AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER
10.1002/2015GL063498

Key Points:
- Permafrost DOC microbial utilization is greater than modern DOC in arctic rivers
- Permafrost DOM has unique molecular signatures (high levels of aliphatics)
- Unique molecular signature of permafrost DOM lost on biodegradation

Supporting Information:
- Supporting Information S1

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Citation:
Spencer, R. G. M., P. J. Mann, T. Dittmar, T. I. Eglinton, C. McIntyre, R. M. Holmes, N. Zimov, and A. Stubbins (2015), Detecting the signature of permafrost thaw in Arctic rivers, *Geophys. Res. Lett.*, *42*, 2830–2835, doi:10.1002/2015GL063498.

Received 13 FEB 2015
Accepted 5 APR 2015
Published online 27 APR 2015

Detecting the signature of permafrost thaw in Arctic rivers

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Abstract Climate change induced permafrost thaw in the Arctic is mobilizing ancient dissolved organic carbon (DOC) into headwater streams; however, DOC exported from the mouth of major arctic rivers appears predominantly modern. Here we highlight that ancient (>20,000 years B.P.) permafrost DOC is rapidly utilized by microbes (~50% DOC loss in <7 days) and that permafrost DOC decay rates (0.12 to 0.19 day^{-1}) exceed those for DOC in a major arctic river (Kolyma: 0.09 day^{-1}). Permafrost DOC exhibited unique molecular signatures, including high levels of aliphatics that were rapidly utilized by microbes. As microbes processed permafrost DOC, its distinctive chemical signatures were degraded and converged toward those of DOC in the Kolyma River. The extreme biolability of permafrost DOC and the rapid loss of its distinct molecular signature may explain the apparent contradiction between observed permafrost DOC release to headwaters and the lack of a permafrost signal in DOC exported via major arctic rivers to the ocean.

1. Introduction

Frozen soils or permafrost regions in the Arctic are estimated to contain 1700 Pg of organic carbon (OC), more than twice the carbon (C) stock of the entire current atmospheric C pool [*Tarnocai et al.,* 2009; *Schuur et al.,* 2013]. Climate change in the Arctic is amplified with current warming estimates leading to the projected release of 41–288 Pg C by 2100 and up to 616 Pg C by 2300 [*Schaefer et al.,* 2011; *Schuur et al.,* 2013] as a consequence of permafrost thaw. As the OC that has been locked away in permafrost thaws into the contemporary C cycle it can be metabolized by microorganisms in soils and exported into aquatic ecosystems where it can be further metabolized by microorganisms and becomes susceptible to photochemical degradation [*Striegl et al.,* 2005; *Osburn et al.,* 2009; *Cory et al.,* 2014; *Mann et al.,* 2014]. If these processes are efficient at mineralizing thawed permafrost OC, ultimately this large ancient C reservoir will be transferred to the atmosphere driving a positive feedback on climate change [*Schuur et al.,* 2013; *Vonk et al.,* 2013].

Numerous studies have highlighted long-term permafrost degradation and a deepening in the active layer in arctic watersheds [*Payette et al.,* 2004; *Zhang et al.,* 2005; *Osterkamp*, 2007]. However, the fate of liberated OC in arctic rivers remains unclear and is focused on dissolved organic carbon (DOC) for three reasons. First, approximately 80% of the total OC flux from arctic watersheds is estimated to occur in the form of DOC; second, as permafrost thaws and the active layer deepens this results in a new source pool of OC for DOC production; and finally, DOC is the most important intermediate in the global C cycle fuelling microbial metabolism [*Striegl et al.,* 2005; *Battin et al.,* 2008; *Frey and McClelland*, 2009]. Headwater streams in arctic watersheds have exhibited DOC with ancient permafrost-derived radiocarbon ages [*Neff et al.,* 2006; *Vonk et al.,* 2013]. However, major arctic rivers export predominantly modern DOC to the ocean that is derived from recently fixed plant material and organic-rich surface soils [*Neff et al.,* 2006; *Raymond et al.,* 2007; *Spencer et al.,* 2008; *Aiken et al.,* 2014]. This raises the question, where is the ancient OC mobilized by permafrost degradation and deepening of the active layer?

