was recorded (Figure 3). This is consistent with a higher proportion of DIC originating from plant-derived CO_2 [*Kendall and Doctor*, 2003], supporting a transient input of a terrestrial source of carbon in Fardalen. Based on the presence of *pmoA* genes at Site O and the ubiquity of methane cycling in similar catchments, the low δ^{13}C-DOC end-member is likely a mixture of DOC derived from methanotrophy (<−60‰) and typical terrestrial DOC (∼−27‰) resulting in an end-member value of −45.1 ± 1.0‰ in Dryadbreen and −43.3 ± 0.3‰ in Fardalen (errors 1 SE, Figure 4). These end-member values are in agreement with C isotope measurements of macroinvertebrates in food chains inferred to have a methanotrophic contribution [*Kohzu et al.*, 2004; *Trimmer et al.*, 2009].

We propose that the low δ^{13}C-DOC values occur as a result of stream water interacting with the active layer [*Cooper et al.*, 2002; *Greenwald et al.*, 2008; *Cooper et al.*, 2011] where methane cycling occurs, enabling the water to acquire a methanotrophic signature. Interaction is enhanced by the presence of braided stream networks in both catchments, which merge before the water sampling locations (Figures 2a and 2b). Conversely, the high δ^{13}C-DOC values could occur because the system received a greater input from snow (and ice) melt due to the sunny weather and this meltwater was dominated by typical terrestrial DOC values derived from autotrophs using the Calvin-Benson-Bassham cycle. The relative contribution of DOC from the active layer was therefore diminished. Although the increase in δ^{13}C-DOC values was only observed once, it could indicate that the hydrological history has an important control over δ^{13}C-DOC values in these catchments.

6. Implications and Conclusions

The carbon isotopic composition of DOC was sensitive to antecedent hydrological conditions in both a glaciated and a permafrost-dominated catchment in the High Arctic. Crucially, the δ^{13}C-DOC value was around −40‰ for extended periods of time, with the lowest value recorded being −43.8 ± 0.6‰ which is, to our knowledge, the lowest value thus far reported for surface waters. These values are far removed from the carbon isotopic composition of POC (−26‰) and are consistent with ^{13}C-depleted DOC produced by methane oxidation. A lack of strong evidence in the local sediments for methanogens and methanotrophs would indicate that the production of ^{13}C-depleted DOC occurs in upstream environments. Interestingly, the low δ^{13}C-DOC values are observed in both catchments suggesting a common process not linked to present-day glaciation.

Permafrost and glaciated areas overlying carbon-rich sedimentary bedrock are widespread throughout the Arctic, and thus, we would expect low δ^{13}C-DOC to be more widespread. However, the conditions leading to the low δ^{13}C-DOC values may be unique to small headwater streams, which are relatively undersampled compared to large Arctic rivers. Compared to water flowing in a single channel, water in small, shallow, braided streams interacts with the active layer over a greater area, enabling the water to acquire a δ^{13}C-DOC composition heavily influenced by methane cycling. In contrast, the δ^{13}C isotopic composition of DOC in larger rivers becomes increasingly dominated by runoff with δ^{13}C values derived from C3 plants and soil organic matter.

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