

RESEARCH LETTER

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Key Points:

- Aged, biolabile forms of DOC are present in Pleistocene permafrost
- Reducing conditions in yedoma produce biolabile DOC and characteristic solutes over time
- Both reducing conditions and mineral dissolution are related to permafrost DOC production

Supporting Information:

- Text S1 and Data Set S1 caption
- Data Set S1

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Long-term anoxia and release of ancient, labile carbon upon thaw of Pleistocene permafrost

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Abstract The fate of permafrost carbon upon thaw will drive feedbacks to climate warming. Here we consider the character and context of dissolved organic carbon (DOC) in yedoma permafrost cores from up to 20 m depth in central Alaska. We observed high DOC concentrations (4 to 129 mM) and consistent low molecular weight organic acid concentrations in three cores. We estimate a DOC production rate of 12 $\mu\text{mol DOC m}^{-2} \text{ yr}^{-1}$ based on model ages of up to ~200 kyr derived from uranium isotopes. Acetate C accounted for 24 $\pm$ 1% of DOC in all samples. This proportion suggests long-term anaerobiosis and is likely to influence thaw outcomes due to biolability of acetate upon release in many environments. The combination of uranium isotopes, ammonium concentrations, and calcium concentrations explained 86% of the variation in thaw water DOC concentrations, suggesting that DOC production may be related to both reducing conditions and mineral dissolution over time.

1. Introduction

Permafrost stores about half of terrestrial organic carbon (C; ~1300 Pg [Hugelius *et al.*, 2014]), equivalent to about twice the C currently in the atmosphere. This large reservoir of organic C is subject to release with permafrost thaw and may represent a positive feedback to climate warming [Koven *et al.*, 2011; Schaefer *et al.*, 2014]. Large uncertainties remain with respect to the timing and magnitude of this permafrost C feedback [Schuur *et al.*, 2013]. One source of uncertainty is variability in the chemical composition of permafrost C as a control on its decomposability. Recent incubation studies have documented the biolability of permafrost C [Elberling *et al.*, 2013; Mann *et al.*, 2014; Drake *et al.*, 2015; Mueller *et al.*, 2015] and of dissolved organic carbon (DOC) delivered to surface waters from permafrost landscapes [Wickland *et al.*, 2012; Vonk *et al.*, 2013; Mann *et al.*, 2015; Spencer *et al.*, 2015]. Moreover, the age of DOC in arctic rivers is relatively young [Neff *et al.*, 2006; Aiken *et al.*, 2014; O'Donnell *et al.*, 2014] compared to observations of permafrost C in solid or gas phase [Schuur *et al.*, 2009; Kanevskiy *et al.*, 2011] and ice [Froese *et al.*, 2008; Reyes *et al.*, 2011]. By contrast, ancient DOC (>20 kyr) has been observed in streams draining yedoma thaw water sources [Vonk *et al.*, 2013; Mann *et al.*, 2015; Spencer *et al.*, 2015] and also in in-tact yedoma cores [Ewing *et al.*, 2015]. Optical properties of DOC in rivers and streams also suggest a shift in composition over time [Aiken *et al.*, 2014], and within seasons [Koch *et al.*, 2013a], with evidence of hydrologic connection to thaw waters at several meters depth along preferential flow paths in ice-rich permafrost (e.g., yedoma) [Koch *et al.*, 2013b], as well as in abrupt thaw features [Schuur *et al.*, 2015]. In this study, we evaluate the chemical character of DOC in Pleistocene yedoma cores and quantify the net rate of DOC production in ground ice associated with these deposits in central Alaska.

The biolability of DOC is a function of both its chemical character and its physical environment. In terrestrial and aquatic settings, low molecular weight organic acids—particularly acetate—are typically highly biolabile because of their energetically favorable status for pairing with terminal electron acceptors in key metabolic processes (e.g., methanogenesis and sulfate reduction) [Van Hees *et al.*, 2005; Payn *et al.*, 2014]. However, in low-oxygen environments with high organic C, such as peatlands, fermentation and acetogenesis can result in accumulation of these compounds, and acetate has received particular attention because of its role in methanogenesis [Hines *et al.*, 2008; Hädrich *et al.*, 2012]. In permafrost, these effects may be similar, with

microbial process rates limited by low temperature and scarce liquid water but sustained by stability of these environments over millennia. Unfrozen water is known to be present in relatively warm permafrost [Romanovsky and Osterkamp, 2000], allowing for microbial activity [Rivkina *et al.*, 2000]. With permafrost thaw, the microbial communities that control C transformation shift rapidly, reflecting changes in temperature, nutrient and substrate availability, and oxygen status [Waldrop *et al.*, 2010; Mackelprang *et al.*, 2011]. These circumstances will differ with modes of thaw favoring oxic conditions (thermal erosion and exhumation) or maintaining anoxic conditions (thermokarst lake and peatland collapse-scar formation) [Schuur *et al.*, 2008; Jorgenson *et al.*, 2013].

The character and biolability of C in permafrost are also likely to be affected by the mode of permafrost formation and preservation, which dictates ice content and C density [O'Donnell *et al.*, 2011b]. Syngenetic permafrost forms in response to sediment or peat accumulation at the land surface that causes the permafrost table to propagate upwards, with volumetric expansion due to ice aggradation and burial of large C stocks [Zimov *et al.*, 2006; Grosse *et al.*, 2011; O'Donnell *et al.*, 2011b]. The thickness of syngenetically frozen yedoma silts in some areas of Siberia and Alaska exceeds 40 m [Shur *et al.*, 2010; Kanevskiy *et al.*, 2011, 2012]. At shallower depths, ice-poor zones may indicate more recent shallow thaw, while ice-rich zones may indicate formation of quasi-syngenetic permafrost by virtue of plant community succession (e.g., post-fire moss regrowth) or downslope sedimentation processes [Pewe, 1975; Shur and Jorgenson, 2007; Shur *et al.*, 2010]. Because these modes of ice development and transformation in permafrost dictate unfrozen water content, mineral interaction, and C density, they likely affect C transformation within permafrost and fate upon thaw.

