LETTER

Permafrost-derived dissolved organic matter composition varies across permafrost end-members in the western Canadian Arctic

Erin N MacDonald1,4, Suzanne E Tank1, Steven V Kokelj, Duane G Froese and Ryan H S Hutchins1,5

1 Department of Biological Sciences, University of Alberta, Edmonton, Canada
2 Northwest Territories Geological Survey, Government of Northwest Territories, Yellowknife, Canada
3 Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada
4 Current address: Woodwell Climate Research Center, Falmouth, Massachusetts, United States
5 Current address: Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Canada

E-mail: enmacdon@ualberta.ca

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Abstract

Organic matter, upon dissolution into the aqueous state as dissolved organic matter (DOM), can undergo mineralization by microbes. There has been increasing effort to characterize DOM released from thawing permafrost because it may perpetuate a permafrost carbon feedback. Permafrost-derived DOM often has a composition that can be highly susceptible to mineralization by microbes, but most studies to date that characterize permafrost-derived DOM have been limited to select regions, and tend to focus on a single type of permafrost (sometimes unspecified) that reflects a particular deposit type. Importantly, diversity in the nature of the deposit, formation of permafrost, and thaw modification processes leads to spatial and stratigraphic variability in its properties, but our understanding of variation in the composition of DOM derived from differing permafrost types (end-members) is poor. Here, we used ultrahigh-resolution mass spectrometry to characterize DOM composition derived from a series of permafrost end-member types that are commonly found within the thaw-vulnerable western Canadian Arctic, including: tills (glacially deposited), diamicton (thawed and remobilized material of mixed origin), lacustrine (lake basin sediments into which permafrost has aggraded), peat (partially decomposed organic material), and Yedoma (syngenetic silty loess) deposits. We identified marked variation in DOM composition among permafrost end-member types. Tills were compositionally dissimilar to all other permafrost end-members. Compounds unique to Yedoma were predominantly aliphatic, while compounds unique to peat, lacustrine, and diamicton spanned saturation and oxygenation gradients. All permafrost leachates were generally higher in aliphatics, lower in aromatics, and less oxygenated than active layer leachates. Compositional differences appear to reflect variation in permafrost parent materials, and particularly strong effects from past modification processes while in the unfrozen or thawed state. Constraining DOM composition and assessing its stratigraphic variability will become more pressing as the spatial and stratigraphic extent of thaw increases with future warming.

1. Introduction

There has been increasing effort to characterize organic matter that may be released from permafrost, since decomposition of the large stocks of carbon stored in permafrost soils may perpetuate a permafrost carbon feedback [1, 2]. Decomposition of organic matter can occur via different mechanistic pathways, and upon dissolution into the aqueous state as dissolved organic matter (DOM), it can undergo mineralization by microbial organisms (biodegradation) [3]. DOM released from permafrost has been shown to be highly susceptible to biodegradation, and is therefore generally considered to be biolabile [4–8]. The susceptibility of DOM to biodegradation is strongly related to its composition [9], but characterizing the complex, heterogeneous mixture that comprises the bulk DOM pool requires highly...
detailed techniques, such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) [10, 11].

There has been a surge in studies utilizing FT-ICR MS to characterize DOM composition over the past decade, which has provided insight into DOM composition in peatlands [12], fluvial systems [13], and lakes [14] affected by permafrost thaw. To assess DOM that is directly available to be leached from permafrost soils, the water-extractable fraction of organic matter (WEOM) has been employed to assess the composition and biolability of permafrost in Alaska [8, 15, 16] and China [17]. These studies have tended to conclude that DOM derived from permafrost soils is comprised of highly saturated, aliphatic compounds (e.g. lipids, proteins and carbohydrates), which tend to be more biolabile than less saturated (e.g. lignins and tannins), or aromatic (e.g. phenolics or combustion-derived black carbon) compounds [12, 17, 18]. Importantly, most studies to date that examine DOM composition have compared permafrost-derived DOM extracts to those from the active layer (e.g. [15–17]), or have focused on a single type of permafrost ‘end-member’ (e.g. Yedoma deposit in [8]), but have not yet accounted for how variation in deposit type, past modification, or history of permafrost formation may influence DOM composition.

