Preferential export of permafrost-derived organic matter as retrogressive thaw slumping intensifies

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Abstract

Enhanced warming of the Northern high latitudes has intensified thermokarst processes throughout the permafrost zone. Retrogressive thaw slumps (RTS), where thaw-driven erosion caused by ground ice melt creates terrain disturbances extending over tens of hectares, represent particularly dynamic thermokarst features. Biogeochemical transformation of the mobilized substrate may release CO₂ to the atmosphere and impact downstream ecosystems, yet its fate remains unclear. The Peel Plateau in northwestern Canada hosts some of the largest RTS features in the Arctic. Here, thick deposits of Pleistocene-aged glacial tills are overlain by a thinner layer of relatively organic-rich Holocene-aged permafrost that aggraded upward following deeper thaw and soil development during the early Holocene warm period. In this study, we characterize exposed soil layers and the mobilized material by analysing sediment properties and organic matter composition in active layer, Holocene and Pleistocene permafrost, recently thawed debris deposits and fresh deposits of slump outflow from four separate RTS features. We found that organic matter content, radiocarbon age and biomarker concentrations in debris and outflow deposits from all four sites were most similar to permafrost soils, with a lesser influence of the organic-rich active layer. Lipid biomarkers suggested a significant contribution of petrogenic carbon especially in Pleistocene permafrost. Active layer samples contained abundant intrinsically labile macromolecular components (polysaccharides, lignin markers, phenolic and N-containing compounds). All other samples were dominated by degraded organic constituents. Active layer soils, although heterogeneous, also had the highest median grain sizes, whereas debris and runoff deposits consisted of finer mineral grains and were generally more homogeneous, similar to permafrost. We thus infer that both organic matter degradation and hydrodynamic sorting during transport affect the mobilized material. Determining the relative magnitude of these two processes will be crucial to better assess the role of intensifying RTS activity in CO₂ release and ecosystem carbon fluxes.

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1. Introduction

Abrupt thaw caused by enhanced warming has become a widespread phenomenon throughout the northern permafrost zone, causing increased geomorphic disturbances such as thermo-erosional gullies, thermokarst lakes, active layer detachment slides and retrogressive thaw slumps (RTS; e.g. Kokelj and Jorgenson 2013, Nitze et al 2018). Recent studies estimate that up to 20% of the northern permafrost zone may become affected by rapid thaw processes by 2300, leading to disturbance of up to half of the total organic matter stored in permafrost (Olefeldt et al 2016, Turetsky et al 2020). Upon thaw, this large carbon pool is subjected to photochemical and microbial degradation, potentially releasing CO$_2$ to the atmosphere and thus amplifying global warming (e.g. Schuur et al 2015), as well as affecting downstream ecosystems (e.g. Vonk et al 2015). Runoff from RTS features increases stream total organic carbon (OC) yields by orders of magnitude, almost entirely due to increasing particulate OC mobilization (Shakil et al 2020). In contrast, the loads of dissolved OC can decrease in RTS-impacted streams (Littlefair et al 2017, Shakil et al 2020). This pattern of a strong dominance of particulate over dissolved organic matter mobilization can be widespread (Kokelj et al 2020), and stands in contrast to other permafrost environments characterized by a gradual increase in active layer thickness and talik formation (Vonk et al 2015). Rates of CO$_2$ efflux can be disproportionately high in RTS runoff, yet the majority of the eroded particulate organic matter (POM) is transported downstream (Zolkos et al 2019, Kokelj et al 2020), where it may be deposited en-route or eventually exported to the Arctic Ocean (e.g. Wild et al 2019). In the Arctic coastal shelf seas, permafrost-derived material can be further degraded (e.g. Vonk et al 2012, Bröder et al 2018) or buried and sequestered in marine sediments (e.g. Hilton et al 2015).

Sediment properties of mobilized permafrost soils have been shown to play a crucial role in stabilizing organic matter, as close associations with the mineral matrix may protect it from microbial decomposition and additionally shield it from photodegradation (Opfregert 2020, and references therein). Mineral grain sizes furthermore determine downstream fluvial transport behaviour, as larger grains require greater stream velocity to remain in suspension, causing hydrodynamic sorting during aquatic transport (e.g. Tesi et al 2016).

Besides organic matter quantity and its mineral associations, its (chemical) composition may be an additional factor regulating decomposition rates. In permafrost environments, different carbon pools have been shown to be mobilized and transported differently (e.g. lignin phenols as plant debris vs plant-wax lipids associated with mineral surfaces; Feng et al 2013, 2015, Tesi et al 2014, 2016). Furthermore, on shorter timescales (i.e. decadal or less), certain macro-molecular components (e.g. polysaccharides) may inherently be more labile and susceptible to degradation, while others are expected to be chemically more recalcitrant (e.g. condensated aromatic structures such as black carbon) (Sparkes et al 2016, Lehmann et al 2020). Environmental controls together with intrinsic sediment and organic matter properties thus conspire to create a complex interplay between different—currently poorly understood—factors that ultimately regulate the degree to which, and timescales over which thawed permafrost organic matter represents a source of greenhouse gases to the atmosphere.

On the Peel Plateau in northwestern Canada, in addition to rapidly rising temperatures, increases in the frequency and intensity of summer precipitation events are main driving factors for RTS initiation and growth (Kokelj et al 2015, Segal et al 2016). This region, located at the former margin of the Laurentide Ice Sheet (LIS), is prone to thaw-driven mass wasting due to the prevalence of ice-rich permafrost and the fluvially incised terrain (Kokelj et al 2017). RTS features comprise the most prominent form of mass wasting and sediment mobilization in the area, the largest of which can move 1000–10 000 m$^3$ of thawed materials per year downslope (e.g. Van Der Sluijs et al 2018, Kokelj et al 2020), thereby overwhelming the sediment transport capacity of the fluvial network and forming large (on the order of $\sim$100 000 m$^3$) debris tongues in the valley bottom (e.g. Kokelj et al 2013, 2020, Van Der Sluijs et al 2018). RTS headwalls can expose a complex combination of materials reflecting variation in depositional and climate legacy (Lacelle et al 2019). Stratigraphically (a) the deepest layers consist of Pleistocene-aged permafrost associated with glacial tills that were deposited by the advance and retreat of the LIS (e.g. Kokelj et al 2017); (b) above these, a relict-thaw layer (consisting of mineral soils that developed during a particularly warm period in the early Holocene) was incorporated into Holocene-aged permafrost during subsequent regional cooling (Burn 1997, Lacelle et al 2019); (c) on top lies the organic-rich, present-day active layer, sustaining modern and recent vegetation.