Here we focus on the chemical composition of ground ice thawed from yedoma cores collected in interior Alaska [Ewing *et al.*, 2015]. This region is characterized by discontinuous permafrost, with the distribution and thermal state of permafrost strongly affected by aspect and soil drainage class in upland settings [Ping *et al.*, 2005; Jorgenson *et al.*, 2013]. North-facing, loess-mantled slopes tend to host permafrost and support black spruce ecosystems typical of the discontinuous permafrost zone in Alaska [Kane *et al.*, 2005]. Substantial C storage and permafrost resilience have been observed in this area [O'Donnell *et al.*, 2011b], along with DOC and dissolved inorganic nitrogen efflux and processing in streams [Koch *et al.*, 2013a, 2013b] and rivers [Wickland *et al.*, 2012]. Previous analyses of U isotope activities and radiocarbon (^{14}C) contents of DOC in deep cores collected to schist bedrock from this area suggest U series model ages up to ~200 kyr with depth, with uncertainties up to an order of magnitude [Ewing *et al.*, 2015]. We present solute analysis from the cores described by Ewing *et al.* [2015], including acetate and ammonium (NH_4^+), as a measure of the biolability and antiquity of DOC that will be released upon permafrost thaw in this region.

2. Methods

Details of core sampling have been described elsewhere [Kanevskiy *et al.*, 2012; Ewing *et al.*, 2015]. Briefly, we collected core samples from Pleistocene ice-rich loess deposits (i.e., yedoma) within the Hess Creek watershed near Livengood, Alaska (65.568 N, 148.925 W, NAD83), approximately 150 km north of Fairbanks, Alaska. All core locations were on forested north-facing slopes underlain by permafrost. Cores were collected in May 2008 by hollow stem drilling [Shur *et al.*, 2010; Kanevskiy *et al.*, 2012], from an area that burned in 2003. Permafrost genesis within the core sequence is interpreted to be both syngenetic and quasi-syngenetic [French and Shur, 2010; Shur *et al.*, 2010] based on detailed description of cryostructures in the cores [Shur *et al.*, 2010; Kanevskiy *et al.*, 2012]. Subsections of five deep cores (A2, A4, A5, A6, and A9) were shipped and stored frozen prior to analysis and age interpretation using $^{234}\text{U}/^{238}\text{U}$ activity ratios, DOC concentrations, and ^{14}C ages as presented in Ewing *et al.* [2015]. Core subsections were thawed in preweighed polypropylene jars, solutions were separated by centrifugation, and the supernatant was filtered (0.45 μm) for solute analysis. Uranium activity ratios ($^{234}\text{U}/^{238}\text{U}$ values), radiocarbon values, and DOC concentrations were determined as previously described [Ewing *et al.*, 2015]. Solutions were also analyzed for inorganic solutes and low molecular weight organic acids at U.S. Geological Survey (USGS) as described in the supporting information (Text S1).

3. Results and Discussion

Thaw water samples from the yedoma permafrost cores contained substantial DOC (up to 129 mM or 1551 mg L^{-1} ; Figure 1, Table 1, and Data Set S1) that generally increased with core depth, particularly in core

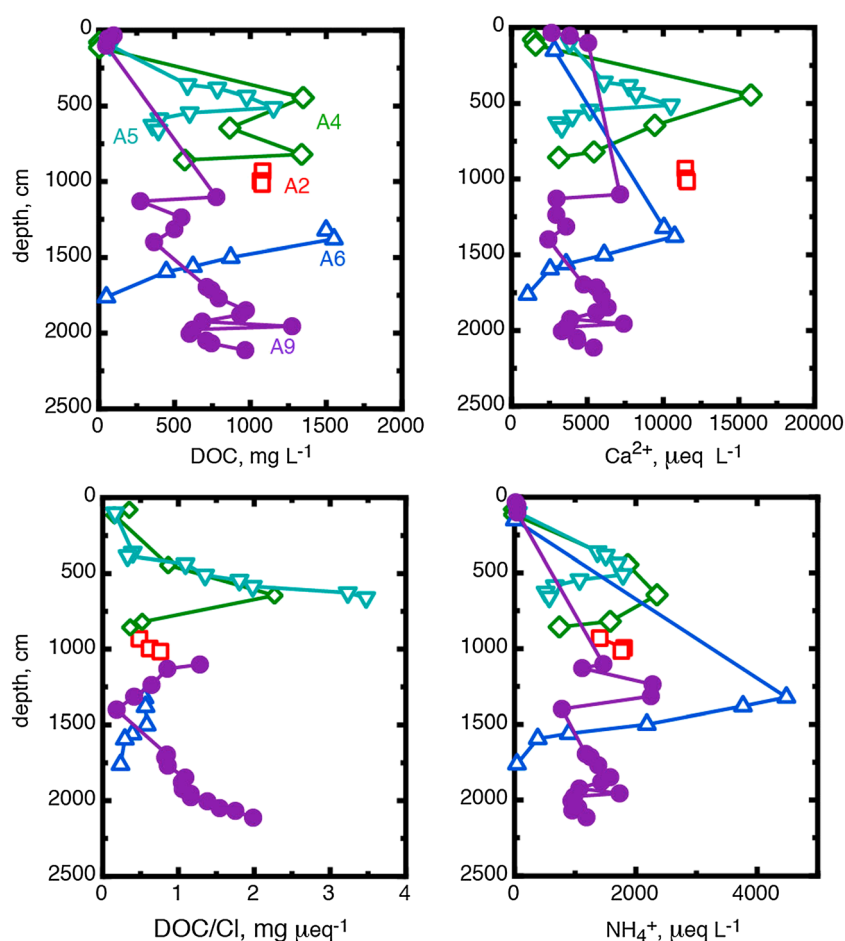


Figure 1. Select solutes with depth in syngenetic loess permafrost cores. (top left) Core numbers are indicated, including cores A2 (red squares), A4 (green diamonds), A5 (aqua inverse triangles), A6 (blue triangles), and A9 (purple circles). Lines connect points as a visual aid.

A9, the deepest core (Figure 1). The DOC concentrations were remarkably high (4–129 mM) in comparison to levels documented by other studies in subarctic peatlands and temperate soils ($<1\text{--}10\text{ mM}$) [e.g., *Sanderman et al.*, 2008; *Kane et al.*, 2010]), in thaw streams draining yedoma ($11 \pm 1\text{ mM}$) [*Mann et al.*, 2015], and in comparison to levels observed in pore waters and streamflow within this catchment ($<1\text{--}5\text{ mM}$) [*O'Donnell et al.*, 2010, 2012, 2014; *Koch et al.*, 2013a]. Below 1 m, observed $\Delta^{14}\text{C}$ values ($-989 \pm 37\text{‰}$ to $-994 \pm 33\text{‰}$) indicated ages of $>40\text{ kyr}$ (Table 1) and were comparable to values for yedoma thaw streams reported by *Mann et al.* [2015]. Values of ($^{234}\text{U}/^{238}\text{U}$) in thaw water also generally increased with depth, indicating increasing age of ice, with model ages of ~ 1 to 200 kyr and uncertainties up to an order of magnitude (Table 1 and Data Set S1; [*Ewing et al.*, 2015]).