In this study, the term ‘end-member’ refers to seasonally frozen sediments as active layer, or differing perennially frozen sediments (i.e. permafrost) that formed under varying geologic, geomorphic, climate, and ecosystem histories. Differentiating permafrost into end-member types enables consideration of differences in the nature of the deposit, history of formation, and modification processes, which can vary significantly across regional (e.g. outside of vs. within past glacial limits), local (e.g. locations of organic matter accumulation), and stratigraphic (e.g. depth or stratigraphic position) scales. In addition to differing modes of permafrost formation, such as through syngenetic (deposits are incorporated through upward aggradation of the permafrost and sediments) or epigenetic (downward aggradation of permafrost into previously deposited material) [19] processes, thaw-driven modification can also vary substantially based on changing environmental conditions over time. A detailed description of the permafrost end-members is provided below in section 1.2 (study region description), but four contrasting examples are highlighted briefly: (a) glacial-origin unconsolidated deposits (tills) [20, 21] that thaw can be reworked to form diamicton, which may induce geochemical alteration and initiate the onset of soil formation [22, 23]; (b) thermokarst lake development creates thermal disturbances that thaw underlying permafrost, and the sediments can persist in an unfrozen state for long periods of time (talik), then following the drainage of thermokarst lakes, permafrost aggrades into exposed lake bottom sediments (lacustrine) [24] that initially include organic matter of both the parent materials (terrestrial) and those that developed in the aquatic environment (e.g. algal) [24]; (c) flat, poorly-drained terrestrial environments can facilitate peat formation, which then transitions into a frozen state through syngenetic aggradation of permafrost [24–27]; (d) permafrost will incorporate past vegetation of different types, such as the steppe-tundra associated with Yedoma deposits, in which low molecular weight organic acids can accumulate from anaerobic fermentation over long time scales [6]. This diversity of parent materials, formation, and modification highlights the need to consider how DOM derived from differing permafrost end-members may vary in its composition, since differences in composition could tie to differences in biolability, thus affecting the amount of carbon that may be mineralized and released to the atmosphere [1, 2].

To examine if spatial and stratigraphic variation leads to differences in extractable DOM composition, we sampled diverse end-member types from a broad latitudinal and permafrost gradient across the western Canadian Arctic. We obtained samples from sites with contrasting geomorphic, climate, and ecosystem histories. A majority of sites are from previously glaciated landscapes within the continuous permafrost zone that span the treeline transition in the Northwest Territories (NT) [27]. This region is a dynamic depositional environment, where variation in Holocene climate and post-glacial terrain modification have produced a high degree of landscape heterogeneity suggesting variable sensitivities to impacts from climate change [28, 29]. To explore how variation in permafrost end-member types compares to variation across different landscapes, we also collected near-surface soil samples from hillslips, peatlands, and riparian zones. Additionally, a small number of samples were collected from the extensive-discontinuous permafrost zone in the unglaciated region of central Yukon, which is characterized by substantial aggradation of loessial silts (i.e. Yedoma) [30].

Here, we assess (a) how DOM leachate composition varies across permafrost end-members that have contrasting formational history and have been subject to varying degrees of past modification, and (b) how contemporary active layer samples from multiple terrain types compare to variation among permafrost end-members. We used ultrahigh-resolution mass spectrometry to characterize DOM composition for the WEOM fraction leached from diverse permafrost end-members, including tills, diamicton, lacustrine, peat, and Yedoma deposits, as well as from contemporary active layer samples from multiple landscape types (peatland, riparian and hilltop). We hypothesized that permafrost end-members that have more recent soil formation (diamicton, peat)
will be characterized by WEOM leachates that are less saturated (lower proportion of aliphatic compounds) than those where permafrost deposits are older (Yedoma), have not undergone processes of soil formation (till), or include some aquatic-origin organic matter compounds incorporated into frozen deposits (lacustrine). We also hypothesized that (2) active layer samples will reflect contemporary soil formation and thus will contain fewer saturated compounds, but more oxygenated compounds, relative to permafrost leachates.

1.1. Study region description

The broad study area spans ca. six degrees of latitude in the western Canadian Arctic, from the northern NT to the Klondike region in central Yukon. Sites in the NT are in a previously glaciated terrain within the zone of continuous permafrost spanning the forest to tundra transition zone (south to north) [27, 29]. As a result, material in this region has a glacial origin, while post-glacial modification by thaw and ecological succession contribute to permafrost variability. This region is divided into two physiographic subdivisions. The southern sites (BH1–6; figure 1; supplementary figure 1 (available online at stacks.iop.org/ERL/16/024036/mmedia) are located in the Anderson Plains, which is characterized by gently sloping topography with some basins and valleys, where poor drainage can facilitate formation of peatlands [25, 31]. The northern sites (BH7–10; figure 1; supplementary figure 1) are in the Tuktoyaktuk Coastlands, which is characterized by rolling hummocky topography with intervening valleys [25] and abundant depressions where lakes form [32].

