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Dissolved organic carbon loss from Yedoma permafrost amplified by ice wedge thaw

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Abstract
Pleistocene Yedoma permafrost contains nearly a third of all organic matter (OM) stored in circum-arctic permafrost and is characterized by the presence of massive ice wedges. Due to its rapid formation by sediment accumulation and subsequent frozen storage, Yedoma OM is relatively well preserved and highly biologically available (biolabile) upon thaw. A better understanding of the processes regulating Yedoma degradation is important to improve estimates of the response and magnitude of permafrost carbon feedbacks to climate warming. In this study, we examine the composition of ice wedges and the influence of ice wedge thaw on the biolability of Yedoma OM. Incubation assays were used to assess OM biolability, fluorescence spectroscopy to characterize the OM composition, and potential enzyme activity rates to examine the controls and regulation of OM degradation. We show that increasing amounts of ice wedge melt water in Yedoma-leached incubations enhanced the loss of dissolved OM over time. This may be attributed to the presence of low-molecular weight compounds and low initial phenolic content in the OM of ice wedges, providing a readily available substrate that promotes the degradation of Yedoma OC. The physical vulnerability of ice wedges upon thaw (causing irreversible collapse), combined with the composition of ice wedge-engrained OM (co-metabolizing old OM), underlines the particularly strong potential of Yedoma to generate a positive feedback to climate warming relative to other forms of non-ice wedge permafrost.

Keywords: Yedoma, permafrost, ice wedges, biodegradable dissolved organic matter, enzymes, fluorescence

S Online supplementary data available from stacks.iop.org/ERL/8/035023/mmedia

1. Introduction

Northeast Siberian permafrost is dominated by frozen Yedoma deposits (figure 1(a)) containing ~500 Gt of organic carbon (OC), nearly a third of all belowground OC that is stored in circum-arctic permafrost (Zimov *et al* 2006a,

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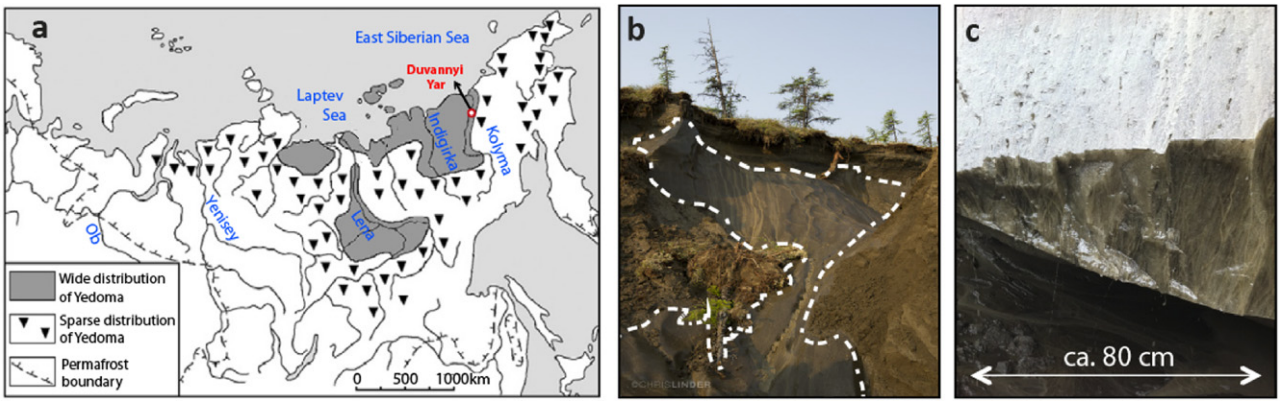

Figure 1. (a) Distribution of Yedoma in Siberia (Romanovskii 1993) overlain with major Russian-Arctic Rivers and study site Duvannyi Yar, (b) eroding Yedoma containing massive ice wedges (outline as white dashed line) on the bank of Kolyma River at the Duvannyi Yar exposure, and (c) close-up of an old ice wedge (age about 30–40 ky, Vasil'chuk and Vasil'chuk 1997) revealing (annual) ice veins formed through melt of the snow pack seeping into existing frost cracks.

2006b, Tarnocai *et al* 2009). Degradation of Yedoma is identified as a key trigger in the debate on permafrost carbon feedback mechanisms to global climate (Zimov *et al* 1993, Khvorostyanov *et al* 2008a, 2008b). Yedoma deposits were formed during glacial times when the northern regions on Earth (Siberia but also parts of Central Alaska and NW Canada) were occupied by extremely dry and cold steppe–tundra ecosystems. There are several existing hypotheses on Yedoma genesis: alluvial, colluvial, nival, eolian, or a combination thereof (Sher *et al* 1979, Tomirdiaro 1982, Kanevskiy *et al* 2011 and references therein), but there typically is agreement on the leading factors being a cold climate and continuous long-term sedimentation.