High concentrations of dissolved NH_4^+ (up to 4.5 mM ; Figure 1), calcium (Ca^{2+} , up to 7.9 mM ; Figure 1), and acetate C (up to 30.0 mM) were correlated with high concentrations of DOC (Figure 2). Correlation of acetate and DOC with Ca^{2+} concentrations may indicate a mineral weathering interaction and/or that carbonate dissolution may provide a bicarbonate precursor for acetogenesis. For DOC, relationships were strongest with acetate ($R^2 = 0.92$; Figure 2, top), NH_4^+ ($R^2 = 0.67$; Figure 2, bottom), and Ca^{2+} ($R^2 = 0.62$; data not shown). The striking correlation of acetate C with DOC indicates that $24 \pm 1\%$ of DOC is present in the form of acetate regardless of depth (Figure 2). Considered together, acetate, lactate, and malate constitute $30 \pm 2\%$ of DOC (Data Set S1). These consistent proportions of low molecular weight organic acids suggest that production of DOC over time includes a fixed component of fermentation dictated by limited oxygen. SUVA_{254} values in core A9 were low (0.5 to 1.4; Data Set S1) and showed a weak inverse relationship with acetate

Table 1. Solutes, Uranium Activity Ratios, Radiocarbon Ages, and Model Ages in Thaw Waters, and Cores A5, A6, and A9

Sample Name ^a	Thaw Water $A_{f,t}$ ($^{234}\text{U}/^{238}\text{U}$) ^b	DOC $\Delta^{14}\text{C}$ (‰) ^c ($\delta^{13}\text{C}$)	Linear With Depth Model Age (kyr) ^d	DOC (mM)	CH_3CO_2^- (mM C)	NH_4^+ (mM)	Ca^{2+} (mM)	SO_4^{2-} (mM)
HCDT.A5.0101	1.195	-710 ± 4 (-24.84)	6	6.24		0.054	1.918	3.20
HCDT.A5.0361	1.373		23	48.71		1.368	3.045	0.07
HCDT.A5.0384	1.271		24	65.11	16.52	1.504	3.873	0.12
HCDT.A5.0437	1.261		28	81.18	19.50	1.696	4.107	0.18
HCDT.A5.0511	1.251		32	95.92	21.51	1.788	5.255	0.94
HCDT.A5.0545	1.248	-994 ± 32 (-28.83)	35	49.88	10.99	1.072	2.582	0.27
HCDT.A5.0585	1.26		37	33.22	8.83	0.664	2.006	0.07
HCDT.A5.0627	1.273		40	29.48	5.60	0.513	1.502	0.06
HCDT.A5.0660	1.251		42	32.72	8.10	0.573	1.657	0.15
HCDT.A6.0151	1.173		10			0.004	1.412	0.03
HCDT.A6.1322	1.495	-992 ± 32 (-26.15)	84	124.81		4.483	5.026	0.52
HCDT.A6.1380	1.502		87	129.14	29.96	3.767	5.379	0.35
HCDT.A6.1500	1.497		95	72.44	16.58	2.182	3.055	0.27
HCDT.A6.1560	1.379		99	51.71	14.24	0.895	1.799	0.14
HCDT.A6.1594	1.551		101	37.05	5.66	0.383	1.271	0.20
HCDT.A6.1762	1.271	-638 ± 4 (-26.96)	112	4.16	0.38	0.04	0.529	0.11
HCDT.A9.0035	1.163		2	8.16		0.016	1.325	
HCDT.A9.0055	1.168		3	5.00		0.045	1.922	
HCDT.A9.0102	1.182		6	4.08		0.045	2.529	
HCDT.A9.1102	1.322		70	64.53	10.66	1.465	3.574	0.18
HCDT.A9.1130	1.297	-989 ± 37 (-26.55)	72	22.90	3.22	1.115	1.482	0.15
HCDT.A9.1237	1.386		78	45.38	8.26	2.275	1.477	0.00
HCDT.A9.1315*	1.468		83	41.55	6.62	2.249	1.803	0.14
HCDT.A9.1399	1.366		89	30.31	1.66	0.781	1.213	1.37
HCDT.A9.1695	1.366		107	59.28	14.50	1.174	2.375	0.24
HCDT.A9.1715	1.716	-991 ± 28 (-28.81)	109	61.87	14.73	1.253	2.801	0.20
HCDT.A9.1770	1.703		112	65.78	15.37	1.379	2.973	0.16
HCDT.A9.1849	1.529		117	80.77	19.81	1.575	3.168	0.22
HCDT.A9.1879	1.594		119	77.52	16.98	1.429	2.793	0.14
HCDT.A9.1924	1.772		122	56.79	12.38	1.071	1.932	
HCDT.A9.1956	1.904		124	106.16	22.16	1.731	3.700	
HCDT.A9.1977	1.768		125	51.46	9.52	0.981	1.814	
HCDT.A9.2005	1.655		127	49.79	9.05	0.939	1.660	
HCDT.A9.2050	1.638		130	59.03	10.38	1.05	2.157	
HCDT.A9.2069	1.589		131	61.87	10.91	0.953	2.164	
HCDT.A9.2114	1.541		134	80.43	14.38	1.186	2.712	

^aSample names indicate location, core, and depth in centimeters, separated by decimal points.^bUranium activity ratio uncertainties (2σ) of 0.003 to 0.078.^cRadiocarbon results are the mean of two analyses (separate aliquots from same core section) for A6.1594 and A9.1770.^dEstimated ages using linear fit for the relationship between mean model age and depth in all cores but A2 [Ewing *et al.*, 2015].

concentration (Figure 2, top (inset)). Decreased SUVA_{254} and absorbance values have been observed in surface waters of central Alaska over the last decade [O'Donnell *et al.*, 2012, 2014] and may indicate an increasing base flow contribution of low molecular weight DOC derived from deep yedoma via subsurface flow paths, for example, along thawing ice wedge networks at depth [Koch *et al.*, 2013b].

Acetate is a central intermediate in organic matter degradation and a precursor of methane formation [Hädrich *et al.*, 2012; Bridgman *et al.*, 2013]. The presence of substantial acetate in these cores indicates anaerobic decomposition via fermentation, as has been observed previously in northern bog and fen environments [Duddleston *et al.*, 2002; Hädrich *et al.*, 2012] but not in ice-rich mineral soils, such as yedoma. The process of fermentation occurs under strongly reducing conditions as more energetically favored terminal electron acceptors (i.e., O_2 , NO_3^- , and SO_4^{2-}) have been utilized, in a characteristic sequence dictated by thermodynamics. This relationship can be directly observed along environmental gradients in conjunction with increased levels of electron donors, namely, DOC and NH_4^+ [Hedin *et al.*, 1998]. Our observation of high and correlated DOC and NH_4^+ concentrations in yedoma thaw waters points to conditions conducive to rapid DOC turnover upon thaw.