Glacial legacy and post-glacial landscape development have strongly shaped the NT region. Diverse depositional environments together with variation in Holocene climate and thaw-driven modification have produced multiple permafrost end-member types throughout this region. The Laurentide Ice Sheet glaciated this area during the late Wisconsinan [33], depositing abundant till often derived from carbonate- and sulfide-rich shale bedrock [20, 21]. At depth, tills in this region have likely remained frozen since deposition, whereas near-surface deposits thawed during a warming period in the early Holocene, and were reworked as diamicton (we distinguish diamicton from tills when it has undergone some degree of thaw and modification) before re-incorporation into permafrost during a subsequent cooling period [22]. Driven by the transition from warmer to cooler temperatures in the Holocene, a similar pattern of processing and freezing affected other types of soils and sediments. Warming enhanced plant productivity and increased production of organic matter in the early Holocene [25], and in areas with poor drainage, saturated soils led to incomplete decomposition, allowing continued accumulation of peat which was sequestered by an upward aggrading permafrost table. During warm or wet conditions, thaw lakes commonly formed [32] resulting in the accumulation of lacustrine sediments, which typically contain a mixture of terrigenous (allochthonous) and within-lake (autochthonous) organic matter [24]. Thermal disturbance of lakes results in talik formation, and thus the accumulated lacustrine sediments and underlying materials would have been completely thawed for a significant amount of time. Drainage or drying of lake basins is associated with gradual peat accumulation and concurrent upward aggradation of the permafrost table. In addition to the permafrost end-member types described here, we also sampled contemporary active layer soils from multiple landscapes (peatland, riparian and hilltop) to understand how landscape variation in surficial soils compares to that between our permafrost end-members.

In contrast to sites in the NT study area, the Klondike region of the Yukon is an unglaciated area within the extensive-discontinuous permafrost zone (KL; figure 1; supplementary figure 1) [30]. Because
it was too dry to support extensive glaciation, loessal sediments and syngenetic permafrost aggraded during the late Wisconsinan cold stage [30, 34]. In addition to aggrading clastic sediments, a variety of ground ice bodies formed, creating ice-rich sygenetic permafrost, locally known as ‘muck’ (terminology varies by country, and is also described as ‘ice complex’ or ‘Yedoma’ in the Russian literature) [35, 36]. While this region is characterized by substantial aggradation of loessal silts during the last glacial period, variation in climate through the Pleistocene caused marked shifts in vegetation, productivity, and the rapidity of permafrost aggradation, and thus also the organic matter content of these Yedoma soils [37]. Klondike Yedoma has been shown to range from relatively organic-rich sediments (∼5.2% carbon) associated with spruce and shrub macrofossils representative of a warmer and wetter environment (ca. 50 000–36 000 calibrated years before present; cal ybp), to organic-poor grey silts (∼1.5% carbon) that are associated with graminoids and reduced shrub vegetation, representative of a colder, drier period of steppe-tundra (ca. 27 000–13 150 cal ybp) [38]. Samples from the Klondike region provide the opportunity to compare Yedoma permafrost from western Canada to Yedoma from other regions that have been previously characterized (e.g. [13]).

2. Methods

2.1. Sample collection

To better understand the importance of variation in geomorphic and ecological history, we selected a series of end-members that represent distinct formation and modification processes. Till, diamicton, peat, lacustrine, and active layer samples were each obtained from varying depths within cores collected from the NT region, while Yedoma was collected from the Klondike region. We collected bulk active layer soil (which were thawed at time of sample collection) and permafrost samples (which were frozen at time of sample collection) from clusters of hilltops, riparian, and peatland sites across a latitudinal gradient through the forest-tundra transition zone (figure 1). Borehole samples below 2 m (2–15 m depths; table 1) were collected in February 2017 using a LECO corer or an auger with a diamond tooth coring bit, as part of a larger geotechnical program to characterize permafrost conditions along the Inuvik–Tuktoyaktuk Highway [38]. Samples from above 2 m (0.2–2 m depths; table 1) were collected from the same sites in July 2018, using either a gas or electric drill with a diamond tooth coring bit. Samples from the Mint Gulch site in the Klondike region were collected horizontally from a mining exposure using a gas drill with a diamond tooth coring bit, from Yedoma deposits approximately 6–7 m below the surface, dating between ca. 16 100 and 13 530 cal ybp [39]. All permafrost samples were transported from the field to the laboratory in a frozen state, then were stored in a dark freezer (−20 °C) until processing.