The present study investigates the composition and quality of sediment and organic matter mobilized from RTS systems on the Peel Plateau, and draws comparisons with the putative sources described above. We studied active layer soils, Holocene and Pleistocene permafrost, recently thawed materials (debris) located at the base of the headwall, and runoff from slump outflow that was freshly deposited at the edge of the scar zone (i.e. not suspended runoff material, as in e.g. Kokelj et al 2013 or Shakil et al 2020) from four separate RTS features, differing in elevation, age, areal extent and headwall height. In order to assess potential influences
of preferential particle transport on carbon export, composition and degradability, grain size distributions and mineral surface area (SA) properties were analysed. Organic matter composition was characterized on a bulk level in terms of elemental (total nitrogen (TN), OC) and isotopic (13C and 14C) characteristics, as well as on a molecular level based on solvent-extractable (plant-wax lipids), hydrolysable (lignin phenols, cutin acids) and thermally-liberated (via analytical pyrolysis) biomarkers. Together, these methods provide comprehensive insights into the origin and degradation status of specific organic matter pools. When combined with ancillary information on mineral properties, this dataset sheds new light on the likely fate of RTS-mobilized organic matter within the headwater component of the terrestrial-freshwater-ocean continuum, and informs on potential impacts of intensifying RTS activity in a rapidly changing Arctic.

2. Materials and methods

2.1. Study area and sample collection

The Peel Plateau is located in northwestern Canada, stretching along the eastern foothills of the Richardson Mountains with elevations between 750 and 100 masl and an eastward-facing slope (Kokelj et al. 2017). The region was glaciated in the late-Pleistocene, approximately from 18 000 year BP to 15 000 year BP (Lacelle et al. 2013). Advance and retreat of the LIS shaped the plateau and formed an ice-rich hummocky moraine landscape, largely consisting of glacial tills incised by glacial meltwater channels and the modern stream network (Duk-Rodkin and Hughes 1992, Kokelj et al. 2013). Much of this ice-rich, relict permafrost has been preserved (Kokelj et al. 2017), despite a relatively warm and dry early Holocene period that was associated with widespread thermokarst and an increase in the seasonal depth of thaw approaching two meters (Burn 1997). Throughout the middle and late Holocene, the region experienced a gradual cooling, resulting in permafrost aggradation, preserving this relict-thaw layer and the underlying ice-rich Pleistocene till (e.g. Burn 1997, Lacelle et al. 2019). Contemporary active layer depths range between 40 and 100 cm (Lacelle et al. 2019).

Current climatic conditions recorded at Fort McPherson (approximately 40 km from the nearest study site, FM2, figure 1) from 1981 to 2010 report average summer temperatures (June–August) of 13 °C, winter temperatures (December–February) of −26 °C and an average annual precipitation of 298 mm, about half of which falls as snow (Environment Canada 2020). Precipitation is generally greatest in July and August, which accounts for more than a third of the total annual budget (Environment Canada 2020). Mean annual air temperatures in the region have risen rapidly since the 1970s at a rate of approximately 0.77 °C per decade (Burn and Kokelj 2009), along with increases in the frequency and intensity of rain events (Kokelj et al. 2015). These climatic changes, imposed on ice-rich permafrost and sloping terrain, have given rise to the initiation of hundreds of RTS features (e.g. Kokelj et al. 2017, and references therein). Each comprises a steep headwall, where permafrost ground ice is exposed, a gently sloping scar zone and, in some cases, a debris tongue, consisting of thawed material that has been transported downslope (Kokelj et al. 2015). Most RTS features are polycyclic in nature, i.e. they remain active and growing as the headwall retreats for several years before stabilization, during which the scar zone revegetates, and subsequent reactivation and reinitiation of the erosion cycle (e.g. French 2007). The favourable conditions on the Peel Plateau, however, have sustained the development of extremely large ‘mega slumps’ that have been active over decades, with scar zones exceeding 150 000 m2 in area and displacing up to 106 m3 of sediments (Kokelj et al. 2015, 2017, Lacelle et al. 2015).

For this project, we collected material from four separate RTS features along an east to west transect (increasing elevation) that have been the subject of earlier studies (e.g. Kokelj et al. 2013, 2015, Littlefair et al. 2017, Van Der Sluijs et al. 2018, Zolkos et al. 2019, Shakil et al. 2020, Zolkos and Tank 2020), namely FM2, FM3, CB, and SF (see figure 1 and table 1 for exact locations and field photos). This east to west transect also reflects RTS features ordered by decreasing size and age, ranging from the largest and oldest (FM2), with a scar zone area of 48 ha and a maximum headwall height of 25 m, which formed more than 70 years ago (Lacelle et al. 2015), to a relatively recent feature (SF), which is less than five years of age, and extends <1 ha with a maximum headwall height of <6 m (Zolkos and Tank 2019). For each feature, samples were collected from the seasonally thawed active layer, permafrost (Holocene and Pleistocene layers for FM2, see below), freshly thawed debris (collected at the base of the headwall), and slump runoff. To account for the effects of variable discharge and slump runoff, instead of collecting suspended particulate matter, we sampled freshly deposited saturated colluvium from the active thaw slump scar. Samples were collected at the edge of the scar zone, where saturation and surface water (runoff) was derived from ground ice melt. As such, these fresh deposits provide a more integrated signal of the material transported by the stream during variable flow conditions. For simplicity and to distinguish these deposits from the freshly thawed debris collected at the foot of the headwall, we will term these samples ‘runoff deposits’. All unfrozen samples (active layer soils, debris and runoff deposits) were collected with a stainless-steel spoon, for permafrost samples we used a chisel. Total sample weights ranged between about 100–500 g. All samples were gathered in summer 2017 (mid-July to
mid-August), frozen within a few hours of collection, and kept frozen until analysis.

2.2. Sediment physical properties

2.2.1. Mineral SA

Associations with mineral surfaces are considered to promote organic matter stabilization and hence buffer the release of carbon to the atmosphere. Mineral SA analyses were determined by gas adsorption following the 5-point Brunauer-Emmett-Teller (BET) method (Brunauer et al 1938) on a Nova 4200e Surface Area Analyser (Quantachrome) at the Department of Earth Sciences at the Vrije Universiteit Amsterdam (The Netherlands). Freeze-dried subsamples of about 1 g were combusted at 350 °C for 12 h to remove organic material (with slow heating and cooling to avoid incomplete combustion), and samples were degassed under vacuum.