Rapid incorporation of thawed surface layers into permafrost, in combination with frozen storage, is today reflected in relatively high amounts of OC (1–5%, Schirrmeister *et al* 2011, Zimov *et al* 2006a, 2006b) that is relatively well preserved (Zimov *et al* 2006b, Schuur *et al* 2008). Biolability assessments with dissolved OC (19–29 ky old) from small Yedoma thaw streams in NE Siberia clearly illustrate the rapid decomposability of Yedoma, showing OC losses of up to 33% in 14 days (Vonk *et al* 2013). Water isotopic analyses (δ^2H and δ^{18}O) demonstrate that these thaw streams are predominantly derived from ancient ice wedge melt water (Vonk *et al* 2013, Vasil'chuk *et al* 2001).

Ice wedges are a key feature of Yedoma (figure 1(b)) as they penetrate the entire soil sequence and extend to depths of 25 or even 50 m. They are formed when snow melt waters seep into frost cracks during early spring, vertically building up annual ice veins (figure 1(c)) of 1–5 mm thickness. Ice wedges also grow horizontally, parallel to Yedoma build-up, with an average of ∼1 m per 1000 yr (Vasil'chuk and Vasil'chuk 1997). These syngenetic ice structures account for about 50% of the soil volume (Sher *et al* 1979, Schirrmeister *et al* 2011) and render Yedoma deposits particularly vulnerable to warmer temperatures, as ice melt will give rise to surface subsidence and thermal collapse (Strauss *et al* 2012, Vonk *et al* 2012). The yellow, gray or milky-white ice wedges have incorporated sediments and organic matter (Douglas *et al* 2011, Davydova *et al* 2012) that presumably originates from surface soils and vegetation debris that was carried along with the melting snow. Pollen analyses on ice wedge and adjacent Yedoma sediments suggest similar vegetation sources (Sher *et al* 1979, Vasil'chuk and Vasil'chuk 1997). Several studies have reported signs of extant microbial communities in ice wedges (Katayama *et al* 2009, Wilhelm *et al* 2012), as well as in Yedoma (e.g. Gilichinsky and Wagener 1995, Rivkina *et al* 1998, 2000), and Holocene permafrost (e.g. Waldrop *et al* 2010, Coolen *et al* 2011). Additionally, intact soil enzymes have also been found in Yedoma (Shchelchkova 2009). Ice wedges, in addition to providing a source of enzymes and microbial communities, also provide an abundant moisture source necessary for microbial degradation (Zimov *et al* 1993).

Here, we investigate the influence of thawing ice wedges on the biolability of Yedoma OC. We hypothesize that the presence of ice wedge waters may contribute to the high rates of biolability previously reported in Yedoma OC (Vonk *et al* 2013). To test this hypothesis, we set up biolability assays by exposing Yedoma to varying mixtures of ice wedge melt water and river water. In addition to measurement of bulk parameters (DOC, dissolved total nitrogen, nutrients), we utilize fluorescence spectroscopy during the incubations to shed light on the initial composition and compositional changes during degradation. The use of fluorescent-DOM is a broadly applied and well-known technique (Hudson *et al* 2007, Fellman *et al* 2010, Murphy *et al* 2010) to characterize DOM composition. We specifically target dissolved organic matter (OM) instead of particulate OM as these compounds are readily available for microbial metabolism (Battin *et al* 2008). Furthermore, we measure potential enzyme activity rates (exoenzymes) that are released by microorganisms to cleave organic matter into smaller molecules, and thus mediate the degradation of organic matter (Sinsabaugh *et al* 2008). This allows us to assess the initial substrate availability and to clarify which processes regulate OC degradation. A better understanding of the factors regulating degradation of Yedoma is important to improve estimates on the magnitude of the positive feedback mechanism to climate warming from thawing permafrost carbon (Schaefer *et al* 2011).

Table 1. Experimental setup, bulk elemental analyses, nutrient and incubation results.