2.2. Leaching and processing procedure

To remove contamination, the surface (~2 mm) of all permafrost samples was scraped clean using a sterile stainless steel razor blade. A hand tooth saw was then used to isolate the target end-member depth, and a chisel and hammer were used to separate the sub-sample. Subsamples were kept frozen (~−20 °C) in the dark until lyophilization (freeze-drying). Large rocks and debris were removed by hand following lyophilization (supplementary figure 2), then material was homogenized with a natural agate mortar and pestle. Approximately 4 g of homogenized material was placed into pre-cleaned (acid-washed, MilliQ rinsed, then combusted at 475 °C for 4 h) glass 50 ml centrifuge tubes. Sample tubes were sealed with polytetrafluoroethylene (PTFE) -lined caps and stored overnight in a dark fridge (4 °C) until leaching.

To characterize the organic matter relevant for the soil–water interface, we chose to use MilliQ water as the solvent to capture the WEOM fraction (following e.g. [5, 6, 8, 15, 40]). We added 40 ml of MilliQ (1:10 dried soil weight to water volume), shook the samples in the dark for 2 h, centrifuged at 1200 g for 10 min, then collected the supernatant (mean volume was ~37 ml) using a pre-cleaned (acid-washed, MilliQ rinsed, then combusted at 475 °C for 4 h) glass pipette [41]. Leaching with MilliQ was repeated four times to collect a total mean supernatant volume of ~150 ml. The WEOM supernatant was filtered through 0.45 µm polyethersulfone (PES) syringe filters, then the filtrate was collected into pre-cleaned glass beakers (acid-washed, MilliQ rinsed, then combusted at 475 °C for 4 h) and stored in a dark fridge (4 °C) until sample analysis, which was completed within two weeks of leaching. We completed a sequential extraction on the remaining sediment using methanol and chloroform [41, 42], and used the methanol fraction for further analysis since it is able to capture a different range of compounds than the WEOM fraction [41]. We briefly compare the relative abundance of compound classes when using these different solvents (supplementary figure 3), but focus on the WEOM fraction for most of our analyses.

2.3. Ultrahigh-resolution mass spectrometry and ancillary chemical analyses

Following common methodology, the homogenized leachates were analyzed for dissolved organic carbon (DOC) concentration (detailed technique is described in the supplement), which was used to determine the volume of sample (ranging from 0.7 to 743 ml; mean 79.8 ml) to be passed through PPL cartridges (assuming 65% extraction efficiency [11]) to reach a final target mass of 100 µg carbon (C). WEOM leachates were acidified with trace metal grade hydrochloric acid to pH 2, then passed through
Table 1. Coring sites and their associated surficial landscape type indicating end-member sample origin, where listed depths (m) denote mid-depth of the subsample. The compounds refer to those identified using FT-ICR MS, where unique compounds are those that occur only in the specified end-member. Coordinates are given in decimal degrees (DD).

| Site | Latitude (DD)  | Longitude (DD) | Landscape | Active layer (m) | Peat (m) | Till (m) | Lacustrine (m) | Diamicton (m) | Yedoma (m) |
|------|----------------|----------------|-----------|------------------|---------|----------|---------------|--------------|-----------|
| BH1  | 68.53876       | 133.772-98     | Peatland  | 0.32             | 0.82    | —        | —             | —            | —         |
| BH2  | 68.53832       | 133.762-82     | Hilltop   | 0.32             | —       | 11.25    | —             | —            | —         |
| BH3  | 68.53415       | 133.764-51     | Riparian  | 0.32             | —       | —        | —             | —            | —         |
| BH4  | 68.74937       | 133.541-53     | Peatland  | —                | 3.7     | —        | 5.9           | —            | —         |
| BH5  | 68.75214       | 133.541-18     | Hilltop   | —                | —       | 14.25    | —             | —            | —         |
| BH6  | 68.75916       | 133.545-20     | Riparian  | —                | —       | —        | —             | —            | 1.12      |
| BH7  | 69.01883       | 133.275-33     | Hilltop   | 0.32             | —       | 4.75     | —             | —            | —         |
| BH8  | 69.01257       | 133.270-39     | Peatland  | 0.32             | 1.52    | —        | 11.25         | —            | —         |
| BH9  | 69.01289       | 133.306-49     | Riparian  | 0.32             | —       | 9.25     | —             | —            | —         |
| BH10 | 69.27051       | 132.934-57     | Hilltop   | —                | —       | —        | —             | 9.5          | —         |
| KL   | 63.93776       | 138.8897       | Yedoma     | —                | —       | —        | —             | —            | 6.0, 7.0  |

