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## Permafrost Landscape History Shapes Fluvial Chemistry, Ecosystem Carbon Balance, and Potential Trajectories of Future Change

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# Global Biogeochemical Cycles®



## RESEARCH ARTICLE

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### Key Points:

- Permafrost landscape history regulates fluvial carbon (C) sources and export across a transect of continental glaciation and thermokarst
- Fluvial C flux equaled 6%–16% of vegetation C uptake in most watersheds and 60% in those affected by permafrost thaw-driven mass wasting
- Thaw-susceptible terrains will be significant to Arctic ecosystem carbon balance as permafrost thaw and hydrologic carbon fluxes intensify

### Supporting Information:

Supporting Information may be found in the online version of this article.

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## Permafrost Landscape History Shapes Fluvial Chemistry, Ecosystem Carbon Balance, and Potential Trajectories of Future Change

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**Abstract** Intensifying permafrost thaw alters carbon cycling by mobilizing large amounts of terrestrial substrate into aquatic ecosystems. Yet, few studies have measured aquatic carbon fluxes and constrained drivers of ecosystem carbon balance across heterogeneous Arctic landscapes. Here, we characterized hydrochemical and landscape controls on fluvial carbon cycling, quantified fluvial carbon fluxes, and estimated fluvial contributions to ecosystem carbon balance across 33 watersheds in four ecoregions in the continuous permafrost zone of the western Canadian Arctic: unglaciated uplands, ice-rich moraine, and organic-rich lowlands and till plains. Major ions, stable isotopes, and carbon speciation and fluxes revealed patterns in carbon cycling across ecoregions defined by terrain relief and accumulation of organics. In previously unglaciated mountainous watersheds, bicarbonate dominated carbon export (70% of total) due to chemical weathering of bedrock. In lowland watersheds, where soil organic carbon stores were largest, lateral transport of dissolved organic carbon (50%) and efflux of biotic CO<sub>2</sub> (25%) dominated. In watersheds affected by thaw-induced mass wasting, erosion of ice-rich tills enhanced chemical weathering and increased particulate carbon fluxes by two orders of magnitude. From an ecosystem carbon balance perspective, fluvial carbon export in watersheds not affected by thaw-induced wasting was, on average, equivalent to 6%–16% of estimated net ecosystem exchange (NEE). In watersheds affected by thaw-induced wasting, fluvial carbon export approached 60% of NEE. Because future intensification of thermokarst activity will amplify fluvial carbon export, determining the fate of carbon across diverse northern landscapes is a priority for constraining trajectories of permafrost region ecosystem carbon balance.

**Plain Language Summary** Freshwaters are a main component of the global carbon cycle and climate. Yet, their role in climate change is uncertain in permafrost regions, where thaw is releasing large amounts of carbon and enabling production of climate-warming greenhouse gases. To reduce uncertainty, we measured stream chemistry and carbon fluxes across four ecoregions including a global hotspot of permafrost thaw in the western Canadian Arctic. Comparing across ecoregions, lowlands were strong sources of biological carbon dioxide and methane to the atmosphere; mountain rivers ferried products from chemical rock weathering downstream; and streams affected by permafrost thaw-induced wasting transported large amounts of particulate carbon. Typical of northern ecosystems, carbon fluxes in non-thaw-affected streams were equivalent to 6%–16% of carbon uptake by terrestrial vegetation. However, in watersheds affected by thaw-induced wasting, carbon fluxes were up to 100 times higher and approached 60% of vegetation carbon uptake. Together, these findings