![Map of the study area on the Peel Plateau, north-western Canada. Locations of the RTS features that were sampled for this study are marked by red filled circles and field photographs of their respective headwalls are shown in the inserts. Other active RTS features are shown on the map as grey dots and the boundaries of the Stoney Creek and Vittrekwa River watersheds are delineated in blue. Samples were collected of the seasonally thawed active layer, Holocene and Pleistocene permafrost, freshly thawed debris, and slump runoff as exemplified in the pictures of the FM3 headwall and overview, adapted from Zolkos et al (2018). Basemap from Esri ArcGIS Online. Geospatial data for Active RTS (other) from (Segal et al 2016). Zolkos et al (2018) John Wiley & Sons. ©2018. American Geophysical Union. All Rights Reserved.](image)

![Table 1. Locations of the four sampled RTS features and their characteristics.](table)

| RTS feature | Latitude (°N) | Longitude (°E) | Elevation (masl) | Approx.active layer depth (cm) | Max. headwall height (m) | Scar zone (ha) | Approx. age (year) |
|-------------|---------------|----------------|------------------|-------------------------------|--------------------------|----------------|--------------------|
| FM2         | 67.257        | −135.236       | 338              | 23                           | 24.2<sup>b</sup>        | 48<sup>b</sup>  | >70<sup>b</sup>     |
| FM3         | 67.253        | −135.273       | 391              | 65                           | 9.8<sup>b</sup>         | 10<sup>b</sup>  | <25<sup>b</sup>     |
| CB          | 67.182        | −135.732       | 576              | 46                           | 5.8<sup>c</sup>         | 3.4<sup>c</sup> | <15<sup>c</sup>     |
| SF          | 67.183        | −135.811       | 720              | 56                           | 7.6<sup>b</sup>         | <1<sup>b</sup>  | <5<sup>b</sup>      |

<sup>a</sup> Active Layer depth measurements for all sites made on the day of sample collection, using a probe near the thaw slump headwall; measured at one point only and therefore approximate.

<sup>b</sup> Data from Zolkos and Tank (2019).

<sup>c</sup> Data from Kokelj et al (2020).
(300 °C for 3 h) immediately prior to analysis. Reference materials BAM-PM-102 (Lot No. 733, Bundesanstalt für Materialforschung und -prüfung) and SARM (Silica Alumina, Cat. No. 2009, Quantachrome) with specific SAs of 5.41 ± 0.04 m² g⁻¹ and 27.46 ± 3.6 m² g⁻¹, respectively, were analysed regularly to monitor instrument performance. Instrumental measurement uncertainty is 0.1 m² g⁻¹.

2.2.2. Grain size distributions

Mineral grain size is an important parameter determining erosion and hydrodynamic sorting upon transport. Grain size distributions were analysed by laser diffraction using a Helos/KR laser diffraction particle size and particle size distribution analyser (Sympatec) with a Quixel dispersing system (Sympatec) at the Department of Earth Sciences at the Vrije Universiteit Amsterdam (The Netherlands). Freeze-dried subsamples of about 1 g were heated to boil with 5 ml of H₂O₂ in de-ionized water to remove fine organic matter, following the method described in Konert and Vandenbergh (1997). An additional 5 ml of H₂O₂ were used if oxidation was incomplete. If larger plant debris remained, samples were filtered and repeatedly treated with H₂O₂. For CaCO₃ removal, samples were subsequently acidified with hydrochloric acid (HCl) and prior to analysis, samples were dispersed in sodium phosphate (Na₅P₃O₁₀ 10H₂O) and filtered again (1 mm mesh). Results are reported as % clay, % silt and % sand, referring to grain size classes <4 µm, 4–63 µm and 63–1000 µm, respectively. Furthermore, the median grainsize D₅₀ is reported (µm) together with the sorting parameter (inclusive graphic standard deviation, Wentworth φ-scale; Wentworth 1922, Krumbein 1934) to assess the heterogeneity in mineral grain sizes. All results are detailed in table S2 (available online at stacks.iop.org/ERL/16/054059/mmedia) of the supporting information.

2.3. Isotopic and molecular composition of soil and sediment organic matter

2.3.1. Bulk elemental and carbon-isotope analyses

Elemental and carbon-isotope analyses were performed to quantify organic matter stocks and describe their composition on a bulk level. Freeze-dried, homogenized subsamples (~3 g) were solvent-extracted at the Department of Earth Sciences at Vrije Universiteit Amsterdam (The Netherlands), using a MARS 6 microwave (CEM GmbH). Extraction, purification and quantification followed well-established methodology (e.g. Freymond et al 2018), details can be found in the supporting information (S1.1). Resulting quantities of HMW n-alkanes (with carbon chain lengths of C₂₇–C₃₃) and HMW₂₄–₃₄ n-alkanoic acids (with carbon chain lengths of C₂₄–C₃₄) were normalized to the mineral SA of each sample, and are here presented as µg m⁻² to avoid the signals being obscured by changes in other carbon pools. Lipid biomarker concentrations normalized to OC content (mg g OC⁻¹) are reported in the supporting information (table S4). Furthermore, the carbon preference indices (CPI) for HMW₂₇–₃₃ n-alkanes and HMW₂₄–₃₄ n-alkanoic acids, as well as the ratio of even low molecular weight (LMW) n-alkanes (C₁₆, C₁₈, C₂₀) to odd high molecular weight (HMW) n-alkanes (C₂₇, C₂₉, C₃₁) were employed as degradation proxies for plant waxes, as further described in the results, section 3.5 (see supporting information S1.2 and table S5 for calculations and detailed results).

2.3.2. Analysis of solvent-extractable lipid biomarkers

High-molecular weight (HMW) n-alkanes and n-alkanoic acids constitute the major part of epicuticular leaf wax lipids (Eglinton and Hamilton 1967) and have therefore been broadly employed as source-specific biomarkers of vascular plants. Freeze-dried, homogenized subsamples (~3 g) were solvent-extracted at the Department of Earth Sciences at Vrije Universiteit Amsterdam (The Netherlands), using a MARS 6 microwave (CEM GmbH). Extraction, purification and quantification followed well-established methodology (e.g. Freymond et al 2018), details can be found in the supporting information (S1.1). Resulting quantities of HMW₂₇–₃₃ n-alkanes (with carbon chain lengths of C₂₇–C₃₃) and HMW₂₄–₃₄ n-alkanoic acids (with carbon chain lengths of C₂₄–C₃₄) were normalized to the mineral SA of each sample, and are here presented as µg m⁻² to avoid the signals being obscured by changes in other carbon pools. Lipid biomarker concentrations normalized to OC content (mg g OC⁻¹) are reported in the supporting information (table S4). Furthermore, the carbon preference indices (CPI) for HMW₂₇–₃₃ n-alkanes and HMW₂₄–₃₄ n-alkanoic acids, as well as the ratio of even low molecular weight (LMW) n-alkanes (C₁₆, C₁₈, C₂₀) to odd high molecular weight (HMW) n-alkanes (C₂₇, C₂₉, C₃₁) were employed as degradation proxies for plant waxes, as further described in the results, section 3.5 (see supporting information S1.2 and table S5 for calculations and detailed results).