In this study we examine DOC radiocarbon age, biolability, and composition in small-order streams and the main stem of a major arctic river (Kolyma, Siberia), with a focus on the period of maximum permafrost thaw

and active layer depth (late summer). In addition to measuring bulk DOC, we employed Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) on nonfractionated samples to develop molecular fingerprints for the different dissolved organic matter (DOM) samples and their biomodification during 28 day microbial incubations. The resultant changes in the radiocarbon age of ancient permafrost-derived DOC were used to determine whether rapid loss of permafrost DOC in headwater streams could account for the apparent disconnect between extensive permafrost mobilization and the apparent modern age of DOC in major arctic rivers. FTICR-MS characterization allowed us to investigate whether permafrost DOM exhibits unique molecular signatures and if these signatures are persistent enough to show up in the main stems of large arctic rivers, thereby enabling a means to examine catchment-wide permafrost degradation by taking samples at major river outflows.

2. Materials and Methods

The Kolyma River Basin covers ~ 650,000 km^2 of northeastern Siberia and represents the largest watershed on Earth completely underlain by continuous permafrost. Water samples were collected from two sites: one representing the main stem Kolyma River (9 September 2013) approximately 2 km upstream from Chersky (68.767°N, 161.333°E) and one representing small-order permafrost thaw streams which drained from the yedoma exposure known as Duvanni Yar (68.631°N, 159.151°E). The permafrost thaw stream site was sampled twice in early September, and the individual samples are referred to in this manuscript as permafrost stream A (1 September 2013) and permafrost stream B (9 September 2013). Samples were collected in precleaned (acid and Milli-Q rinsed) high-density polyethylene plasticware and kept on ice and in the dark until return to the laboratory (<6 h) where they were filtered through precombusted (450°C) 47 mm 0.7 μm glass fiber filters to remove particulates. Aliquots were then frozen for subsequent DOC concentration, Δ^{14}C-DOC, and FTICR-MS analyses.

To determine the biolability of DOC, dark laboratory incubations were begun immediately, in triplicate, in 60 mL precleaned (acid and Milli-Q rinsed) high-density polyethylene plasticware at 20°C using 0.7 μm filtered waters and established methodology [*Holmes et al.,* 2008; *Vonk et al.,* 2013; *Spencer et al.,* 2014]. These incubations were kept oxygenated, and triplicates were stopped after 2, 7, 14, and 28 days and subsequently frozen. DOC concentration was measured on a Shimadzu TOC-V analyser using established protocols [*Mann et al.,* 2014]. DOC samples for ^{14}C analysis (Δ^{14}C-DOC) were freeze dried directly in precombusted (850°C for 5 h) quartz glass tubes. Samples were then acidified to remove carbonates and flame sealed with precombusted CuO under vacuum. CO_2 was cryogenically captured and quantified (~30 μg carbon) before ^{14}C measurement using a miniaturized radiocarbon dating system and gas feeding system at the Laboratory of Ion Beam Physics, Eidgenössiche Technische Hochschule (ETH) Zurich [*Wacker et al.,* 2010].

Samples for FTICR-MS were analyzed without isolation or fractionation following *Stubbins et al.* [2010, 2014]. Permafrost stream samples A and B were diluted to the concentration of Kolyma River water DOC with ultrapure water (Milli-Q). All samples were then mixed 1:1 with methanol to aid ionization in negative mode electrospray ionization (ESI) and infused into the ESI source of a 15 T FTICR-MS (Solarix Bruker). Molecular formulas were assigned to peaks with signal-to-noise ratios >5 based on published rules [*Stubbins et al.,* 2014] (see Supplemental Methods in Text S1 in the supporting information) Peaks below a standardized detection limit were filled to prevent false negatives for the absence of a peak within samples with low dynamic range. For this assessment elemental formulas were defined as biolabile if they experienced a 40% or greater reduction in relative peak intensity after 28 days. Assigned formulas were categorized by compound class based upon elemental stoichiometries [*Stubbins et al.,* 2014] (see Supplemental Methods in Text S1).