	Relative amounts in incubations			Initial concentrations						DOC loss	
	IW[b] (%)	Kolyma River (%)	Yedoma (g l^{-1})	DOC (mg l^{-1})	TDN (mg l^{-1})	DOC:TDN	NO_3 (μgN l^{-1})	NH_4 (μgN l^{-1})	PO_4 (μgP l^{-1})	T = 3 (%)	T = 11 (%)
Control: no Yedoma added											
Kolyma River[a]	0	100	0	4.9	0.24	20	18	25	6.8	0	1.3
IW[b] 1	100	0	0	9.2	2.6	3.5	3.9	1000	23	—	—
IW[b] 2	100	0	0	15	2.3	6.6	25	510	5.1	—	—
IW[b] 3	100	0	0	8.8	2.0	4.5	32	830	6.3	—	—
IW[b] composite	100	0	0	11	2.4	4.6	—	—	—	22	34
Treatments[c]: Yedoma added											
Kolyma River	0	100	8	9.2	0.60	15	—	—	—	6.5	7.9
IW[b] composite	100	0	8	16	2.9	5	—	—	—	3.5	24
50%	50	50	8	13	1.9	7	—	—	—	2.0	20
25%	25	75	8	11	1.4	8	—	—	—	3.4	17
10%	10	90	8	11	0.71	15	—	—	—	14	15
5%	5	95	8	9.3	0.62	15	—	—	—	0	7.9
1%	1	99	8	9.4	0.58	16	—	—	—	3.9	11

[a] Nutrient concentrations are average values of Kolyma River (above Omolon tributary, i.e. above Duvannyi Yar) of 13 and 21 July 2011 (www.thepolarisproject.org/data/).

[b] IW; ice wedge.

[c] Mixtures of Kolyma River water and ice wedge water with leached Yedoma are represented as % ice wedge water in incubations (i.e. 25% is 25% ice wedge water and 75% Kolyma River water in the incubation).

2. Sampling and methods

2.1. Site description

Duvannyi Yar consists of a 10–12 km long Yedoma outcrop located on the right bank of the lower Kolyma River (NE Siberia, figures 1(a), (b)). The ice-rich cliffs rise up to about 50 m above mean river level, and are subject to rapid erosion by the Kolyma River. The Yedoma bank retreat in this area is estimated to be about 100 m in the last 30 years (Vasil'chuk *et al* 2001). Duvannyi Yar is a relatively well-studied Yedoma site and serves as a reference section for the Omolon-Anui Yedoma massif (Vasil'chuk 2005), and as a stratigraphic key site for the late Quaternary (Kaplina *et al* 1978). Here, the Yedoma deposits accumulated between ~40 and 13 ky BP (Sher *et al* 1979, Vasil'chuk *et al* 2001) and are believed to be of polygenetic (alluvial, fluvial and aeolian) origin (Strauss *et al* 2012). The total OC content averages 1.5 ± 1.4 wt%, and the total average ice content is about 75% by volume (35 wt% for ground ice, plus about 50 vol% for ice wedges) (Strauss *et al* 2012).

2.2. Sampling

Three different ice wedges from Duvannyi Yar were sampled on 8 July 2012 (68.630 48°N, 159.146 80°E; 68.630 37°N, 159.146 62°E; 68.630 40°N, 159.146 33°E), each located about 7 m above river level. Freshly thawed Yedoma deposits surrounding these ice wedges were taken and combined into a composite sample. Kolyma River water was collected upstream of Duvannyi Yar (68.722 60°N, 158.692 65°E), just south of the Omolon tributary. All samples were immediately transported back to the Northeast Science Station in Cherskiy (about 120 km upstream of Duvannyi Yar) and stored cold (about 5 °C) and in the dark.

2.3. Experimental setup

After thaw (about 24 h after sampling) small aliquots were taken from each ice wedge for bulk analyses. The melt water was then combined into a composite sample to mimic the natural mixing that occurs in melt water streams. Both the ice wedge water and the Kolyma River water was filtered through a 0.45 μm cartridge filter. Different ratios of filtered ice wedge to Kolyma River water (table 1) were combined and a standard amount of Yedoma (8 g l^{-1} water) was added to an ice wedge and Kolyma River control, as well as to each experimental treatment (table 1), to form a leachate. These leachates were shaken over a period of six hours and then re-filtered (0.45 μm). Each filtrate, in addition to a Kolyma and ice wedge control (no Yedoma added), was divided into pre-ashed glass scintillation vials (40 ml, half-filled; in triplicate) and left to incubate in the dark at about 15 °C during continuous shaking with loose caps to allow for oxygenated conditions.

At $T = 0$, $T = 3$ and $T = 11$ days, we measured DOC, total dissolved nitrogen (TDN), potential enzyme activity rates (see section 2.5), and fluorescence EEMs of dissolved

organic matter (see section 2.4), all at the Northeast Science Station in Cherskiy. Nutrient analysis (NO_{3-}, NH_{4+}, $PO_{4^{3-}}$; only $T = 0$) and water isotope analysis ($\delta^2H/\delta^{18}O$; only $T = 0$) were completed at the Woods Hole Research Center (Falmouth, US) and ETH-Zürich (Zürich, Switzerland), respectively. DOC and TDN were measured using a Shimadzu TOC-V analyzer using established protocols (Mann *et al* 2012). Nutrients were measured on an Astoria-Pacific Analyzer (Clackamas, US), and water isotopes were run on a Picarro L2120-i Isotopic water analyzer (Santa Clara, US).