2.3.3. Analysis of lignin phenols and cutin acids by CuO oxidation

Lignin is synthesized in vascular plants in order to impart stability to the cell walls. Phenolic monomers liberated upon oxidative hydrolysis of the lignin macromolecule carry information on plant types (Gohi and Hedges 1992), see supporting information (S1.3) for further details. Cutin-derived hydroxy fatty acids obtained from CuO oxidation are another compound class of biomarkers often employed in parallel with
lignin phenols (e.g. Goñi and Hedges 1990, Prahl et al 1994, Goñi et al 2000). Cutin is mainly associated with the soft tissues of vascular plants such as leaves and needles.

Microwave-assisted alkaline CuO oxidations were carried out at the Department of Earth Sciences at Vrije Universiteit Amsterdam (The Netherlands), using a MARS 6 system (CEM GmbH), following the method described by Goñi and Montgomery (2000) and described in more detail in the supporting information (S1.3). As for the lipid biomarkers, lignin phenol and cutin acid concentrations were normalized to the mineral SA of each sample and are reported as loadings (µg m\(^{-2}\)). Concentrations normalized to OC content (mg g OC\(^{-1}\)) can be found in the supplementary information, table S4. Additionally, ratios of syringic acid to syringaldehyde (Sd/Sl) and vanillic acid to vanillin (Vd/Vi), as well as 3,5-dihydroxybenzoic acid to vanillyl phenols (3,5-Bd/V) served as proxies for lignin degradation (see supplementary information, S1.4 and table S6).

2.3.4. Analysis of macromolecular constituents by pyrolysis-gas chromatography-mass spectrometry (Py-GCMS)

Solvent-insoluble macromolecular components, including lignin, proteins, polysaccharides and their degradation products, comprise the majority of organic matter in environmental matrices such as soils and sediments. Py-GCMS enables qualitative characterization of the macromolecular constituents of organic matter. Flash heating in an oxygen-free environment produces pyrolysis products which are identified via GCMS. For this study, a restricted number of dominant compounds were identified to target representative groups of moieties, following an approach by Sparkes et al (2016) (modified from Guo et al 2004, 2009).

Analytical pyrolysis was performed using an Agilent GC/MSD system coupled to a CDS-5200 pyroprobe at the Department of Earth and Environmental Sciences at the University of Manchester (United Kingdom), with details described in the supporting information (S1.5). As samples had not been solvent-extracted prior to Py-GCMS analysis, pyrolysates do not exclusively derive from non-extractable, macromolecular constituents of the organic matter. Extractable lipids likely contributed to the hydrocarbon fraction (aromatics and short-chain alkanes, described below). Resulting ion chromatograms were analysed for a selection of moieties representative of the following six key compound classes using a method described in Sparkes et al (2016): aromatics (toluene, ethylbenzene, naphthalene) and short-chain alkanes (carbon chain lengths C\(_{3-4}\)) indicating reworked organic matter, polysaccharides (3-furaldehyde, furfural, 5-methylfurfural) representing less degraded carbohydrates, lignin markers (guaiacol, creosol and 4-ethylguaiacol), phenols (phenol, 2-methylphenol, 3-methylphenol, 4-methylphenol) likely deriving from polysaccharides and proteins (not from lignin, in contrast to the methylphenols) and N-containing compounds (pyridine, 2-methylpyridine and benzimidazole) as a proxy for microbial residues. All results are given as relative amounts, denoting the chromatogram peak areas of diagnostic ions for each group compared to the total area of all measured compounds identified in that sample. While this approach does not provide absolute concentrations of the different compound classes due to variations in pyrolysis and ionization efficiency (i.e. how efficiently different macromolecular precursors are broken down to measurable pyrolysis products and how efficiently different types of compounds are ionized to yield a mass spectral response), it enables sample-to-sample comparisons of relative compound abundances and derivation of characteristic fingerprints. Furthermore, the different compound classes can be categorized as intrinsically labile (lignin markers, N-containing compounds, phenols, polysaccharides) or intrinsically recalcitrant (alkanes, aromatics), similar to the approach taken in Sparkes et al (2016). The fraction of labile compound classes relative to all identified compounds (as fraction labile; F\(_{\text{lab}}\)) may then serve as a proxy for the freshness of the macromolecular organic matter.

3. Results

3.1. Sediment properties

The mineral matrix of all samples consisted of mostly silt, comprising 50%–70% of the total sediment pool, with the exception of Pleistocene permafrost from FM2 (45%, figure S2, supporting information). Clay accounted for 25%–45%, (52% for FM2 Pleistocene permafrost), whereas sand made up <20% (<10% for all but FM2 debris and active layer, CB active layer). Active layer soils (together with permafrost) from SF had the largest median grain sizes (D\(_{50}\) of 7–11 µm, with a mean ± standard deviation of 8.5 ± 1.2 µm) and were the least well sorted (i.e. a wider grain size distribution and thus higher sorting parameter of 2.3 ± 0.1 on the Wentworth scale). Permafrost substrates, on the other hand, consisted of finer mineral grains (D\(_{50}\) of 4–8 µm, 6.7 ± 2.2 µm) and had a lower sorting parameter of 2.0 ± 0.2, indicating greater homogeneity of sediments. The Pleistocene permafrost of FM2 showed the lowest D\(_{50}\) of 3.6 µm and sorting parameter of 1.9. Freshly thawed debris and slump runoff deposits had median grain sizes of 6.8 ± 1.5 µm and 7.2 ± 2.7 µm, respectively, and sorting parameters of 2.1 ± 0.1 for both. Median grain sizes and sorting parameters were weakly correlated to the \(^{14}\)C content of the bulk organic matter, i.e. coarser and less sorted sediments contained relatively younger OC (R = 0.55, p = 0.012 and R = 0.57, p = 0.0087, respectively). Mineral SA values were highest and most heterogeneous for
active layer samples (36.6 ± 8.0 m² gdw⁻¹, up to 48 m² gdw⁻¹ for FM3), whereas both Holocene and Pleistocene permafrost samples clustered around 20–25 m² gdw⁻¹ (22.1 ± 2.0 m² gdw⁻¹, figure 2(A)). Debris and runoff deposit samples fell into a similar range (23.5 ± 4.3 m² gdw⁻¹ and 23.7 ± 1.7 m² gdw⁻¹, respectively) with the exception of the runoff deposit sample of FM2 (12.2 m² gdw⁻¹).