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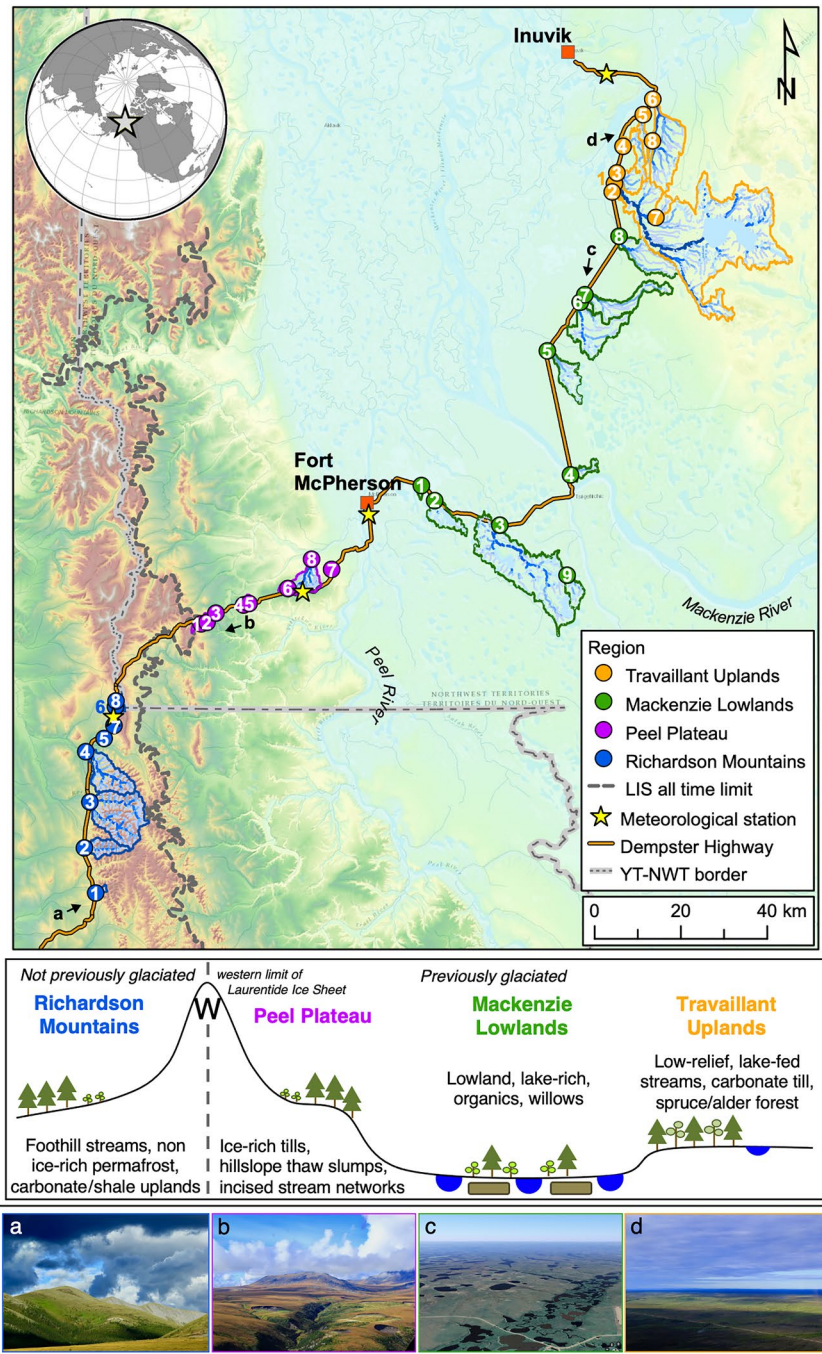
reveal that thermokarst-susceptible terrains are poised to emerge as a significant component of the Arctic ecosystem carbon balance and global climate feedbacks, due to hydrologic carbon fluxes that will intensify as permafrost thaw accelerates.

## 1. Introduction

At northern high latitudes, permafrost thaw and intensifying hydrologic cycles are strengthening terrestrial-freshwater linkages (Vonk et al., 2019) and the aquatic component of ecosystem carbon cycling and climate feedbacks (Plaza et al., 2019; Turetsky et al., 2020). The intensification of these processes across northern watersheds is reflected by multi-decadal increases in riverine solute fluxes and the propagation of thawed permafrost substrate across watershed scales (Drake, Tank, et al., 2018; Kokelj et al., 2021; Toohey et al., 2016; Zolkos et al., 2018). Reactivation of thawed permafrost substrate into modern biogeochemical cycles manifests as perturbation to local and regional carbon cycling. For instance, on the Peel Plateau in the Northwest Territories of Canada, thaw-driven mass wasting of ice- and mineral-rich glacial deposits in fluvial network headwaters (Kokelj et al., 2013) increases particulate organic carbon (POC) export by orders of magnitude (Shakil et al., 2020) and enables production of dissolved inorganic carbon (DIC =  $\Sigma[\text{CO}_2, \text{HCO}_3^-, \text{CO}_3^{2-}]$ ) via chemical weathering of carbonate-bearing tills (Zolkos & Tank, 2020). In comparison, thaw of relatively biolabile permafrost organic carbon in previously unglaciated terrains (Strauss et al., 2017) can fuel relatively high rates of microbial oxidation of dissolved organic carbon (DOC) and increase carbon dioxide ( $\text{CO}_2$ ) loss within fluvial network headwaters (Drake, Guillemette, et al., 2018). Variation in landscape conditions (e.g., topography, hydrology, and geology) across the northern permafrost zone are hypothesized to underlie thaw effects on aquatic carbon cycling (Tank et al., 2020), yet few studies have assessed physiographic controls on aquatic carbon cycling within thaw-susceptible terrains.