2.4. Absorbance and fluorescence spectroscopic analyses

UV–visible absorbance measurements were performed from 200 to 800 nm on a Shimadzu dual beam UV-1800 spectrophotometer at room temperature. Fluorescence measurements were conducted using a Horiba Fluoromax 4 spectrofluorometer. Excitation–emission matrices (EEMs) were collected using excitation wavelengths of 250–400 nm and emission wavelengths of 320–520 nm. All EEMs were post-corrected and normalized using methods outlined previously (Mann *et al* 2012). EEMs were decomposed and validated using parallel factor analyses (PARAFAC) using the methods and code in the DOMFluor toolbox for MATLAB (Stedmon and Bro 2008). In order to generate a robust and more widely applicable PARAFAC model, EEMs collected from the lower Kolyma watershed over the past three years were included in the model. These EEMs included some reported previously (Mann *et al* 2012), as well as additional EEMs collected from waters spanning a range of aquatic ecosystems (lakes, rivers and streams) and years (2010, 2011 and 2012) (www.thepolarisproject.org/data/). In total, 549 individual EEMs were included in the analysis and were decomposed into seven 'KW' (Kolyma Watershed) components.

2.5. Extracellular enzyme activity rates

The potential activity of four extracellular enzymes (phosphatase, β-glucosidase, leucine-aminopeptidase, and phenol oxidase) was assayed using pnp-linked substrates on 96-well microplates (Biotek) following methods developed by Sinsabaugh *et al* (1997, 2001). Filtered waters (200 μl) were added to each well along with 50 μl of substrate. Sample waters were replicated in five wells, and each plate contained replicated substrate and samples controls. Substrate solutions were prepared in distilled water with final substrate concentrations of 5 μM.

Hydrolytic enzymes (e.g. phosphatase, β-glucosidase, and leucine-aminopeptidase) degrade organic matter with simply arranged hydrolyzable bonds whereas oxidative enzymes, like phenol oxidase, break down more complex bonds, such as in aromatic compounds. More specifically, phosphatase targets ester-bound phosphate, β-glucosidase targets simple chain carbon compounds, and leucine-aminopeptidase degrades proteins into amino acids. Phenol oxidase breaks down phenolic compounds; compounds that have been shown to inhibit hydrolase enzyme synthesis in northern peatland soils, impacting organic carbon and nutrient cycling (Fenner and Freeman 2011).

3. Results and discussion

3.1. Bulk chemistry of ice wedges and Kolyma river water

The water isotopic composition of the sampled ice wedges confirm formation during the late Pleistocene. During this time, Duvannyi Yar was situated further inland (due to a lower sea level) and experienced colder winter temperatures. Both factors lead to a stronger rain-out of the heavier isotope, resulting in a more depleted signature of the precipitation that formed the ice wedges (Hubberten *et al* 2004, Meyer *et al* 2002). Deuterium signatures were -259 ± 4‰ (mean $\pm$ stdev) and oxygen signatures -33.2 ± 0.4‰, lying in the same range as previously measured ice wedges at Duvannyi Yar (Vasil'chuk *et al* 2001) or elsewhere in the Yedoma region (Meyer *et al* 2002). Small Yedoma thaw streams from the same location on Duvannyi Yar, sampled in 2011 (Vonk *et al* 2013), also had similar ∂^2H (-246‰) and $\partial^{18}O$ (-32.4‰) signatures. In comparison, Kolyma River water reflects present-day precipitation sources with ∂^2H values of -166‰ and $\partial^{18}O$ of -21.6‰, lying within the seasonal variation (∂^2H -185 to -162‰; $\partial^{18}O$ -24 to -21‰, Cooper *et al* 2008, www.thepolarisproject.org/data/ and http://arcticgreatrivers.org/data.html).

Initial DOC concentrations ranged between 8.8 and 15 mg l^{-1} in the three sampled ice wedges (11 mg l^{-1} for the composite) and measured 4.9 mg l^{-1} in the Kolyma River and between 9.3 and 13 mg l^{-1} for the Yedoma leachate mixtures (table 1). Ratios of DOC:TDN in ice wedges were low compared to the Kolyma (3.5–6.7, compared to 20), whereas Yedoma thaw streams (2011) had DOC:TDN of 14. The unusually low ice wedge DOC:TDN ratios can most likely be attributed to the high inorganic nitrogen content (NH_{4+} is 500–1000 μgN l^{-1}, compared to 25 μgN l^{-1} for the Kolyma; table 1). Nitrate and phosphate concentrations were 4–32 μgN l^{-1} and 5–24 μP l^{-1} for the ice wedges and 18 μgN l^{-1} and 7 μP l^{-1} for the Kolyma River in July (table 1).