3.2. Organic matter concentrations and loadings
Among the RTS sediment sources, OC contents were generally highest and most variable for active layer samples, with values between 20 and 160 mg gdw⁻¹ (54.2 ± 49.2 mg gdw⁻¹, figure 2(A)). In contrast, permafrost samples from all slumps displayed lower and more homogeneous OC contents between 13 and 18 mg gdw⁻¹ (15.1 ± 1.8 mg gdw⁻¹), and were similar to those for debris (16.7 ± 2.3 mg gdw⁻¹) and runoff deposit samples (16.4 ± 3.5 mg gdw⁻¹).

Most samples showed SA-normalized OC loadings between 0.4 and 1 mg OC m⁻² (figure 2(A)), which is the common range reported for aquatic environments, where OC is expected to closely interact with mineral surfaces (e.g. Blair and Aller 2012, and references therein). In organic-rich soils, on the other hand, plant remains and organic matter fragments often exist either as aggregates or as so-called ‘free’ POM (free POM), with no apparent associations to minerals. Notably, some of the active layer samples from CB, FM2 and FM3 showed significantly higher OC loadings of 1.4, 1.9 and 7.0 mg m⁻², respectively, suggesting the existence of aggregates or free POM in these samples, in contrast to the results for permafrost, debris and runoff deposits (0.69 ± 0.06, 0.73 ± 0.13, and 0.79 ± 0.18 mg m⁻², respectively).

3.3. Bulk organic matter composition
Ratios of molar TN to total organic carbon (TN/TOC) have been employed to quantify contributions of petrogenic OC (e.g. for the Mackenzie watershed; Hilton et al 2013), with values between 0.064 and 0.078 typical for the petrogenic endmember (figure 2(B)). TN/TOC values were lowest for active layer samples (0.058 ± 0.011) and highest for permafrost samples (0.073 ± 0.008), with intermediate ratios for debris and runoff deposit samples (0.069 ± 0.009 and 0.068 ± 0.006, respectively). All bulk stable carbon isotope values (δ¹³C) were between −26.9‰ and −25.6‰ and no clear trends or differences were visible (figure S3, supplementary material), similar to earlier findings (Shakil et al 2020). Radiocarbon values (Δ¹⁴C) were highest (i.e. the youngest OC) in the active layer samples for each RTS: ranging from −415‰ to −290‰ for CB, FM2 and SF (corresponding to uncalibrated radiocarbon ages of 4200–2700 years) and from −711‰ to −641‰ (corresponding to 9900–8200 years) for FM3 (figure 2(B)), respectively. Permafrost samples contained substantially older OC (i.e. lower Δ¹⁴C values), with the most westward slump (SF) comprising the youngest Holocene permafrost OC (Δ¹⁴C of −772‰, uncalibrated radiocarbon age of 11 800 years). The oldest OC was found in the Pleistocene permafrost layer of FM2 (Δ¹⁴C of −976‰ or 30 000 years). Δ¹⁴C values of debris and runoff deposit samples (−958‰ to −741‰) were generally similar to those of permafrost samples (−976‰ to −772‰, see above), although debris from SF and runoff deposits from CB had higher Δ¹⁴C values (−678‰ and −591‰, respectively). TN/TOC ratios showed a linear correlation with Δ¹⁴C (R = −0.77,
Figure 3. Biomarker loadings (i.e. normalized to mineral surface area, μg m⁻²) decreased with decreasing radiocarbon content (i.e. increasing radiocarbon age) of the bulk organic carbon (Δ¹⁴C): (A) lignin phenols, (B) cutin acids, (C) high-molecular-weight (HMW₂₇–₃₃, i.e. carbon chain lengths 27–33 carbon atoms) of n-alkanes, and (D) HMW₂₄–₃₄ n-alkanoic acids, for active layer (AL), debris (DB), Holocene (HO) and Pleistocene (PL) permafrost and runoff deposits (RU) from RTS features CB, FM2, FM3 and SF.

3.4. Lignin, cutin and lipid biomarker loadings
Loadings of vascular plant biomarkers (i.e. lignin phenols, cutin acids, high molecular weight (HMW₂₇–₃₃) n-alkanes and HMW₂₄–₃₄ n-alkanoic acids) exhibited similar patterns with respect to organic matter age (figure 3). Generally, active layer samples for each RTS feature displayed the highest biomarker loadings (normalized to mineral SA), whereas biomarker loadings for permafrost samples were much lower. These differences were particularly pronounced for the largest RTS feature, FM2, where the active layer sample had the overall highest, and the Pleistocene permafrost sample by far the lowest loadings for each of the biomarkers. The smallest RTS feature, SF, on the other hand, displayed the least differences between biomarker loadings for the active layer and permafrost samples. Debris and runoff deposit samples showed intermediate biomarker loadings, generally more similar to permafrost than active layer samples. All values can be found in supporting information, table S4.

3.5. Biomarker degradation proxies
Carbon preference indices for HMW n-alkanes and HMW n-alkanoic acids (CPIₐ lk and CPIₐcid) showed dissimilar trends with respect to organic matter age (figures 4(A) and (C)). Values for CPIₐ lk varied over a wide range (1.1–40), with lower values for permafrost samples (<4.2 for samples from CB and FM2, 8.5 and 8.2 for FM3 and SF, respectively). Active layer samples for all but FM3 clustered between 12 and 20, similar to most debris and runoff deposit samples. FM3 active layer and CB runoff deposits had higher values of 32–40. Values for CPIₐcid on the other hand, were lowest for active layer samples from FM3 and SF (2.9–3.4).
Figure 4. Degradation indices based on biomarker data with arrows indicating the change of the proxy value with ongoing degradation. (A) Low carbon preference indices of HMW \( n \)-alkanes (CPI\(_{\text{alk}}\)) likely signalling a notable contribution of rock-derived (petrogenic), \(^{14}\)C-depleted organic matter for the Holocene and Pleistocene permafrost samples of FM2 and CB. (B) High ratios of even low molecular weight \( n \)-alkanes (LMW\(_{16,18,20}\)) to odd high molecular weight \( n \)-alkanes (HMW\(_{27,29,31}\)) are indicative of petrogenic or microbially altered organic matter. (C) Low HMW \( n \)-alkanoic acids CPI\(_{\text{acid}}\) values imply more decomposed material. (D) High acid-to-aldehyde ratios for vanillyl phenols (Vd/Vl) point towards more degraded lignin phenols.

and slightly higher for FM2 and CB (4.2–4.7). Most permafrost, debris and runoff deposit samples displayed higher values (6.0–10, except permafrost and debris of SF with 5.2 and 4.5, respectively).