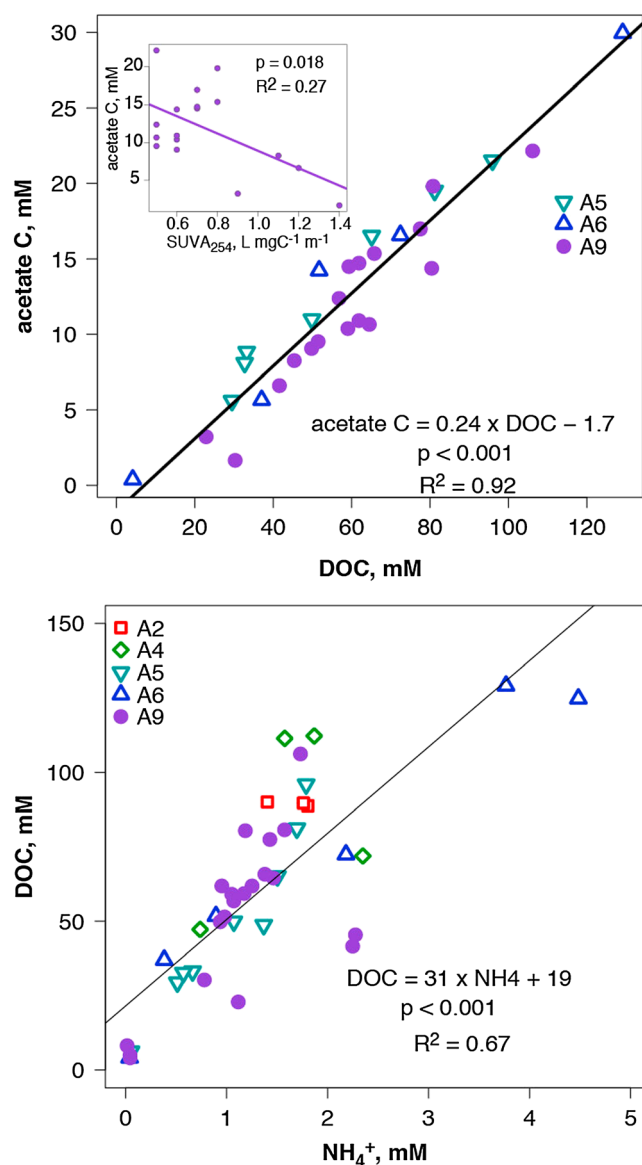


Figure 2. Variation of acetate and ammonium with DOC in syngenetic loess permafrost cores. (Top) The relationship of acetate to DOC (linear fit shown in dark line) implies that roughly one in four DOC atoms is present in acetate throughout 20 m of core in three locations. Inset: Acetate decrease with increasing $SUVA_{254}$; line indicates linear fit. (Bottom) Relationship of ammonium and DOC with line indicating linear fit. All linear regressions performed using the `lm` package in R [RCoreTeam, 2012].

of low molecular weight and potentially labile DOC produced from yedoma deposits as they age, in conjunction with development of reducing conditions. The oldest deposits may contain the largest pool of potentially labile C, here totaling an estimated $11 \text{ kg acetate C m}^{-2}$ in 45 kg DOC m^{-2} over the upper 20 m of core A9. This would suggest an age-dependent response to thaw that ties C dynamics to landscape evolution via spatial pattern of thaw and transformation of hydrologic character such as development of preferential flow paths dictated by ground ice structure [Koch et al., 2013b].

Acetate in surface waters and hyporheic settings can transform in hours to days [Hedin et al., 1998; Baker et al., 1999; Payn et al., 2014], consistent with observed time scales of DOC biolability in permafrost environments [Michaelson et al., 1998; Wickland et al., 2012; Elberling et al., 2013; Vonk et al., 2013; Mann et al., 2014; Spencer et al., 2015]. Pathways of soil C turnover would depend on the degree to which thaw might sustain reducing

We estimated DOC production rates in yedoma from our observed relationship of DOC concentrations to $(^{234}\text{U}/^{238}\text{U})$ values (Figure 3, top). By converting DOC concentration to abundance or stock (units of mmol m^{-2}), as the product of DOC concentrations and volumetric ice content of each sample, a relationship of DOC abundance to depth (Figure 3, bottom) and model ages derived from uranium activity ratios can be derived. This relationship is stronger for core A9 than for other cores, suggesting a DOC production rate of $12 \mu\text{mol C m}^{-2} \text{ yr}^{-1}$, and an acetate C production rate of $3 \mu\text{mol C m}^{-2} \text{ yr}^{-1}$. When all cores are considered together, this rate generally increases with NH_4^+ concentration in intermediate cores (A5 and A6). Using multiple linear regression to empirically model DOC as a function of uranium activity ratio (time), NH_4^+ and Ca^{2+} , we were able to explain 86% of the variability in DOC concentration within these cores (Figure 4). These observations suggest that DOC production is accompanied by both microbial processes under reducing conditions and by mineral dissolution. In addition, DOC production may also be influenced by physical processes that alter solute concentrations in dynamic permafrost landscapes, as suggested by DOC/CI ratios that both increase and decrease with depth (Figure 1) [Kokelj and Burn, 2003, 2005]. Elevated DOC/CI ratios in cores A4 and A5 may relate to past thaw and refreezing, which could have facilitated decomposition to produce DOC and increased DOC/CI ratios in these cores. In general, in situ transformation of organic C appears to result in an increasing pool