3.2. Organic matter composition of ice wedges and Kolyma river water

Seven independent fluorescent components were identified within the EEMs using PARAFAC analyses. Four of the components have been previously identified as UV-C-like humic fractions, two as lower molecular weight UV-A-like humics and one as an amino acid tryptophan-like component (table 2 and references therein). Ice wedge waters, both with and without leached Yedoma, contained high proportions and absolute contributions from lower molecular weight DOM as evidenced by high proportions of the KW4 component (figure 2) (Cory and McKnight 2005, Fellman *et al* 2010, Mann *et al* 2012). This suggests that ice wedge waters contain a DOM pool of reduced aromaticity and lower abundance of phenolic compounds.

Our four target extracellular enzymes (supplementary table 1 available at stacks.iop.org/ERL/8/035023/mmedia) have very different initial ($T = 0$) activity rates. The

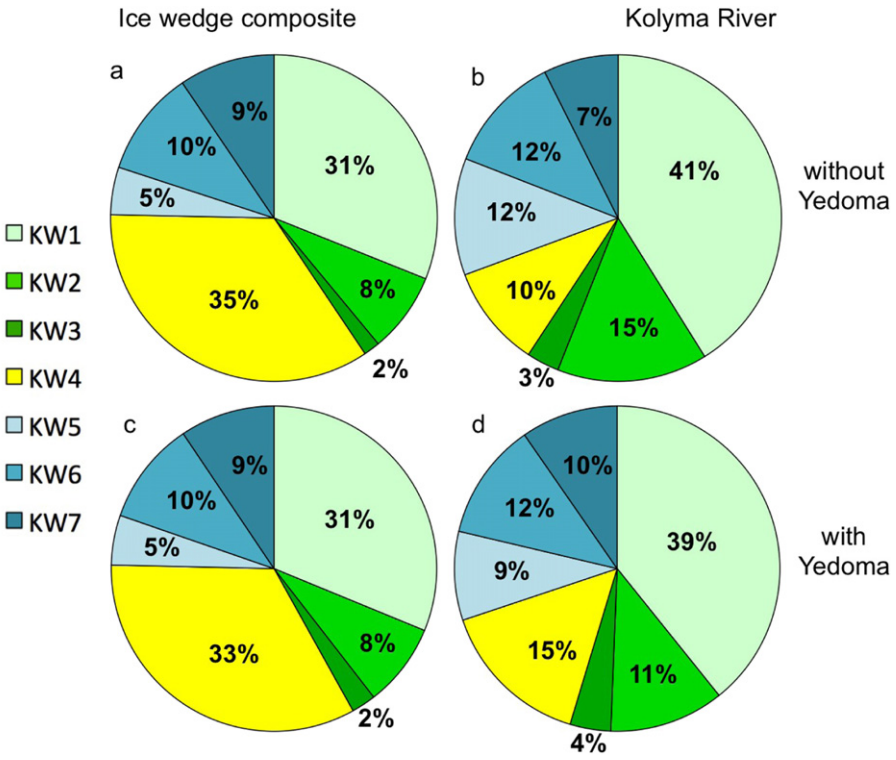

Figure 2. Dissolved organic matter composition expressed as the per cent contribution of PARAFAC components in (a) ice wedge composite, (b) Kolyma River, (c) ice wedge composite with leached Yedoma (8 g l^{-1}), and (d) Kolyma River with leached Yedoma (8 g l^{-1}). The seven PARAFAC components (KW: Kolyma Watershed) are identified from excitation–emission matrices using fluorescence spectroscopy. The methods can be found in section 2.4, and a detailed component description in table 2.

Table 2. Spectral characteristics of the seven components identified using PARAFAC, secondary excitation maxima in parentheses.

Component	Excitation λ_{max} (nm)	Emission λ_{max} (nm)	Description	Description and previous studies (comparative components in Mann *et al* (2012) in parentheses)
KW1	255	444	UV-C humic-like	Terrestrial or soil OM. High-molecular weight/aromatic[a]. (C3)
KW2	255	512	UV-C humic-like	High-molecular weight and aromatic humic[a,b,c]. (C2)
KW3	325	384	UV-A humic-like	Low-molecular weight. Commonly associated with biological activity[a].
KW4	<255(300)	420	UV-A humic-like	Low-molecular weight. Common with biological activity, correlated with aliphatic C content[a,b,c]. (C1)
KW5	365	456	UV-C humic-like	
KW6	325	428	UV-C humic-like	High-molecular weight humic. Common in wetlands/forested regions[a].
KW7	<255(280)	336	Tryptophan-like	Ubiquitous. Free or bound amino acids/proteins[a,b,c]. (C4)

[a] Fellman *et al* (2010).
[b] Mann *et al* (2012).
[c] Cory and McKnight (2005).