The ratio of even low-molecular-weight \( n \)-alkanes to odd HMW \( n \)-alkanes (LMW\(_{16,18,20}\)/HMW\(_{27,29,31}\), figure 4(B)), showed a distinct trend with \( \Delta^{14}\)C of bulk OC. A particularly high value of 2.6 was observed for the radiocarbon-depleted Pleistocene permafrost of FM2, while Holocene permafrost, together with some debris and runoff deposit samples varied between 0.47 and 0.88. More radiocarbon-enriched runoff deposits, debris and permafrost from SF, as well as runoff deposits and debris from CB scored between 0.041 and 0.20. All active layer samples had values between 0.016 and 0.046. Average chain lengths of HMW \( n \)-alkanes and \( n \)-alkanoic acids, also correlated with bulk \( \Delta^{14}\)C values (\( R = 0.75, p < 0.001 \) and \( R = 0.61, p < 0.005 \), respectively, figures S4(A) and (B), supplementary material). For HMW \( n \)-alkanes values ranged between 28.4 and 29.2 for permafrost, between 28.1 and 29.2 for debris, between 28.6 and 29.9 for runoff deposits, and between 28.3 and 30.1 for active layer samples. For HMW \( n \)-alkanoic acids, permafrost, debris and runoff deposit samples showed values between 25.1 and 26.4, while active layer samples had average chain lengths of 26.4–27.4.

A lignin phenol-based degradation proxy, the acid-to-aldehyde ratio of vanillyl phenols (Vd/Vl), showed highest values for active layer samples (0.56–0.86, figure 4(D)). Permafrost, debris and runoff deposit samples recorded values between 0.35 and 0.66. The acid-to-aldehyde ratio for syringyl phenols (Sd/Sl) showed no clear pattern with bulk \( \Delta^{14}\)C, with all samples ranging between 0.17 and 0.52 (exception: active layer from FM3 with 0.72; figure S4(C), supplementary material). The ratio of 3,5-Bd/V did not display a clear trend with bulk \( \Delta^{14}\)C, either. Here, all samples ranged between 0.052 and 0.17 (exception:
runoff deposits from FM2 with 0.028; figure S4(D), supplementary material).

3.6. Macromolecular organic matter characteristics
Analyses by py-GCMS indicated that aromatic hydrocarbons were the most abundant compound group in all samples with relative contributions of 30%-82% (figure 5(A)). Polysaccharide and lignin markers were almost solely found in the active layer samples (6.4-25 and 0.14%-6.0% of total analysed components, respectively, for active layer samples, for all other samples <4.3% and <0.43%, respectively, with the exception of runoff deposits from CB, which had 1.9% lignin markers). The active layer samples also contained a larger proportion of phenolic compounds (18%-36%, in contrast to 0%-29% for all other samples). N-containing compounds were found to comprise 1.5%-12%, and short-chain alkanes the remaining 3.4%-18% of integrated products with no emerging patterns.

The fraction of labile compound classes $F_{lab}$ (sum of lignin markers, N-containing compounds, phenols, polysaccharide markers relative to all identified compound classes) was highest for the active layer for all RTS features except for SF, where $F_{lab}$ for runoff deposits was similar to the active layer (0.35 and 0.36, respectively). With the exception of CB (0.37), $F_{lab}$ values for the active layer samples were significantly higher (0.52-0.59). The Pleistocene permafrost sample from FM2 had by far the lowest $F_{lab}$ values (0.02), while Holocene permafrost samples exhibited intermediate values (0.17-0.22, with CB being an exception, 0.37). $F_{lab}$ values of debris samples were 0.10-0.32, which for FM3, CB and SF was lower than the $F_{lab}$ values recorded for the respective slump runoff deposits for each of these RTS features (0.23-0.38; since debris was not collected for FM2 no comparison can be made for that feature). Generally, samples with high OC concentrations (all from the active layer) also showed the highest $F_{lab}$ values (figure 5(B)), and the
latter decreased in a linear fashion with decreasing bulk radiocarbon content $\Delta^{14}C \ (R = 0.76, p < 0.001, \ \text{figure } 5)(C)$.

4. Discussion

A growing body of research has focused on tracing permafrost substrate in fluvial networks (e.g. Spencer et al 2015, Vonk et al 2015, McClelland et al 2016, Drake et al 2018, Wild et al 2019, Bröder et al 2020, Zolkos and Tank 2020), in the coastal near-shore zone (e.g. Drenzek et al 2007, Winterfeld et al 2015, Grotheer et al 2020, Jong et al 2020), and across Arctic shelf seas (e.g. Vonk et al 2012, Tesi et al 2014, 2016, Bröder et al 2016, 2018, 2019). In the terrestrial realm, slope thermokarst features have been investigated to quantify their carbon stocks and impact on carbon release (e.g. Zolkos et al 2019, Shakil et al 2020, Turetsky et al 2020). This study provides detailed chemical and isotopic information on the sources and release of sediment and organic matter from a specific permafrost disturbance mode (i.e. RTS) to stream networks and thereby offers context for the headwater component of the terrestrial-freshwater-ocean continuum (Kokelj et al 2020).