Total compounds mean (SD) 2747 (484) 3573 (325) 2499 (1010) 4155 (48.7) 1961 (1310) 3449 (18.3)
Unique compounds mean (SD) 136 (14) 14 (3) 151 (92) 11 (2) 3.5 (3) 38 (40)
3 ml 100 mg Bond Elut PPL cartridges (Agilent Technologies) [11]. The solid-phase concentrated samples were eluted with 1 ml methanol into pre-cleaned 2 ml glass amber vials, then were stored in a dark freezer (−20 °C) until they were characterized using the FT-ICR MS. We used a 9.4T Bruker Apex-Qe mass spectrometer (Bruker Daltonics) with an Apollo II electrospray ionization source in negative mode. Samples were injected at a flow rate of 120 μl h⁻¹ to acquire 300 spectra scans. We assigned formulae based on quality-inspected masses, following published protocols with the ICBM-OCEAN tool [43, 44]. The formulae were used to calculate a corresponding oxygen to carbon ratio (O/C), hydrogen to carbon ratio (H/C), and modified aromatic index (AI) [10]. The O/C, H/C, and AI were then used to sort the formulae into five broad compound classes: aliphatic (H/C ⩾ 1.5), low-O unsaturated (H/C < 1.5, O/C ⩽ 0.5, AI < 0.5), high-O unsaturated (H/C < 1.5, O/C > 0.5, AI < 0.5), aromatic (0.5 < AI < 0.67), or condensed aromatic (AI ⩾ 0.67; supplementary figure 4) [45]. For each sample, formulae were expressed in relative abundance using sum-normalized signal intensity. We calculated the proportion of compound classes within sample types, which broadly indicates the relative abundance of compounds that are present in DOM. Briefly, the aliphatic class includes lipids, proteins and carbohydrates, the unsaturated class includes lignins and tannins, the aromatic class includes phenolics, and the condensed aromatic class includes combustion-derived black carbon [12, 17, 18].

WEOM leachate subsamples were also collected for analysis of soil organic matter (SOM) concentration, DOM composition using absorbance (i.e. the slope ratio; Sₘ) [46], dissolved trace metals, and total dissolved phosphorus (TDP). Analyses followed standard techniques as outlined in the supplementary material.

2.4. Statistical analyses
All statistical analyses were completed using R version 3.6.3, including packages ggplot2 [47], dplyr [48], and tidyr [49]. Linear regression was used to determine relationships between SOM and leachate DOC, TDP, and Sₘ. We used vegan [50] to determine Bray-Curtis dissimilarity of FT-ICR MS assigned formulae (normalized intensities), visualized using non-metric multidimensional scaling (NMDS). This was coupled with Spearman’s rank correlation to determine which formulae were most strongly associated with the first NMDS axis (MDS1).

3. Results

3.1. Bulk leachate properties
Across all end-member types, DOC and TDP were positively correlated to SOM (p < 0.001, R² = 0.506 and p = 0.004, R² = 0.532, respectively), which generally declined with depth. Both DOC and TDP were high for peat and active layer samples, but low for till, lacustrine, and Yedoma samples (figure 2). Conversely, Sₘ (a DOM compositional metric that declines with increasing molecular weight) was negatively correlated to SOM (p = 0.002, R² = 0.591) and increased with depth, suggesting a transition from higher molecular weight compounds in active layer sources and permafrost peat samples towards lower molecular weight compounds in other leachate types [46]. While trace metal concentrations showed no clear trends with depth, there were differences among end-member types (see also [23]). Lacustrine leachates had markedly higher concentrations of magnesium, calcium, and strontium than all other end-members (supplementary figure 5). Sodium was higher in diamicton and Yedoma leachates, but slightly lower in till samples. Peat leachates were distinguished by higher zinc and arsenic concentrations than all other end-members.