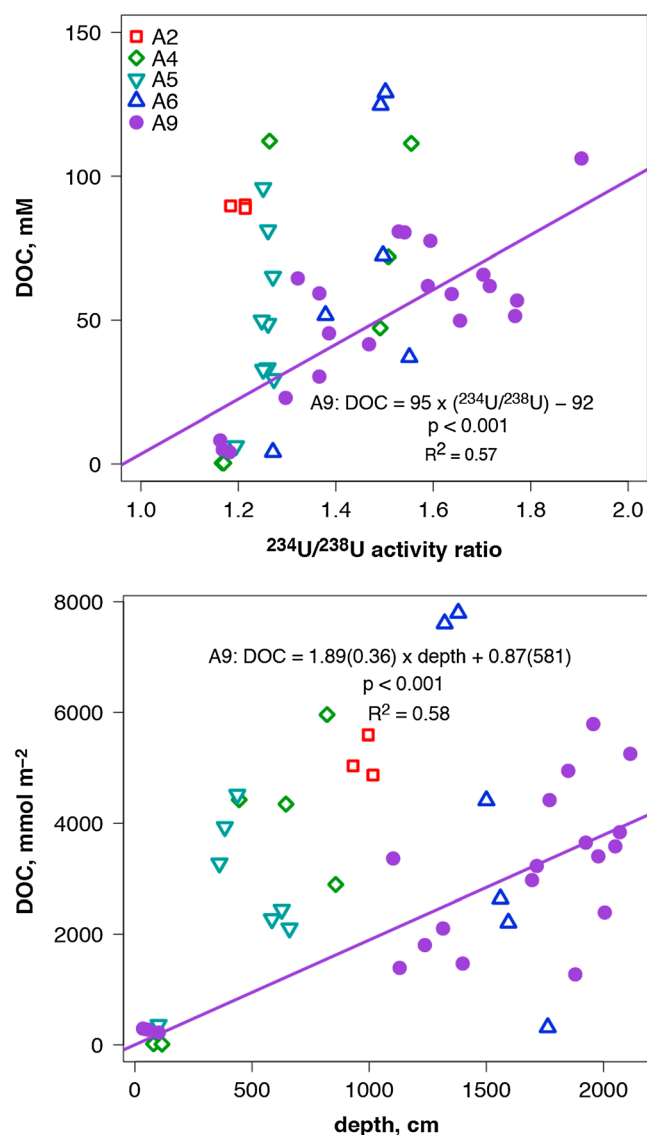


Figure 3. Concentration and stock of thaw water DOC with time and depth in syngenetic loess permafrost cores. (top) DOC concentrations in core thaw waters increase with uranium activity ratios, and (bottom) DOC pool based on DOC concentration and sample ice content, with the linear fit to depth in core A9. Lines indicate linear regressions using the *lm* package in R [RCoreTeam, 2012].

conditions or result in oxidizing conditions [Lawrence *et al.*, 2015]. Poor drainage of yedoma deposits enhances their resilience to thaw [O'Donnell *et al.*, 2011a, 2011b] and sustains reducing conditions in addition to promoting the preservation of thermally protective plant communities [Shur and Jorgenson, 2007]. In situ turnover with preservation of reducing conditions may lead to production and release of old C to the atmosphere [Schuur *et al.*, 2009]. Mobilization of old acetate and other low molecular weight DOC from deep yedoma deposits can occur rapidly through thermoerosional features such as retrogressive thaw slumps. More effective drainage to surface waters resulting from thermal erosion [Kokelj *et al.*, 2013; Malone *et al.*, 2013] could mix old C and inorganic solutes with relatively young DOC along flow paths following thaw, and rapid degradation of the older DOC can then limit the observed ^{14}C age of the residual pool [Spencer *et al.*, 2015]. Recent work has shown that with transport into streams and rivers, ancient labile DOC is rapidly lost, and apparent DOC ^{14}C ages become younger [Mann *et al.*, 2015; Spencer *et al.*, 2015]. Recent biodegradation experiments utilizing DOC from permafrost thaw streams in Siberia showed that about half of thaw stream DOC was consumed during short-term incubations [Mann *et al.*, 2015], consistent with similar recent experiments on yedoma samples [Drake *et al.*, 2015]. Limited observations of old DOC in rivers seems to reflect the increased biolability of old DOC from thawing permafrost, as well as in-mixing of substantial modern C in middle- to

higher-order rivers [Aiken *et al.*, 2014; O'Donnell *et al.*, 2014], masking the signal of permafrost thaw and potentially increasing loads of DIC [Striegl *et al.*, 2005]. Our results suggest that this signal should be evident from inorganic solute characteristics like uranium activity ratios that are not subject to biological transformation.

The fate of DOC with permafrost thaw may also depend on the fate of the substantial inorganic N that we observe in frozen yedoma cores, consistent with other observations of N release upon thaw in permafrost environments [Bowden *et al.*, 2008; Harms *et al.*, 2014; Koch *et al.*, 2014] including yedoma thaw lakes [Walter-Anthony *et al.*, 2014]. This inorganic N could be converted to nitrate and exported or lost to denitrification in streams [Mulholland *et al.*, 2008]. While some fertilization experiments in permafrost settings have indicated that inorganic N will facilitate decomposition and hence loss of C [Mack *et al.*, 2004; Mann *et al.*, 2014], recent observations also note no significant effect of nutrient addition [Mann *et al.*, 2015]. Our observation of high inorganic N in frozen yedoma permafrost on hillslopes, coupled with the observation of limited

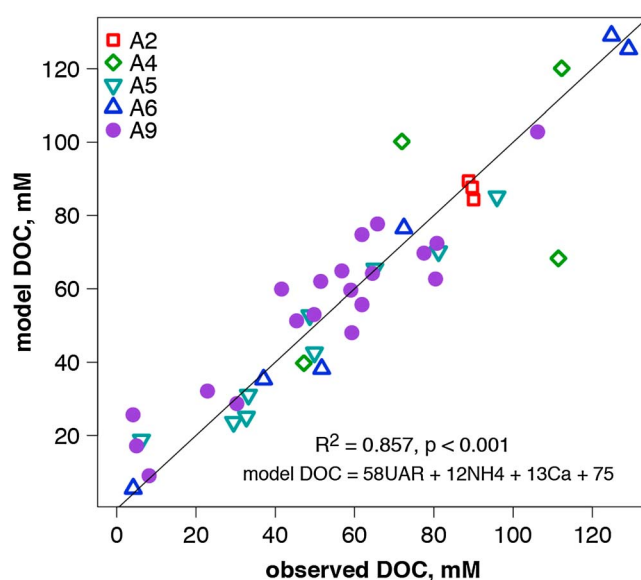


Figure 4. Modeled versus observed DOC in deep syngenetic loess permafrost cores. Results of multiple linear regression using UAR, NH_4^+ , and Ca^{2+} to explain DOC concentration. Regression performed using *lm* package in R [RCoreTeam, 2012], with the resulting linear equation as shown, explaining 86% of the variation in DOC.

inorganic N reaching streams in this area [Koch et al., 2013b], provides additional evidence that DOC loss upon thaw will not be N limited and will be rapid enough to limit stream export. Ultimately, these rates and circumstances will depend on the geomorphic and hydrologic conditions of thaw.