4.1. Sedimentological and biogeochemical characteristics of RTS features

Large differences in sediment properties, as well as bulk and (macro-)molecular organic matter composition were observed between the active layer, Holocene and Pleistocene permafrost. In general, active layer soils were more heterogeneous with respect to grain size distribution, mineral SA, and organic matter content and composition, likely reflecting a mixture of organic and mineral soil horizons. The permafrost that was sampled, was generally more homogeneous, yet the Pleistocene permafrost showed some clear differences to the Holocene permafrost (the relict thaw layer). While OC contents and loadings of Pleistocene permafrost were not substantially lower than for the other samples (17.8 mg gdw$^{-1}$, 0.74 mg m$^{-2}$), it was strongly depleted in $\Delta^{14}C \ (\Delta^{14}C \text{ of } -976\%)$, plant biomarker (plant wax lipid, lignin and cutin) loadings were very low or below levels of determination, and on a macromolecular level, it was virtually devoid of labile components. These results corroborate findings that RTS-mobilized particulate organic material is more recalcitrant than particulate organic material present in non-impacted streams (Shakil et al 2020), and are consistent with the observation of more biodegradable OC (e.g. O-alkyl-C) in the active layer compared to more aromatic compounds in permafrost based on $^{13}C$ nuclear magnetic resonance (NMR) analysis (Lacelle et al 2019). The high fraction of aromatics in Pleistocene permafrost may derive from thermally mature rock fragments (i.e. petrogenic hydrocarbons), which is consistent with the low CPI$_{lab}$ value. This is supported by earlier findings of mineral sulphides in Peel Plateau permafrost sediments and prior evidence for black shale incorporation into these local deposits (Norris and Walter 1985, Calmels et al 2007, Allen et al 2015, Zolkos and Tank 2020). The high LMW$_{16,18,20}$/HMW$_{27,29,31}$ n-alkane ratio also suggests that Pleistocene permafrost contains rock-derived (petrogenic) OC. Alternatively, a low LMW/HMW n-alkane ratio may be an indication for a relatively high contribution of microbial residues (necromass) that has been preserved in these glacial deposits (Grimalt and Albàgés 1987). The small median grain size of the deeper, Pleistocene permafrost sample here indicates that it could be easily eroded and transported by fluvial processes once thawed at the RTS headwall, while the refractory characteristics and close mineral associations confer resistance of mobilized organic matter to decomposition during export.

Although Holocene permafrost had similar OC contents and loadings to that of Pleistocene permafrost, it was characterized by higher bulk $\Delta^{14}C$ values, vascular plant biomarker loadings, CPI$_{lab}$ and F$\text{lab}$ values, indicating enhanced contributions of biogenic organic matter. This aligns with increased plant productivity and incorporation of organic matter into deeper soils when materials were thawed either as part of a thicker active layer or as colluvium during the Holocene warm interval, and preservation of this material within aggrading permafrost during subsequent cooling (Kokelj et al 2017). The overall larger grain sizes for Holocene permafrost entail that these deposits would be less easily eroded and transported than their Pleistocene counterparts. However, these differences in grain sizes may be specific to the collected sample suite and not represent regional patterns.

Active layer samples had the highest OC concentrations and loadings, suggesting the presence of discrete fragments of plant debris or aggregates not intimately associated with the mineral matrix. The higher $\Delta^{14}C$ values and lower TN/TOC ratios, together with high biomarker loadings and F$\text{lab}$ values, are indicative of younger, biogenic, relatively fresh and labile organic matter stored in these soils. The relatively high median grain sizes and heterogeneous nature infer that upon mobilization, some parts of this material may be less prone to fluvial transport and instead may be retained within the scar zone or be moved downslope as part of the slower debris flow, which is less sensitive to grain size (Kokelj et al 2020).

Recently eroded debris accumulating at the foot of the RTS headwall most closely resembles Holocene and Pleistocene permafrost with respect to grain size distribution, OC and radiocarbon content, biomarker loadings and F$\text{lab}$ values. Slump runoff deposits also exhibited similarities to debris, yet displayed some macromolecular characteristics consistent with elevated proportions of intrinsically labile
organic matter. The latter may reflect entrainment of materials from the active layer or biospheric OC recently developed on the slump itself (i.e. re-colonizing vegetation or microbial biomass). Overall, slump runoff deposits appear to be dominated by Holocene and Pleistocene permafrost sources. This inference is in good agreement with other recent studies in the area (e.g. Lacelle et al 2019, Shakil et al 2020).

4.2. Site-specific variability in organic matter composition and export

The four RTS features sampled for this study differ substantially in size and complexity (see section 2.1, figure 1 and table 1). The larger RTS features, FM2 and FM3 with maximum headwall heights of 24.2 and 9.8 m, respectively, result in greater thaw of deeper Pleistocene permafrost because scar area is positively related with volume and scar concavity depth by power-law relationships (Kokelj et al 2020), and thus export older organic matter (runoff deposits ∆14C = -846‰ and -948‰, respectively, see also Shakil et al 2020). They also display larger differences between permafrost and active layer organic matter composition than the smallest RTS feature SF, as evident from ∆14C values, biomarker loadings and macromolecular organic matter compositions. However, this could also be due to the fact that SF is located farthest west and at a higher elevation (720 m asl, as opposed to 338 and 391 m asl for FM2 and FM3, respectively). These apparent differences could therefore also be a result of contrasting substrates, i.e. herb tundra soils developed on colluvial debris in the mountains vs. tundra forest soils in the lower parts of the Peel Plateau (Kokelj et al 2017). Even though the westernmost sites were subjected to glacial retreat earlier, the lower lying sites towards the east have presumably experienced deeper root penetration and increased soil development, as well as deeper percolation of leached dissolved organic matter from surface soils. The differences in vegetation are also reflected in the lignin phenol composition of the active layer samples, showing enhanced contributions from gymnosperm (non-flowering) plants for the low-lying RTS features FM2 and FM3 (see figure S5, supporting information). Taken together, glacial, climate and ecosystem history influence the composition of the mobilized material as thermokarst features continue to increase in size and number throughout this region.

4.3. Organic matter evolution and downstream implications

Assessing the degradation status of different organic matter pools may help to predict its fate upon mobilization in RTS systems and downstream export. Different proxies have been employed in this study; while the low CPIalk values suggested a petrogenic OC source mainly in the deeper permafrost layers, the lower CPIacid values suggested more degraded biogenic OC in the active layer samples (figure 4(C)). On the other hand, the latter samples displayed the highest biomarker loadings (figure 3(D)), which would typically be at odds with the expectation of extensive degradation. The same appears to be true for lignin phenols, where active layer samples had higher degradation-indicative acid-to-aldehyde ratios for vanillyl phenols (VDv/VI) than most permafrost-associated samples (figure 4(D)), despite higher concentrations of vanillyl phenols in the former. The correlation between these two independent degradation proxies (R = -0.73, p < 0.001) suggests that the observed patterns are robust. Goñi et al (2000) reported VDv/VI ratios of 0.46–0.80 for Mackenzie River suspended sediments and 0.55–0.90 for Beaufort Shelf sediments with no clear spatial trends. These values are similar to those observed here, suggesting that most degradation occurs prior to entrainment in the aquatic continuum. The apparent contradictions of relatively young and labile organic matter with high biomarker concentrations showing a degraded signal may result from much slower degradation of organic matter sequestered in permafrost deposits due to the permanently frozen condition and close associations with mineral surfaces. In contrast, although the active layer receives input from growing vegetation (hence the high OC content), it is subject to more intense recycling under the prevailing conditions of seasonal thaw and more oxygenated conditions, leading to higher microbial activity, and thus a potentially stronger degradation fingerprint in the biomarkers. Additionally, the larger abundance of free or possibly occluded organic matter (i.e. not tightly associated with mineral surfaces) may further increase its degradability. An alternative explanation could be the preferential leaching of dissolved lignin during multiple freeze-thaw cycles in the active layer, which may result in elevated acid-to-aldehyde ratios independent of actual organic matter degradation (Hernes et al 2007).