3.2. FT-ICR MS reveals differences among permafrost end-member types
Across all samples, FT-ICR MS detected 6450 unambiguously assigned molecular formulae (henceforth referred to as compounds). The number of these compounds detected within end-member types ranged substantially, from 4155 ± 48.7 (mean ± standard deviation; n = 2) in lacustrine leachates to 1961 ± 1310 (n = 2) in diamicton leachates (table 1). While active layer leachates were clearly distinct in their DOM composition compared to those from permafrost, we also found substantial differences in compound class proportions among permafrost end-member types (figure 3). Active layer leachates had a higher proportion of both aromatic and condensed aromatic compounds, and a lower proportion of aliphatic compounds, compared to all permafrost end-members. Within the permafrost end-members, the proportion of aliphatic compounds generally increased, while aromatics decreased, moving from diamicton, to lacustrine, to Yedoma, to peat, to till leachates. Diamicton and till leachates had relatively high proportions of low-oxygen unsaturated compounds, while till also had relatively low proportions of high-oxygen unsaturated compounds. Notably, these trends changed when using chloroform-methanol (instead of MilliQ) as the solvent (supplementary figure 3). In this case, methanol fractions captured a higher proportion of aliphatics in all but till leachates, and slightly reduced overall proportions of aromatic and condensed aromatic classes, compared to WEOM leachates. Methanol extractions had fewer high-oxygen unsaturated compounds, but more low-oxygen unsaturated compounds, and showed less variation across active layer and permafrost end-members relative to WEOM leachates.
Figure 2. Soil and DOM characteristics with increasing depth from soil surface showing (a) soil organic matter content; (b) dissolved organic carbon concentration; (c) total dissolved phosphorus concentration; and (d) absorbance slope ratio, a metric of DOM composition that is inversely related to molecular weight. Sample sizes are $n = 19$ for both (a) and (b); $n = 12$ for both (c) and (d) due to some missing Yedoma, till and diamicton samples.

Figure 3. Boxplots to illustrate the proportional abundance (normalized to total intensity) of compounds identified by FT-ICR MS, sorted into broad class groups. Briefly, the aliphatic class includes lipids, proteins and carbohydrates, the unsaturated class includes lignins and tannins, the aromatic class includes phenolics, and the condensed aromatic class includes combustion-derived black carbon [12, 17, 18]. Boxes show median, 25th, and 75th percentiles, whiskers span 1.5 times the interquartile range, and points are outliers.
Figure 4. Leachate DOM composition displayed using (a) non-metric multidimensional scaling (k = 2, stress = 0.102) showing Bray–Curtis dissimilarity of the relative abundance of compounds (normalized to total signal intensity) detected by FT-ICR MS. Samples that are further apart are less compositionally similar. Panel (b) shows a van Krevelen plot of oxygen:carbon (O/C) and hydrogen:carbon (H/C) ratios for compounds detected by FT-ICR MS, where rho ($\rho$) is the correlation between individual compounds and MDS1 (pink points are associated with more negative MDS1 values, while blue points are associated with more positive MDS1 values).

The NMDS reinforced the findings of the compound class assessment, and further illustrated that active layer leachates were compositionally similar to each other regardless of landscape type. Similarly, permafrost leachates showed little to no variation among surficial landscape types within end-members, but demonstrated a clear demarcation among end-member types (figure 4(a)). Along MDS1, diamicton leachates were most compositionally similar to active layer leachates, and were relatively similar to peat, lacustrine, and Yedoma leachates. Till leachates were most dissimilar from other end-member types, and also display more compositional variation within this end-member type. There was muted divergence along MDS2, which separated single hilltop diamicton and till samples from all other leachates. A van Krevelen plot of the correlation between individual compounds and MDS1 demonstrates that leachates positively associated with MDS1 (i.e. tills) were predominantly associated with low-oxygen compounds, mostly in the unsaturated classes (figure 4(b)). In contrast, leachates negatively associated with MDS1 (i.e. active layer) were predominantly associated with moderate-oxygen unsaturated and aromatic classes. Leachates located more centrally along MDS1 (i.e. peat, lacustrine, Yedoma, diamicton) displayed a range of compounds across oxygenation, saturation, and compound classes.

To further explore differences among end-member types, we identified compounds that were common to all or unique to one end-member type. While $\sim$31% of the compounds detected were present in all six end-member types, $\sim$12% were found to be unique to one end-member type alone (table 1; figure 5). Compounds unique to active layer leachates covered a broad range of classes, but were mostly high-oxygen aromatics and low-oxygen condensed aromatics (figure 5(a)). Diamicton, lacustrine, and peat leachates all had fewer unique compounds that spanned the oxygenation gradient, but were primarily aliphatic, with some unsaturated and aromatic compounds (figure 5(b)). Till leachates had unique compounds that were predominantly low-oxygen and spanned a range of saturation (H/C) from aromatic to aliphatic (figure 5(c)). Yedoma contained a moderate amount of unique compounds in the low- to moderate-oxygen aliphatic class, with sparse compounds in aromatics and high-oxygen aliphatic classes (figure 5(d)).