3. Results and Discussion

Concentrations of DOC varied greatly between the study sites, from 5.5 mg C L^{-1} in the Kolyma River main stem to 152.4 to 165.8 mg C L^{-1} in permafrost thaw streams A and B (Figure 1). DOC in permafrost streams A and B ranged in radiocarbon age from 21,000 to 22,100 years B.P. (Δ^{14}C-DOC: −927 to −937‰), whereas Kolyma River main stem DOC was modern (Δ^{14}C-DOC: 22‰) consistent with DOC ages in previous studies of permafrost headwater sites in the Kolyma and the main stem of major arctic rivers [*Raymond et al.,* 2007; *Vonk et al.,* 2013; *Aiken et al.,* 2014]. In 28 day bioincubations permafrost thaw streams A and B exhibited

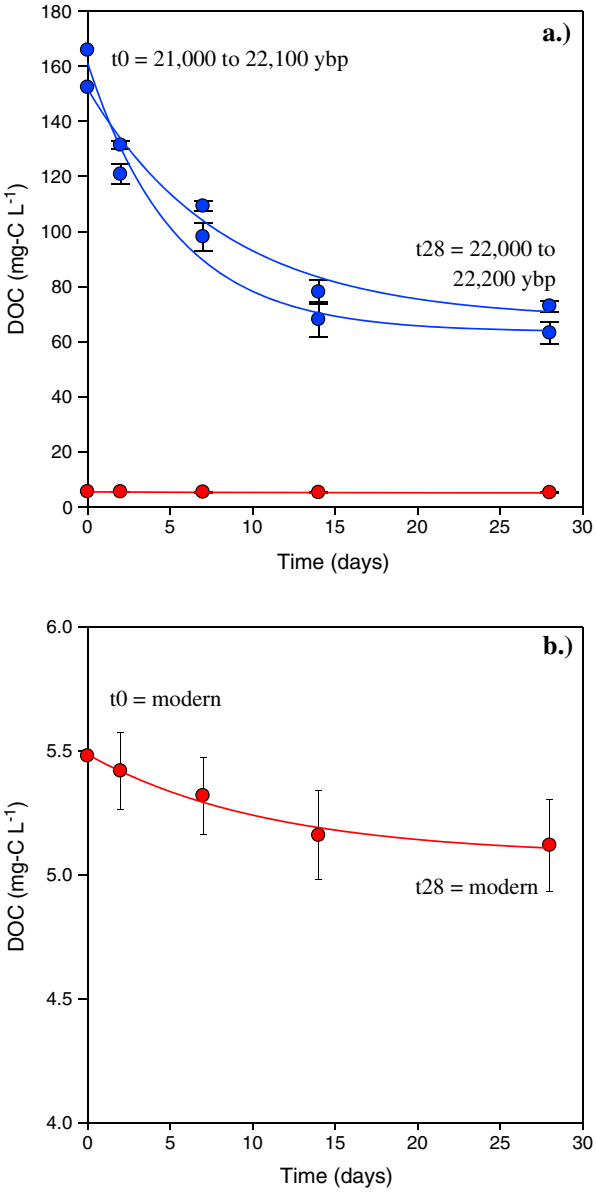

Figure 1. DOC loss and radiocarbon ages in 28 day bioincubations: (a) Blue circles, blue lines and red circles, red lines are permafrost thaw streams (A and B) and Kolyma River main stem, respectively, and (b) red circles and red lines represent Kolyma River main stem.

high biolability as evidenced by large DOC loss (79.5 to 102.7 mg C L^{-1}; 52.2 to 61.9%) in comparison to modern Kolyma River water (DOC loss = 0.36 mg C L^{-1}; 6.6%; Figure 1). Comparable bioincubations from major arctic rivers during late summer have shown similar DOC losses to the Kolyma main stem (<10%) whereas the >50% loss of DOC observed in the permafrost headwater site bioincubations represent the largest DOC losses reported to date from arctic fluvial systems [*Holmes et al.,* 2008; *Wickland et al.,* 2012; *Vonk et al.,* 2013]. The permafrost-derived DOC utilized by microbial communities was always >20,000 years B.P. Conversely, in the Kolyma River main stem bioincubation, the DOC utilized was always modern as determined from the lack of significant changes in the Δ^{14}C-DOC values during the bioincubations (Figure 1).