Py-GCMS data, targeting the larger, non-extractable, macromolecular components of the organic matter, indicated higher proportions of readily degradable organic components in the active layer, while permafrost, debris and runoff deposits displayed proportionally greater abundances of more recalcitrant organic material indicating reworked organic matter as well as potential contributions from petrogenic carbon. Using a similar approach, Sparkes et al (2016) also found a correlation between the bulk ∆14C and the relative contribution of aromatics for sediments from the East Siberian Arctic Shelf. While the relative contributions of aromatics are much lower for that sample set (between ~3% and ~16%, compared to between 30% and 82% for this study), the general trend appears to be similar. Besides a potential contribution from extractable lipids to the aromatic fraction for this sample set (as discussed
earlier), the lower values for those sediments may in part also be due to the dilution with marine organic matter (Sparkes et al. 2016). More importantly, however, the Mackenzie River drainage basin contains extensive regions underlain by organic-rich sedimentary rocks (as described in section 4.1), while this pedogenic OC source is virtually absent from the Siberian Arctic.

While clearly simplistic, our classification of intrinsically labile and intrinsically recalcitrant fractions enables a first assessment of potential degradability of sediment organic matter following thaw and exposure by RTSs on the Peel Plateau. Recent studies have shown that environmental factors such as close interactions with mineral surfaces or the composition of microbial communities present in the soil exert greater control over the degradability of organic matter than its original chemical structure (Schmidt et al. 2011, Blattmann et al. 2019, Hemingway et al. 2019). However, the majority of these studies have been performed in temperate and tropical systems, whereas in cold, high-latitude environments, chemical structure may play a larger role for soil organic matter decomposition rates as the temperature sensitivity of the metabolizing chemical reactions is expected to increase with chemical complexity (Hobbie et al. 2000). The striking differences between active layer samples and all other samples, together with the coherent characteristics that emerge from the different lines of geochemical enquiry, begin to paint a consistent picture with respect to the origin and fate of organic matter and sediments mobilized in RTS systems. According to the data presented here, the organic matter fraction that is easily degraded is relatively small for debris within the RTS scar zone (between 10% and 32%), yet slightly larger in slump runoff deposits (between 23% and 38%) for each of the RTS features. This increase implies either that a small contribution of organic matter from the active layer is incorporated in the runoff as it flows through the slump, or (more likely) that slump runoff deposits entrain some younger, fresher carbon derived from vegetation or microbial biomass growing directly on the recently eroded deposits (as also mentioned above). Either way, this relatively labile organic matter—comprising a smaller proportion of exported RTS substrate than permafrost—is likely subject to rapid downstream decomposition. It thus primarily fuels respiration in headwaters of fluvial ecosystems, as recently observed in the Eastern Siberian Arctic (Dean et al. 2020).

### 4.4. Implications of intensifying RTS activity for climate feedbacks

The majority of OC exported from RTS features appears to be derived from permafrost deposits. This may simply reflect the relative proportions of materials at the headwall, where the active layer comprises less than 1 m and Holocene and Pleistocene permafrost layers account for the majority of the stratigraphic profile exposed by the ablating slump headwall (of up to 23, 9, 5 and 7 m for RTS features FM2, FM3, CB and SF, respectively). However, given the abundance of organic matter in the active layer and recent vegetation growth on stabilized parts of the scar zone, the apparent lack of recently synthesized organic matter in debris and runoff deposits from the RTS features implies that this material is either retained within the scar zone (due to generally larger particle sizes and/or physical stabilization by extensive root networks) or efficiently degraded, thereby returning its carbon (relatively quickly) to the atmosphere. This would, in turn, suggest that ongoing Arctic greening and increasing thaw depths primarily contribute to (relatively) fast cycling OC pools.

In contrast, abrupt thermokarst-driven permafrost thaw and mass wasting processes on the Peel Plateau, leading to the exposure of deeper permafrost deposits, appear to mobilize a reservoir of carbon comprised of two distinct pools: a minor fraction that may be labile and readily respired, and a much larger fraction of less labile, slow cycling permafrost OC that includes pedogenic carbon. The latter pool of material may escape rapid degradation and instead make its way in largely unaltered form to downstream reservoirs, leaving open the question whether it is ultimately respired or reburied along the aquatic continuum (e.g. Hilton et al. 2015, Horan et al. 2019). With ongoing RTS growth affecting larger parts of landscapes across Canada and similar landscapes across the circumpolar Arctic (Segal et al. 2016, Swanson and Nolan 2018, Lewkowicz and Way 2019, Kokelj et al. 2020) and progressive exposure of deeper permafrost layers, fluvial fluxes of relatively recalcitrant organic matter may increase, with its slow degradation possibly leading to a relatively subdued, yet long-term positive feedback to climate change.

### 5. Conclusions

(a) RTS headwalls expose different materials with contrasting sediment properties, organic matter content, age and composition. Deep, Pleistocene permafrost deposits hold a substantial contribution of rock-derived organic matter, while Holocene permafrost (relict thaw layer) contains more biogenic organic matter. The organic-rich active layer comprises relatively labile organic matter from current and recent vegetation, yet paradoxically biomarker degradation proxies suggest this material may have already undergone considerable reworking.

(b) Recently eroded debris and slump runoff sediments are dominated by relatively recalcitrant permafrost-derived organic matter, with a smaller contribution of fresh organic matter emanating either from active layer soils or the revegetated scar zone.
(c) The differences between permafrost type and history (e.g. Pleistocene tills vs relicth thaw layer) play an important role in the biogeochemical behaviour of the eroded material and its ultimate fate downstream, which will determine its impact on climate.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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