4. Discussion

Detailed DOM compositional analyses revealed differences among permafrost end-members types, and while some results were similar to our hypothesized expectations, other results were surprising. We hypothesized that permafrost end-members that have more recent soil formation (diamicton, peat) would be characterized by WEOM leachates that are less saturated (lower proportion of aliphatic compounds) than those where permafrost deposits are older (Yedoma), have not undergone processes of soil formation (till), or include some aquatic-origin organic matter incorporated into frozen deposits (lacustrine). Diamicton and peat results were generally consistent with our expectations, showing lower proportions of aliphatic compounds. In contrast, we also observed similarly low proportions of aliphatic compounds in
lacustrine leachates, and a relatively lower proportion of aliphatic compounds in Klondike Yedoma, when compared to till leachates. We explore how differences in past modification, sample regions, and climate may contribute to these observed trends in the sections below. As hypothesized, and similar to previous studies [8, 13, 15, 17, 51], active layer leachates had fewer saturated (high H/C) compounds and were more oxygenated (high O/C) than permafrost end-members, while also showing compositional similarity across a ~100 km latitudinal gradient that encompassed divergent landscape types (peatland, riparian, and hilltop). While leachable DOC, TDP, molecular weight, and proportion of aromatic compounds generally declined through stratigraphic profiles, there was marked variation observed in these constituents, as well as in trace metals, which may reflect differences in permafrost formation processes [46].

4.1. Permafrost end-members display unique DOM compositions
While compounds unique to the active layer spanned oxygenation and saturation, compounds unique to the permafrost end-members were predominantly low- and moderate-oxygenated compounds, with sparse highly-oxygenated compounds in the aliphatic class. We observed an increasing proportion of aliphatic compounds, coupled with decreasing aromatic compounds, moving from diamicton, to lacustrine, to Yedoma, to peat, and finally, to till leachates. Although some of these end-members were collected from the same permafrost core (table 1), the formation and modification processes of deposits differed greatly. Unmodified tills were substantially dissimilar from all other end-member types, and also contained the highest proportions of aliphatic compounds. Since tills were sampled at depths greater than 10 m, it is unlikely they had been affected by thaw [22, 23]. In contrast, diamicton, lacustrine, and peat deposits were either unfrozen for long periods of time or were previously thawed and modified before incorporation into permafrost. These end-members demonstrated compositional similarity not only to each other, but were also more similar to active layer leachates than they were to tills. This suggests that modification while in the unfrozen state, whether
prior to freezing or after thawing, may play a key role in shaping DOM composition, and appears to enable compositions that were distinct from both contemporary active layer soils and glacially derived, unmodified till deposits.

The proportion of aliphatic compounds was lower than expected in lacustrine and Yedoma leachates, which were also surprisingly similar to diamicton and peat leachates. While we expected to see some influence from autochthonous sources within lacustrine leachates, this within-lake organic matter can be preferentially mineralized in lakebed sediments, such that residual sediments may reflect accumulation of allochthonous (i.e. terrigenous origin) sources [52]. Peat porewaters have previously demonstrated lower proportions of aliphatic compounds [53] than our results, but can also release protein-rich DOC following experimental thawing [54]. Although Yedoma appeared similar to lacustrine and peat leachates in NMDS space, the unique compounds from Yedoma leachates were well constrained to low oxygen (see also [6]), aliphatic species, while compounds unique to lacustrine and peat have more variation in oxygenation and saturation. The predominance of low oxygen, aliphatic compounds in Yedoma, which were also observed in tills, could reflect sorption processes due to higher mineral content, since less saturated and more oxygenated compounds are preferentially adsorbed to mineral particles [55].

Though the proportion of aliphatic compounds was lower than expected, the detection of unique aliphatic compounds in Yedoma are congruent with studies of Yedoma from other regions of the Arctic [13, 56, 57]. The organic carbon (SOM and extractable DOC) content in our Yedoma samples was comparable to our lacustrine and till samples, with SOM content similar to, to slightly lower than, SOM for Yedoma from the North Slope of Alaska (radiocarbon dated to between 37 000 and 9000 cal ybp) [58]. Interestingly, Klondike Yedoma DOC concentrations were orders of magnitude lower than those reported for Yedoma leachates from Interior Alaska [5, 6, 8] and from streams draining thaw features in Siberia [13, 59]. The differences in DOC concentrations could result from regional variability, or may reflect differences in the age of the material and associated vegetation at the time of permafrost aggradation. The higher DOC reported in other studies has been associated with older material (~134 000–21 000 cal ybp), while our Klondike Yedoma samples are slightly to considerably younger (radiocarbon dates from samples immediately below and above our Yedoma samples range between ca. 16 100 and 13 280 cal ybp; supplementary figure 1). This age range is representative of a cooler, drier period with low, graminoid-dominated plant productivity and reduced incorporation of organic matter prior to a transition to a relatively warmer, wetter period in the late Pleistocene [37]. It is also possible that these temporal differences in climate are interacting with regional differences across a broad spatial scale, creating a range of organic matter content and characteristics for spatially diverse Yedoma deposits, and likely other permafrost materials.