All bioincubation data were fitted to a single, three-parameter exponential decay model: $f = y0 + a \times \exp(-b \times x)$, in which y0 = nonbiodegradable component, a = biodegradable component at t0, and b = rate of decay. The decay model fit the data well ranging from $r^2 = 0.97$ to 0.98 across the sites (Figure 1). The rate of decay of DOC was greater in permafrost thaw streams A and B (0.12 to 0.19 day^{-1}) than for the Kolyma River main stem (0.09 day^{-1}). These results clearly show the high biolability of ancient (>20,000 years B.P.) permafrost-derived DOC in small-order streams and the rapid loss (<7 days) of approximately 50% of the DOC in these systems. Although we recognize the limitation of extrapolating DOC loss data from bottle bioincubations it is worth noting here that water residence times from the permafrost thaw stream sites to the Kolyma River main stem site are typically 3–7 days [*Vonk et al.,* 2013]. This rapid loss of ancient permafrost DOC subverts the perception that young, freshly produced DOC will be the most biolabile in arctic fluvial systems and argues for a strong disconnect between permafrost thaw inputs and the DOC that is ultimately exported to the ocean from major arctic rivers. This is the first time that the age of permafrost-derived DOC has been determined prebioincubation and postbioincubation (Figure 1). As such, this is the first definitive demonstration that ancient DOC derived from permafrost C stores will be rapidly mineralized when released into contemporary aquatic ecosystems.

The rapid loss of ancient permafrost DOC suggests that bulk-level measurements of Δ^{14}C-DOC in major arctic rivers may not provide a good integrative tracer of permafrost thaw throughout their catchments. Therefore, we characterized the bioincubation samples using FTICR-MS to determine if the molecular signature of permafrost DOM might offer an alternate tracer. The ultrahigh resolution and mass accuracy of FTICR-MS