three hydrolytic enzymes (phosphatase, β-glucosidase and leucine-aminopeptidase) show higher activity rates for the ice wedge samples, whereas the oxidative phenol oxidase is similar in all controls and treatments. The fact that ice wedges have freshly thawed, after being frozen for several millennia, could contribute to the initial spike in enzymatic activity. A more likely suggestion however, is that the distinct difference between hydrolytic and oxidative enzyme activities is caused by a relatively low abundance of phenolic compounds in ice wedges. These compounds inhibit organic matter degradation (Freeman *et al* 2001) and prevent decay via hydrolytic enzyme activity (Fenner and Freeman 2011). Here, hydrolytic enzymes are active from the start, indicating that there are few inhibitory compounds present. This is supported by a study by Mann *et al* (2013) that suggests that Yedoma-influenced waters at Duvannyi Yar contain low

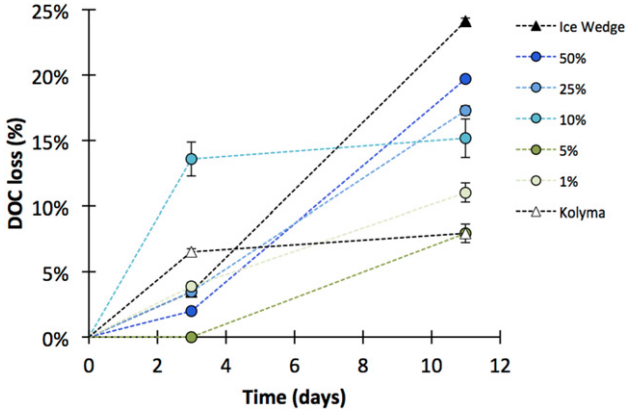

Figure 3. Bioavailability of Yedoma in (mixtures of) ice wedge and Kolyma river water. Dissolved organic carbon (DOC) loss (%) over time for incubations of Yedoma in: ice wedge water (black triangles), mixtures of ice wedge and Kolyma River water (colored circles; reported as %Ice Wedge) and Kolyma water (white triangles). Error bars represent one standard deviation. All incubations contain 8 g l^{-1} leached Yedoma.

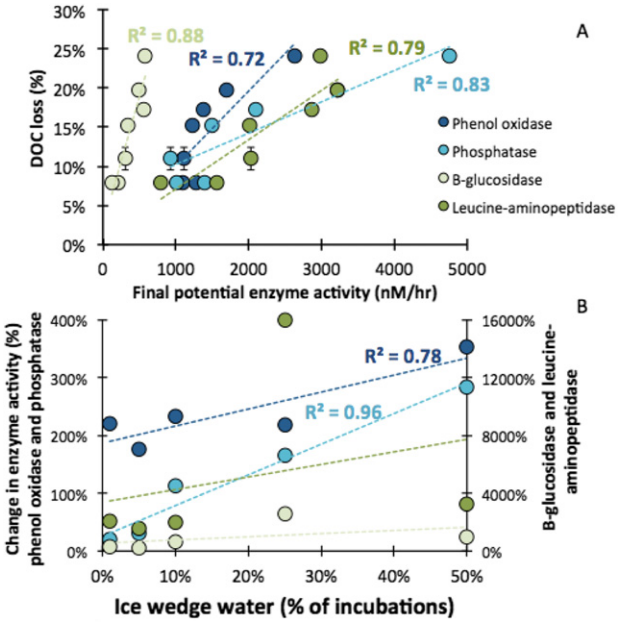

Figure 4. (a) Final potential enzyme activity (nM h^{-1}) at $T = 11$ against total dissolved organic carbon loss (%) for all incubations with leached Yedoma, and (b) change in potential enzyme activity at $T = 11$d (%) against content of ice wedge water (%) in the incubations with leached Yedoma. Note that phosphatase and phenol oxidase activities are on the left y-axis and β-glucosidase and leucine-aminopeptidase on the right.

initial polyphenol concentrations, as derived from limited response of these waters to removal of phenolic content, in contrast to a strong response of contemporary waters in the Kolyma lower basin. Furthermore, elevated phosphatase and β-glucosidase activities (Coolen *et al* 2011), and relatively low phenol oxidase activities (Waldrop *et al* 2010) were also observed in freshly thawed (Holocene) Alaskan permafrost.