While some permafrost end-member types were more compositionally similar to one another than others, the presence of unique compounds for all end-member types emphasizes the heterogeneity in permafrost carbon biogeochemistry, and its relationship to mode of permafrost formation and past thaw modification processes (see also [60]). Compositional differences among end-member types were independent of latitude (across the ~6° span reported here). These clear compositional differences indicate varying susceptibility to decomposition across permafrost types of differing origin, with subsequent implications for organic carbon fate.

4.2. Linking DOM composition with biolability

Although we did not measure susceptibility to decomposition, other studies have established strong links between DOM composition and biodegradation, providing a basis to assess how the differences that we quantify may affect biolability. The aliphatic class that we demarcate can be further distinguished by the degree of oxygenation, including lipids (low O:C), proteins and peptides (moderate O:C) [12], as well as carbohydrates (high O:C) [13]. Because this class is highly saturated and energy-rich, it is generally preferentially consumed and considered to be the most biolabile class of compounds [16]. The unsaturated class is associated with lignins (moderate O:C), and tannins (high O:C), which are considered to be more recalcitrant [12], although highly-oxygenated unsaturated compounds can also be biolabile under anoxic conditions [8]. Aromatics are associated with phenolic compounds derived from vascular plants, though may also represent microbial biomass, while the more condensed aromatics can include combustion-derived black carbon [17, 18]. Both of these aromatic classes are generally considered to be recalcitrant [15], though this interpretation can vary based on specific experimental conditions (i.e. soil- vs. aquatic-based).

Based on the increased biolability of aliphatic compounds, the relative proportion of compounds in this class can be used to predict potential susceptibility to biodegradation [16]. Relating this to the DOM composition in our samples, till leachates had the highest proportion of aliphatic compounds overall, although the aliphatic class contributed only a small portion of the compounds unique to this end-member. The abundant aliphatic compounds in tills may be a consequence of more mineral-rich particles that facilitate preferential sorption of organic matter [15], potentially coupled with high desorption that allows this aliphatic DOM to be leached with
permafrost biolability (e.g. [63]). This may help to explain the variation in biolability observed here, and how this variation may be linked to the history of formation, and in particular how the material incorporated into permafrost is modified by past processing in the unfrozen or thawed state before incorporation into permafrost. We can qualitatively say that tills have likely undergone some processing prior to syngenetic permafrost aggradation, followed by long-term anaerobic fermentation in the frozen state [6, 34–36]. Future work could investigate distinguishing between drivers of DOM compositional differences, which in addition to formation and modification, could also include comparing rates of productivity and rates of permafrost aggradation, anaerobic fermentation, or mineral sorption and desorption processes [61].

4.3. Implications of key findings

The DOM compositional differences among end-members observed here appear to be strongly influenced by history of formation, and in particular how past processing in the unfrozen or thawed state can modify organic matter which later becomes incorporated into permafrost. These differences have clear implications for biolability, and thus how the substantial DOM that is lost to aquatic flowpaths following permafrost thaw [64] impacts the permafrost carbon feedback, as well as downstream biogeochemical and ecological processes [2]. Our findings serve as a reminder that the WEOM fraction most easily leached to aquatic flow paths is representative of only a portion of the SOM pool (supplementary figure 3). This may help to explain differences between soil-based measurements of permafrost biolability (e.g. [65]) and those that focus on DOM, while also reinforcing the need for a more thorough integration of organic matter characterization across terrestrial-aquatic continua [66]. Most importantly, these results act as a call for other studies to include geologic/geomorphic context and permafrost history as an underpinning to understand the fate of permafrost-origin DOM, and incorporate this variation into projections of future change. Constraining DOM composition, lability, and assessing its stratigraphic variability will become more pressing as the spatial and stratigraphic extent of thaw increases with future warming.

Data availability

The data that support the findings of this study [67] are openly available at the following URL/DOI: [https://doi.org/10.21963/13187].

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Author contributions

The experimental design was developed by EM and ST. Sample collection was completed by SK, DF, and EM. Data analysis was completed by EM and RH. All authors contributed to interpretation of the results and writing the manuscript.

Conflict of interest

The authors declare no competing financial interests.
ORCID iDs
Erin N MacDonald  https://orcid.org/0000-0002-8418-6695
Suzanne E Tank  https://orcid.org/0000-0002-5371-6577
Ryan H S Hutchins  https://orcid.org/0000-0002-1694-9394

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