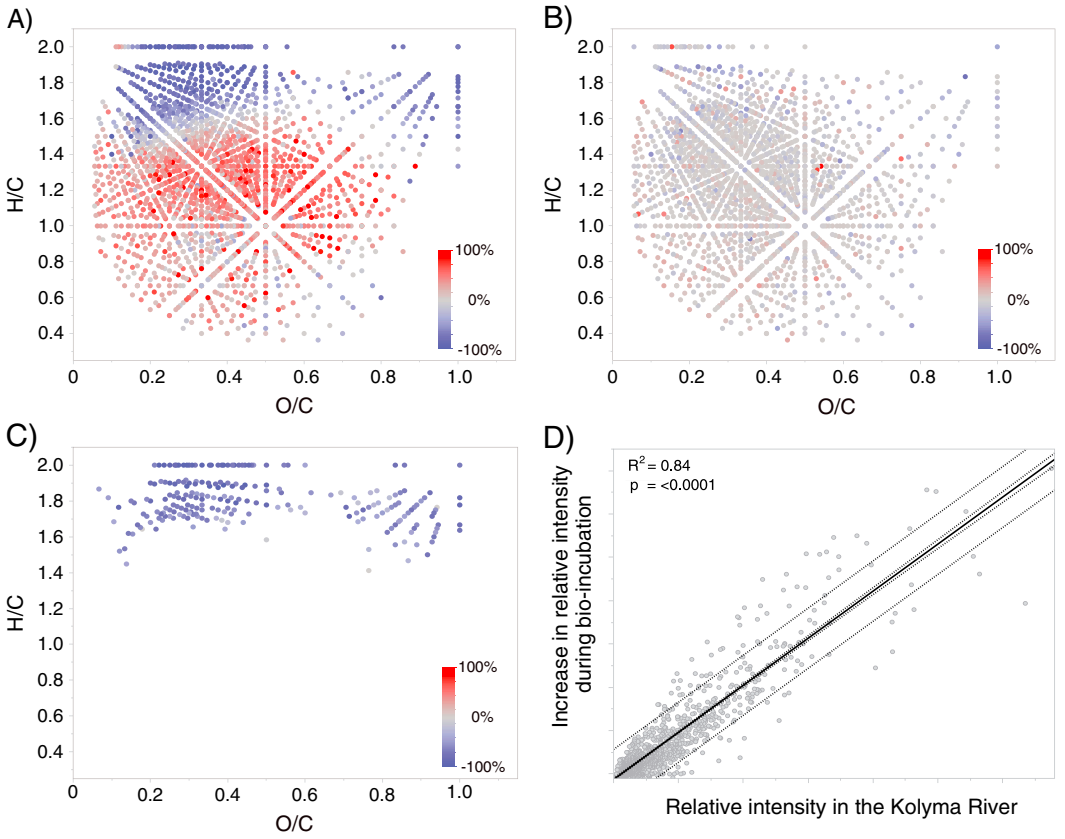

Figure 2. (a) Van Krevelen diagram of permafrost thaw stream A DOM where the color scale from blue (100% decrease) to red (100% increase) indicates the change in molecular formulas relative peak intensities during the 28 day bioincubations. (b) Van Krevelen diagram of Kolyma River main stem water where the color scale from blue (100% decrease) to red (100% increase) indicates the change in molecular formulas relative peak intensities during the 28 day bioincubation. (c) Van Krevelen diagram of the unique molecular formula found solely in permafrost thaw stream A DOM (color scaling as in Figure 2a). (d) Linear regression of the relative increase in molecular formula peak intensities that increased during the incubation of permafrost thaw stream A DOM versus initial peak intensities in Kolyma River main stem water.

enabled exact molecular formulas to be assigned to thousands of mass spectral peaks based solely upon mass [*Stubbins et al.,* 2010; *Flerus et al.,* 2012]. Encouragingly, the permafrost thaw DOM had unique molecular characteristics, including the presence of a suite of high H/C compounds (aliphatic) not normally observed in whole water riverine DOM samples (Figure 2 and Tables 1, and S1) [*Stubbins et al.,* 2010]. During the 28 day bioincubations of permafrost DOM, more pronounced changes in molecular signatures were observed than in the Kolyma River DOM (Figures 2a and 2b and Tables 1 and S1) or than within previous bioincubation studies of natural riverine DOM [*Rossel et al.,* 2013]. These modifications, even visible as a reduction in the intensity of biolabile peaks in the raw FTICR mass spectra (Figure S1), were characterized by reductions in the peak intensities of hydrogen-rich, aliphatic molecules and carbohydrates, and concurrent increases in relative peak intensity in the area of van Krevelen space generally associated with high intensity peaks in both riverine and marine DOM (Figure 2a) [*Stubbins et al.,* 2010; *Flerus et al.,* 2012]. The aliphatic and carbohydrate-like molecular formulas unique to permafrost-derived DOM (i.e., peaks present in permafrost DOM but absent in Kolyma River DOM; Figure 2c and Table 1) could provide a means to track permafrost DOM through fluvial networks. However, 83% (including 96–97% of CHO-only peaks) of them were degraded during the bioincubation (Table 1), suggesting that the majority of these unique molecular formulas are unlikely to be found in the Kolyma River main stem.

The decreasing intensities of aliphatics and carbohydrates are interpreted as indicating these moieties were biodegraded. However, as these peaks are degraded, the relative peak intensities of compounds that were

Table 1. Molecular Formula Identified in Initial and t28 Bioincubation Kolyma River and Permafrost Thaw Stream (A and B) Samples[a]