3.3. The impact of ice wedge melt water on biolability of Yedoma

Increasing amounts of ice wedge water in the Yedoma leachate incubations enhanced DOC loss over time (figure 3; table 1). Kolyma waters containing leached Yedoma lost 7.9 ± 0.5% of its initial DOC content after 11 days, whereas ice wedge melt water containing identical amounts of leached Yedoma lost 24 ± 0.2% (figure 3; table 1). The leachate mixtures of Kolyma and ice wedge waters showed a general increase in DOC loss with an increasing proportion of ice wedge melt water; 11 ± 0.7%, 7.9 ± 0.2%, 15 ± 1%, 17 ± 0.4%, and 20 ± 0.1% DOC loss for 1, 5, 10, 25 and 50% ice wedge melt water content in the leachate incubations respectively (figure 3; table 1). Control incubations of Kolyma River and ice wedge water without leached Yedoma lost 1.3 ± 0.04%, and 34 ± 1% of initial DOC after 11 days, respectively. The relatively low DOC loss for the control Kolyma River (1.3 ± 0.04%) compared with the Yedoma-leached Kolyma River water (7.9 ± 0.5%) is likely related to the degree of pre-processing of Kolyma River DOC; the control waters having already undergone extensive processing, but the leached waters contain an additional DOM source with a lower degree of pre-processing (i.e. Yedoma DOC). In contrast, DOC loss was higher for the ice wedge control (34 ± 1%) as compared with the Yedoma-leached ice wedge water (24 ± 0.2%). This reduction is likely caused by the addition of (relatively) more complex, phenolic compounds into the ice wedge waters, slowing the overall rate at which the microbial community could degrade OC. Additionally, microbial communities in ice wedges might need time to adjust to the introduced Yedoma OM.

Incubations with DOC from thaw streams on Duvannyi Yar (Vonk *et al* 2013) showed a 33 ± 1% loss after 14 days. These thaw streams can be considered as natural leachates of Yedoma and contained between 150 and 330 mg l^{-1} of DOC that was 19–29 ^{14}C ky old (2010 and 2011). Ice wedge melt water was the main source of these streams, supporting the previous observation that the presence of ice wedges appears to result in high Yedoma-derived OC degradation.

3.4. Compositional and enzymatic insights into Yedoma biolability

Extracellular enzyme activities provide a tool to examine the controls and regulation of organic matter degradation, and prior studies have successfully related potential activity rates, particularly of β-glucosidase, to bacterial production and carbon loss (Chróst and Rai 1993).

In our treatments, β-glucosidase activity demonstrated the strongest correlation to DOC loss (figure 4(a)), but each of the enzymes studied showed significant positive correlations with DOC removal. The total change in enzyme activity across our incubation period may serve as an indicator of which processes are mediating the continued degradation of the DOM pool. Significant increases in the % activity of each of the enzymes over the incubation period (11 d) demonstrated the production of both specific oxidative and hydrolase enzymes during this period (figure 4(b)). Furthermore, significant linear correlations between the per cent enzyme

activity rates for phenol oxidase ($R^2 = 0.78$) and phosphatase ($R^2 = 0.96$) with the proportion of ice wedge water were observed across the incubations (figure 4(b)). These results suggest that as ice wedge water contribution increases, enzymes targeting the acquisition of P from organic matter are produced. This is probably either due to reduced inorganic P availability (due to increased OC losses) or the increased supply of favorable substrates (e.g. low-molecular weight compounds) for microbial utilization, enabling an enhanced production of enzymes at lower energetic cost. Increases in phenol oxidase demonstrate that the microbial community were acting to degrade more complex substrates, either due to the depletion of more easily used substrates earlier in the incubation, or due to the increased availability of energy for their synthesis.

The loss of DOC in the Yedoma leachate mixtures is also related to initial DOC:TDN; treatments with a lower initial DOC:TDN ratio showed larger DOC losses (figure 5(a)). As outlined above, the lower DOC:TDN ratios in the Yedoma streams probably relate to the high NH_4^+ abundance, which is likely enhancing remineralization. Furthermore, a lower initial abundance of component KW1 (high-molecular weight, aromatic OM) also relates to %DOC loss (figure 5(b)). After a 3 day incubation the loss of the low-molecular component KW4 in all of the incubations containing ice wedge water or Yedoma is remarkably consistent (supplementary table 2 available at stacks.iop.org/ERL/8/035023/mmedia). This confirms the previous suggestion that an increased supply of favorable low-molecular weight substrates is correlated to the presence of ice wedge melt water. It is therefore not surprising that the initial proportion of component KW4 also appears to be correlated ($R^2 = 0.92$) with %DOC loss at $T = 11$ (figure 5(b)). This DOM region may therefore represent a lower molecular weight substrate that provides energy for microbial use through enzyme synthesis supporting OC loss. A shift toward less aromatic, low-molecular weight OM as inferred from fluorescence characteristics was also observed in waters with increasing input of Yedoma (Mann *et al* 2013). Furthermore, Neff *et al* (2006) showed a linear relationship between $\Delta^{14}C$ and $SUVA_{254}$ in Kolyma basin waters, supporting our observation that (older) Yedoma-influenced waters display lower DOM aromaticity.