4. Conclusions

The presence of a substantial biolabile C pool in permafrost is increasingly evident [Mann et al., 2015] and represents an important contributor to the character of the positive warming feedback resulting from permafrost thaw [Drake et al., 2015]. Here we present evidence that this biolability is likely the result of long-term anaerobiosis in the high-C, low-oxygen circumstances of syngenetic permafrost accumulated through loess deposition over millennia. In rivers, the signal of this thaw contribution is

likely to be lost over time scales of hours to days from the DOC pool under oxic conditions but preserved in the signal provided by biologically nonlabile inorganic phases, such as dissolved uranium. We observed substantial acetate C in ice-rich loess permafrost thaw waters, along with substantial NH_4^+ , in concentrations that increased with permafrost age. The fate of this biolabile C will depend strongly upon the conditions of permafrost thaw. Rapid turnover of biolabile DOC (>20% of the total pool) and transport along newly established flow paths may help to explain increased DIC loads in surface waters draining permafrost environments.

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References

- Aiken, G. R., R. G. M. Spencer, R. G. Striegl, P. F. Schuster, and P. A. Raymond (2014), Influences of glacier melt and permafrost thaw on the age of dissolved organic carbon in the Yukon River basin, *Global Biogeochem. Cycles*, **28**, 525–537, doi:10.1002/2013GB004764.
- Baker, M. A., C. N. Dahm, and H. M. Valett (1999), Acetate retention and metabolism in the hyporheic zone of a mountain stream, *Limnol. Oceanogr.*, **44**(6), 1530–1539, doi:10.4319/lo.1999.44.6.1530.
- Bowden, W. B., M. N. Gooseff, A. Balser, A. Green, B. J. Peterson, and J. Bradford (2008), Sediment and nutrient delivery from thermokarst features in the foothills of the North Slope, Alaska: Potential impacts on headwater stream ecosystems, *J. Geophys. Res.*, **113**, G02026, doi:10.1029/2007JG000470.
- Bridgman, S. D., H. Cadillo-Quiroz, J. K. Keller, and Q. Zhuang (2013), Methane emissions from wetlands: Biogeochemical, microbial, and modeling perspectives from local to global scales, *Global Change Biol.*, **19**(5), 1325–1346, doi:10.1111/gcb.12131.
- Drake, T. W., K. P. Wickland, R. G. M. Spencer, D. M. McKnight, and R. G. Striegl (2015), Ancient low-molecular-weight organic acids in permafrost fuel rapid carbon dioxide production upon thaw, *Proc. Natl. Acad. Sci. U.S.A.*, **112**, 13,946–13,951, doi:10.1073/pnas.1511705112.
- Duddleston, K. N., M. A. Kinney, R. P. Kiene, and M. E. Hines (2002), Anaerobic microbial biogeochemistry in a northern bog: Acetate as a dominant metabolic end product, *Global Biogeochem. Cycles*, **16**(4), 1063, doi:10.1029/2001GB001402.
- Elberling, B., A. Michelsen, C. Schadel, E. A. G. Schuur, H. H. Christiansen, L. Berg, M. P. Tamstorf, and C. Sigsgaard (2013), Long-term CO_2 production following permafrost thaw, *Nat. Clim. Change*, **3**, 890–894, doi:10.1038/nclimate1955.
- Ewing, S. A., J. B. Paces, J. A. O'Donnell, M. T. Jorgenson, M. Z. Kanevskiy, G. R. Aiken, Y. Shur, J. W. Harden, and R. Striegl (2015), Uranium isotopes and dissolved organic carbon in loess permafrost: Modeling the age of ancient ice, *Geochim. Cosmochim. Acta*, **152**, 143–165, doi:10.1016/j.gca.2014.11.008.
- French, H., and Y. Shur (2010), The principles of cryostratigraphy, *Earth Sci. Rev.*, **101**(3–4), 190–206, doi:10.1016/j.earscirev.2010.04.002.
- Froese, D. G., J. A. Westgate, A. V. Reyes, R. J. Enkin, and S. J. Preece (2008), Ancient permafrost and a future, warmer Arctic, *Science*, **321**(5896), 1648, doi:10.1126/science.1157525.
- Grosse, G., et al. (2011), Vulnerability of high-latitude soil organic carbon in North America to disturbance, *J. Geophys. Res.*, **116**, G00K06, doi:10.1029/2010JG001507.
- Hädrich, A., V. B. Heuer, M. Herrmann, K.-U. Hinrichs, and K. Küsel (2012), Origin and fate of acetate in an acidic fen, *FEMS Microbiol. Ecol.*, **81**(2), 339–354, doi:10.1111/j.1574-6941.2012.01352.x.
- Harms, T. K., B. W. Abbott, and J. B. Jones (2014), Thermo-erosion gullies increase nitrogen available for hydrologic export, *Biogeochemistry*, **117**(2–3), 299–311, doi:10.1007/s10533-013-9862-0.