Initial Sample	All Peaks (*n*)	Only CHO (*n*)	Mean Mass CHO CHO (Da)	Mean H/C	Mean O/C	Condensed Aromatics	Aromatics	Moderately Unsaturated	Aliphatics	Carbohydrates	Peptides
Initial Sample											
Kolyma River	2011	1533	335.9	1.27	0.38	123	268	1129	435	12	44
Permafrost Stream A	2075	1599	335.2	1.29	0.38	126	268	1123	495	17	46
Permafrost Stream A (absent in Kolyma River)	86	68	323.2	1.77	0.45	3	2	4	65	5	7
Permafrost Stream B	2079	1601	335.6	1.29	0.38	125	268	1126	497	17	46
Permafrost Stream B (absent in Kolyma River)	86	68	323.6	1.77	0.44	3	2	4	65	5	7
Biolabile (t28)											
Kolyma River	60 (3%)	17 (1%)	300.1	1.46	0.34	2 (2%)	9 (3%)	14 (1%)	27 (6%)	2 (17%)	6 (14%)
Permafrost Stream A	285 (14%)	272 (17%)	312.5	1.74	0.38	4 (3%)	4 (1%)	5 (0%)	249 (50%)	17 (100%)	6 (13%)
Permafrost Stream A (absent in Kolyma River)	71 (83%)	66 (97%)	326.7	1.84	0.43	2 (67%)	0 (0%)	1 (25%)	61 (94%)	5 (100%)	2 (29%)
Permafrost Stream B	279 (13%)	265 (17%)	311.1	1.75	0.37	3 (2%)	4 (1%)	4 (0%)	246 (49%)	16 (94%)	6 (13%)
Permafrost Stream B (absent in Kolyma River)	71 (83%)	65 (96%)	326.8	1.84	0.42	2 (67%)	0 (0%)	1 (25%)	61 (94%)	5 (100%)	2 (29%)

[a]The unique molecular formulas in permafrost thaw stream samples A and B (absent in Kolyma River) are shown for initial and t28 biodegraded samples with the percentage of peaks biodegraded during the bioincubation presented in parentheses.

biorefractory (i.e., conserved during the incubation) are expected to increase in relative intensity. Thus, those peaks that showed increasing intensities over the course of the incubation are likely dominated by conserved molecules rather than bioproducts. The peaks that increased in intensity throughout the permafrost DOM incubations were identified. The relative increase in peak intensity of these peaks was then plotted against the intensity of those same peaks in the original Kolyma River sample. The resultant plot reveals a significant linear correlation (Figure 2d), indicating that the peaks that demonstrated the highest increases in intensity during the permafrost DOM bioincubations (i.e., those that were likely preserved during incubations with potential minor contributions from bioproducts) also occurred at high intensity in the Kolyma River initial sample. Thus, the microbial reworking of permafrost DOM will rapidly result in a molecular fingerprint similar to that found in the Kolyma River.

The finding that the molecular signatures of permafrost DOM rapidly converge toward those of DOM in major arctic rivers such as the Kolyma highlights the difficulty of tracking permafrost inputs utilizing DOM characterization approaches on samples from the mouths of major arctic rivers. That said, despite the convergence of average molecular properties, subtle differences exist between the molecular populations within the Kolyma and biodegraded permafrost DOM (Tables 1 and S1), offering hope that collection of larger sample numbers may reveal statistically significant signatures of permafrost DOM transport and modification within arctic river networks. However, the rapid utilization of ancient (>20,000 years B.P.) DOC in bioincubations of permafrost small-order streams may help to explain the apparent offset between mobilization of permafrost-derived OC in arctic watersheds and the current predominantly modern age of DOC at the mouth of major arctic rivers. Small headwater streams are disproportionally important sites for

carbon dioxide (CO_2) outgassing, and estimates of stream areas continue to grow as measurement techniques increase in accuracy [*Battin et al.,* 2008; *Mann et al.,* 2014; *Benstead and Leigh*, 2012]. Thus, while tracking the fate of permafrost DOC through river networks is required to assess its translocation to the atmosphere as CO_2, improved studies of small, permafrost-impacted streams appear to represent the highest priority sites for capturing the signature and influence of permafrost thaw-derived DOC in fluvial networks. Further study of the impact of climate warming upon these small stream ecosystems is essential as our current data clearly demonstrates that the ancient permafrost DOC entering these streams is rapidly metabolized, adding to the buildup of ancient CO_2 in the contemporary atmosphere with clear ramifications for positive feedback between permafrost thaw and climate.

Acknowledgments

Anna Davydova and Ekaterina Bulygina are thanked for help with measurements of DOC concentrations, and we thank members of the Laboratory for Ion Beam Physics (ETH Zurich) for instrumental support. This work was funded by the U.S. National Science Foundation (ANT-1203885/PLR-1500169). All data are directly available within the manuscript text (e.g., Δ^{14}C-DOC, DOC concentration, and bioincubation DOC loss data) or are provided in the supporting information Table S1 (e.g., FTICR-MS data).

The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

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