Incubation experiments with Kolyma River spring freshet DOC showed higher DOC loss with increasing proportions of component C2 (here KW2, table 2), a component that is characterized by humic-like, higher aromatic structures that are also observed in fresh plant sources (Mann *et al* 2012). The spring freshet DOC can be described as a 'fresh–contemporary' source, whereas ice wedge–Yedoma DOC appears to be better categorized as a 'fresh–old' source. The 'fresh–contemporary' OC pool is characterized by a high content of aromatic compounds, whereas the 'fresh–old' Yedoma OC pool is characterized by a high content of low-molecular weight compounds, yet both pools appear to be highly biolabile. Structural and compositional differences are the foundation for this apparent contradiction, contributing to the growing evidence (Hood *et al* 2009, Caraco *et al* 2010) for a shift in the prevailing paradigm that old OC is recalcitrant.

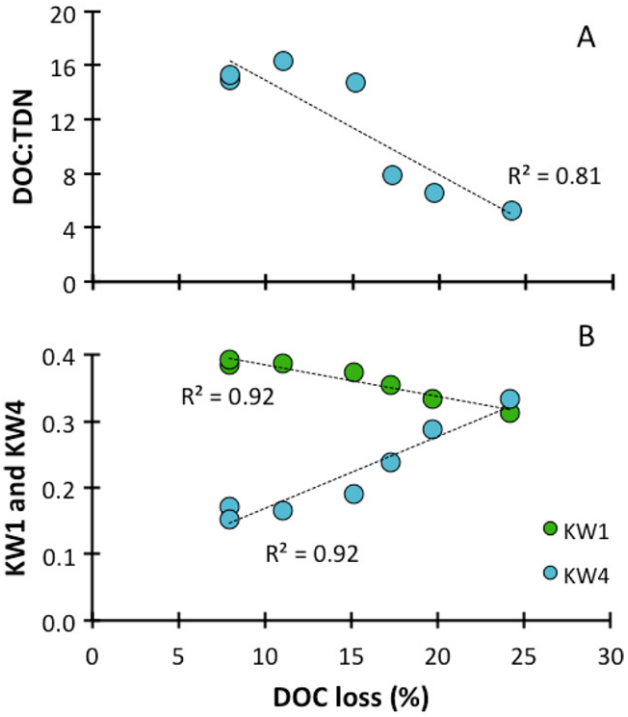

Figure 5. Dissolved organic carbon loss at $T = 11$ (DOC; in %) of all leached Yedoma incubations against (a) DOC:TDN (total dissolved nitrogen), and (b) fraction of total fluorescence of components KW1 and KW4 (KW; 'Kolyma Watershed') derived from PARAFAC analyses on excitation–emission matrices (EEMS). The PARAFAC components are described in table 2.

3.5. Implication of the results

As ice wedges are an integral part of Yedoma, the thaw of Yedoma deposits is inherently coupled to thaw of associated ice wedges. Previous studies that have tested the decomposability of Yedoma deposits have either performed incubations with Yedoma soil (e.g. Dutta *et al* 2006), or have measured *in situ* soil respiration (Zimov *et al* 2006b, Khvorostyanov *et al* 2008b). In both cases, a representative amount of ice wedge melt water (at least 50% of incubation volume or respiration area) is typically not included in the experiments. Our results suggest that by disregarding the co-metabolizing effect of the release of ice wedge OM, one might underestimate the decomposition rates of Yedoma. Furthermore, this also demonstrates the tight coupling between the carbon and the hydrological cycle (e.g. Battin *et al* 2009) and the need to include the aquatic pathway to obtain a complete picture of carbon loss from permafrost.

4. Conclusions

Yedoma is a particularly old type of permafrost covering large portions of northeast Siberia. It contains nearly a third of all the OC globally stored in permafrost, and is characterized by the presence of massive syngenetic ice wedges comprising ~50% of the total volume. As temperatures rise, melt of ice wedges physically destabilizes complete Yedoma profiles

causing massive and irreversible bank collapse, enabling mineralization of OC (Vonk *et al* 2012).

We show here that the presence of low-molecular weight compounds in combination with a low phenolic content in the OM of ice wedges provide a readily available substrate that promotes degradation of Yedoma OC, presumably through co-metabolism. The composition of ice wedge-engrained OM and the physical vulnerability of ice wedges (i.e. profile collapse upon melt) in Yedoma underline the uniqueness of this type of permafrost. Together with the proposed mechanism of self-sustaining decomposition of Yedoma (Khvorostyanov *et al* 2008a), where the production of heat from decomposition continues to thaw frozen soils, this renders a much stronger potential for a positive feedback mechanism to climate warming than other forms of non-ice wedge permafrost.

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