- Hedin, L. O., J. C. Von Fischer, N. E. Ostrom, B. P. Kennedy, M. G. Brown, and G. P. Robertson (1998), Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces, *Ecology*, 79(2), 684–703.
- Hines, M. E., K. N. Duddleston, J. N. Rooney-Varga, D. Fields, and J. P. Chanton (2008), Uncoupling of acetate degradation from methane formation in Alaskan wetlands: Connections to vegetation distribution, *Global Biogeochem. Cycles*, 22, GB2017, doi:10.1029/2006GB002903.
- Hugelius, G., et al. (2014), Estimated stocks of circumpolar permafrost carbon with quantified uncertainty ranges and identified data gaps, *Biogeosciences*, 11(23), 6573–6593, doi:10.5194/bg-11-6573-2014.
- Jorgenson, M. T. T., et al. (2013), Reorganization of vegetation, hydrology and soil carbon after permafrost degradation across heterogeneous boreal landscapes, *Environ. Res. Lett.*, 8(3), 1–13, doi:10.1088/1748-9326/8/3/035017.
- Kane, E. S., D. W. Valentine, G. J. Michaelson, J. D. Fox, and C.-L. Ping (2005), Controls over pathways of carbon efflux from soils along climate and black spruce productivity gradients in interior Alaska, *Soil Biol. Biochem.*, 38, 1438–1450, doi:10.1016/j.soilbio.2005.11.004.
- Kane, E. S., M. R. Turetsky, J. W. Harden, A. D. McGuire, and J. M. Waddington (2010), Seasonal ice and hydrologic controls on dissolved organic carbon and nitrogen concentrations in a boreal-rich fen, *J. Geophys. Res.*, 115, G04012, doi:10.1029/2010JG001366.
- Kanevskiy, M., Y. Shur, and D. Fortier (2011), Cryostratigraphy of late Pleistocene syngenetic permafrost (yedoma) in northern Alaska, Itkillik River exposure, *Quat. Res.*, doi:10.1016/j.yqres.2010.12.003.
- Kanevskiy, M., Y. Shur, B. Connor, M. R. Dillon, E. Stephani, and J. A. O'Donnell (2012), Study of the ice-rich syngenetic permafrost for road design (Interior Alaska), in *Tenth International Conference on Permafrost*, vol. 1, edited by K. M. Hinkel, pp. 191–196, The North. Publisher, Salekhard, Russia.
- Koch, J. C., R. L. Runkel, R. Striegl, and D. M. McKnight (2013a), Hydrologic controls on the transport and cycling of carbon and nitrogen in a boreal catchment underlain by continuous permafrost, *J. Geophys. Res. Biogeosci.*, 118, 698–712, doi:10.1002/jgrg.20058.
- Koch, J. C., S. A. Ewing, R. Striegl, and D. M. McKnight (2013b), Rapid runoff via shallow throughflow and deeper preferential flow in a boreal catchment underlain by frozen silt (Alaska, USA), *Hydrol. J.*, 21(1), 93–106, doi:10.1007/s10040-012-0934-3.
- Koch, J. C., K. Gurney, and M. S. Wipfli (2014), Morphology-dependent water budgets and nutrient fluxes in Arctic thaw ponds, *Permafrost Periglacial Processes*, 25(2), 79–93, doi:10.1002/ppp.1804.
- Kokelj, S. V., and C. R. Burn (2003), Ground ice and soluble cations in near-surface permafrost, Inuvik, Northwest Territories, Canada, *Permafrost Periglacial Processes*, 14, 275–289, doi:10.1002/ppp.458.
- Kokelj, S. V., and C. R. Burn (2005), Geochemistry of the active layer and near-surface permafrost, Mackenzie delta region, Northwest Territories, Canada, *Can. J. Earth Sci.*, 42, 37–48, doi:10.1139/e04-089.
- Kokelj, S. V., D. Lacelle, T. C. Lantz, J. Tunnicliffe, L. Malone, I. D. Clark, and K. S. Chin (2013), Thawing of massive ground ice in mega slumps drives increases in stream sediment and solute flux across a range of watershed scales, *J. Geophys. Res. Earth Surf.*, 118, 681–692, doi:10.1002/jgrf.20063.
- Koven, C. D., B. Ringeval, P. Friedlingstein, P. Ciais, P. Cadule, D. Khvorostyanov, G. Krinner, and C. Tarnocai (2011), Permafrost carbon-climate feedbacks accelerate global warming, *Proc. Natl. Acad. Sci. U.S.A.*, 108(36), 14,769–14,774, doi:10.1073/pnas.1103910108.
- Lawrence, D. M., C. D. Koven, S. C. Swenson, W. J. Riley, and A. G. Slater (2015), Permafrost thaw and resulting soil moisture changes regulate projected high-latitude CO₂ and CH₄ emissions, *Environ. Res. Lett.*, 10, 094011.
- Mack, M. C., E. A. G. Schuur, M. S. Bret-Harte, G. R. Shaver, and F. S. Chapin (2004), Ecosystem carbon storage in arctic tundra reduced by long-term nutrient fertilization, *Nature*, 431(7007), 440–443, doi:10.1038/nature02887.
- Mackelprang, R., M. P. Waldrop, K. M. DeAngelis, M. M. David, K. L. Chavarria, S. J. Blazewicz, E. M. Rubin, and J. K. Jansson (2011), Metagenomic analysis of a permafrost microbial community reveals a rapid response to thaw, *Nature*, 480, 368–371, doi:10.1038/nature10576.
- Malone, L., D. Lacelle, S. Kokelj, and I. D. Clark (2013), Impacts of hillslope thaw slumps on the geochemistry of permafrost catchments (Stony Creek watershed, NWT, Canada), *Chem. Geol.*, 356, 38–49, doi:10.1016/j.chemgeo.2013.07.010.
- Mann, P. J., et al. (2014), Evidence for key enzymatic controls on metabolism of Arctic river organic matter, *Global Change Biol.*, 20(4), 1089–1100, doi:10.1111/gcb.12416.
- Mann, P. J., T. I. Eglinton, C. P. McIntyre, N. Zimov, A. Davydova, J. E. Vonk, R. M. Holmes, and R. G. M. Spencer (2015), Utilization of ancient permafrost carbon in headwaters of Arctic fluvial networks, *Nat. Commun.*, 6, 7856, doi:10.1038/ncomms8856.
- Michaelson, G. J., C. L. Ping, G. W. Kling, and J. E. Hobbie (1998), The character and bioactivity of dissolved organic matter at thaw and in the spring runoff waters of the arctic tundra North Slope, Alaska, *J. Geophys. Res.*, 103, 28,939–28,946, doi:10.1029/98JD02650.
- Mueller, C. W., J. Rethemeyer, J. Kao-Kniffin, S. Loppmann, K. Hinkel, and J. Bockheim (2015), Large amounts of labile organic carbon in permafrost soils of northern Alaska, *Global Change Biol.*, doi:10.1111/gcb.12876, in press.
- Mulholland, P. J., et al. (2008), Stream denitrification across biomes and its response to anthropogenic nitrate loading, *Nature*, 452(7184), 202–205.
- Neff, J. C., J. C. Finlay, S. A. Zimov, S. P. Davydov, J. J. Carrasco, E. A. G. Schuur, and A. I. Davydova (2006), Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams, *Geophys. Res. Lett.*, 33, L23401, doi:10.1029/2006gl028222.
- O'Donnell, J. A., G. R. Aiken, E. S. Kane, J. B. Jones, J. A. O. Donnell, G. R. Aiken, E. S. Kane, and J. B. Jones (2010), Source water controls on the character and origin of dissolved organic matter in streams of the Yukon River basin, Alaska, *J. Geophys. Res.*, 115, G03025, doi:10.1029/2009JG001153.
- O'Donnell, J. A., J. W. Harden, A. D. McGuire, and V. E. Romanovsky (2011a), Exploring the sensitivity of soil carbon dynamics to climate change, fire disturbance and permafrost thaw in a black spruce ecosystem, *Biogeosciences*, 8(5), 1367–1382, doi:10.5194/bg-8-1367-2011.
- O'Donnell, J. A., J. W. Harden, A. D. McGuire, M. Z. Kanevskiy, M. T. Jorgenson, and X. Xu (2011b), The effect of fire and permafrost interactions on soil carbon accumulation in an upland black spruce ecosystem of interior Alaska: Implications for post-thaw carbon loss, *Global Change Biol.*, 17(3), 1461–1474, doi:10.1111/j.1365-2486.2010.02358.x.
- O'Donnell, J. A., G. R. Aiken, M. A. Walvoord, and K. D. Butler (2012), Dissolved organic matter composition of winter flow in the Yukon River basin: Implications of permafrost thaw and increased groundwater discharge, *Global Biogeochem. Cycles*, 26, GB0E06, doi:10.1029/2012GB004341.
- O'Donnell, J. A., G. Aiken, M. Walvoord, P. Raymond, K. Butler, M. Dornblaser, and K. Heckman (2014), Using dissolved organic matter age and composition to detect permafrost thaw in boreal watersheds of interior Alaska, *J. Geophys. Res. Biogeosci.*, 119, 2155–2170, doi:10.1002/2014JG002695.
- Payn, R. A., A. M. Helton, G. C. Poole, C. Izurieta, A. J. Burgin, and E. S. Bernhardt (2014), A generalized optimization model of microbially driven aquatic biogeochemistry based on thermodynamic, kinetic, and stoichiometric ecological theory, *Ecol. Modell.*, 294, 1–18.
- Pewé, T. L. (1975), *Quaternary Geology of Alaska*, U.S. Geol. Surv., U.S. Gov. Print. Off., Washington, D. C.
- Ping, C. L., G. J. Michaelson, E. C. Packee, C. A. Stiles, D. K. Swanson, and K. Yoshikawa (2005), Soil catena sequences and fire ecology in the boreal forest of Alaska, *Soil Sci. Soc. Am. J.*, 69(6), 1761–1772, doi:10.2136/sssaj2004.0139.

- RCoreTeam (2012), *R: A Language and Environment for Statistical Computing*, R Found. for Stat. Comput., Vienna.
- Reyes, A. V., G. D. Zazula, S. Kuzmina, T. A. Ager, and D. G. Froese (2011), Identification of last interglacial deposits in eastern Beringia: A cautionary note from the Palisades, interior Alaska, *J. Quat. Sci.*, 26(3), 345–352, doi:10.1002/jqs.1464.
- Rivkina, E. M., E. I. Friedmann, C. P. McKay, and D. A. Gilichinsky (2000), Metabolic activity of permafrost bacteria below the freezing point, *Appl. Environ. Microbiol.*, 66, 3230–3233, doi:10.1128/AEM.66.8.3230-3233.2000.
- Romanovsky, V. E., and T. E. Osterkamp (2000), Effects of unfrozen water on heat and mass transport processes in the active layer and permafrost, *Permafrost Periglacial Processes*, 11(3), 219–239, doi:10.1002/1099-1530(200007/09)11:3<219::aid-ppp352>3.0.co;2-7.
- Sanderman, J., J. A. Baldock, and R. Amundson (2008), Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils, *Biogeochemistry*, 89(2), 181–198, doi:10.1007/s10533-008-9211-x.
- Schaefer, K., H. Lantuit, V. E. Romanovsky, E. A. G. Schuur, and R. Witt (2014), The impact of the permafrost carbon feedback on global climate, *Environ. Res. Lett.*, 9, 085003, doi:10.1088/1748-9326/9/8/085003.
- Schuur, E. A. G., et al. (2008), Vulnerability of permafrost carbon to climate change: Implications for the global carbon cycle, *BioScience*, 58(8), 701–714, doi:10.1641/b580807.
- Schuur, E. A. G., J. G. Vogel, K. G. Crummer, H. Lee, J. O. Sickman, and T. E. Osterkamp (2009), The effect of permafrost thaw on old carbon release and net carbon exchange from tundra, *Nature*, 459, 556–559, doi:10.1038/nature08031.
- Schuur, E. A. G., et al. (2013), Expert assessment of vulnerability of permafrost carbon to climate change, *Clim. Change*, 119, 359–374, doi:10.1007/s10584-013-0730-7.
- Schuur, E. A. G., et al. (2015), Climate change and the permafrost carbon feedback, *Nature*, 520(7546), 171–179, doi:10.1038/nature14338.
- Shur, Y. L., and M. T. Jorgenson (2007), Patterns of permafrost formation and degradation in relation to climate and ecosystems, *Permafrost Periglacial Processes*, 18(1), 7–19, doi:10.1002/ppp.582.
- Shur, Y. L., M. Z. Kanevskiy, M. Dillon, E. Stephani, and J. A. O'Donnell (2010), Geotechnical investigations for the Dalton Highway Innovation Project as a case study of the ice-rich syngenetic permafrost.
- 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.
- Striegl, R. G., G. R. Aiken, M. M. Dornblaser, P. A. Raymond, and K. P. Wickland (2005), A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn, *Geophys. Res. Lett.*, 32, L21413, doi:10.1029/2005GL024413.
- Van Hees, P. A. W., D. L. Jones, R. Finlay, D. L. Godbold, and U. S. Lundstrom (2005), The carbon we do not see—the impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: A review, *Soil Biol. Biochem.*, 37, 1–13, doi:10.1016/j.soilbio.2004.06.010.
- Vonk, J. E., et al. (2013), High biolability of ancient permafrost carbon upon thaw, *Geophys. Res. Lett.*, 40, 2689–2693, doi:10.1002/grl.50348.
- Waldrop, M. P., K. P. Wickland, R. White, A. A. Berhe, J. W. Harden, and V. E. Romanovsky (2010), Molecular investigations into a globally important carbon pool: Permafrost-protected carbon in Alaskan soils, *Global Change Biol.*, 16, 2543–2554, doi:10.1111/j.1365-2486.2009.02141.x.
- Walter-Anthony, K. M., et al. (2014), A shift of thermokarst lakes from carbon sources to sinks during the Holocene epoch, *Nature*, 511(7510), 452–456, doi:10.1038/nature13560.
- Wickland, K. P., G. R. Aiken, K. Butler, M. M. Dornblaser, R. G. M. Spencer, and R. G. Striegl (2012), Biodegradability of dissolved organic carbon in the Yukon River and its tributaries: Seasonality and importance of inorganic nitrogen, *Global Biogeochem. Cycles*, 26, GB0E03, doi:10.1029/2012GB004342.
- Zimov, S. A., S. P. Davydov, G. M. Zimova, A. I. Davydova, E. A. G. Schuur, K. Dutta, and F. S. I. Chapin (2006), Permafrost carbon: Stock and decomposability of a globally significant carbon pool, *Geophys. Res. Lett.*, 33, L20502, doi:10.1029/2006GL027484.