At the landscape scale, vertical exchange of fluvial  $\text{CO}_2$  and methane ( $\text{CH}_4$ ) with the atmosphere (henceforth, “efflux”) and lateral downstream fluxes of DIC, DOC, and particulate carbon (PC) represent carbon losses from watersheds that are counterbalanced by vegetation photosynthesis. The degree to which ecosystem carbon uptake via photosynthesis offsets aquatic and terrestrial carbon losses determines the net ecosystem carbon balance (NECB), which broadly describes whether landscapes are carbon sources or sinks (Chapin et al., 2006). From a watershed perspective, the ecosystem carbon balance is comprised of net terrestrial carbon uptake as  $\text{CO}_2$  (i.e., net ecosystem exchange [NEE], the difference between two large component fluxes, gross primary productivity [GPP] and ecosystem respiration), and vertical exchange of carbon gases ( $\text{CO}_2$ ,  $\text{CH}_4$ , CO, and volatile organic carbon) between the land and atmosphere, and lateral aquatic export of dissolved and PC (Chapin et al., 2006). Previous comparisons of aquatic carbon fluxes and NEE in western Siberia (Karlsson et al., 2021), Scandinavia (Lundin et al., 2016; Wallin et al., 2013), sub-arctic Canada (Hutchins et al., 2020), Alaska (McGuire et al., 2018), and the Qinghai-Tibet Plateau (Song et al., 2020) indicate that aquatic carbon fluxes in northern environments are generally equivalent to 10%–20% of NEE, but vary regionally. In remote northern regions, where field-based measurements of NEE can be sparse (Pallandt et al., 2022), estimates of ecosystem carbon balance are supported by measurements of aquatic carbon fluxes combined with modeled estimates of NEE informed by remotely sensed ecosystem properties (Kimball et al., 2018). Using this approach in the Ob’ river basin in western Siberia, where low terrain relief and carbon accumulation over millennia have promoted development of vast peat wetlands, Karlsson et al. (2021) found that aquatic carbon efflux was almost 10 times larger than lateral export to the Arctic Ocean and was equivalent to 35%–50% of the net terrestrial carbon uptake. Across Sweden and Alaska, aquatic carbon efflux is similar in magnitude to lateral carbon fluxes (Humborg et al., 2010; Stackpoole et al., 2017). Observations on the species comprising aquatic carbon fluxes, physiographic controls on aquatic carbon fluxes, and estimates of aquatic contributions to NECB remain sparse for arctic Canada, where continental glaciation shaped the evolution of high-latitude ecosystems.

In this study, we measure fluvial chemistry across diverse permafrost terrains to understand how geology and landscape evolution since the last glacial maximum (LGM) have shaped modern-day variation in carbon sources, fluxes, and ecosystem carbon balance. We focus on the western Canadian Arctic, where variation in geology, topography, hydrology, and glacial history have driven four adjacent ecoregions to evolve along different trajectories (Figure 1). These four ecoregions cover nearly 84,000 km<sup>2</sup> of the northern Yukon Territory and western Northwest Territories (Ecosystem Classification Group, 2009, 2010; Kokelj, Tunnicliffe, et al., 2017; Smith et al., 2004) and include: (a) the previously unglaciated Richardson Mountains; (b) the ice-rich and thermokarst-susceptible



**Figure 1.** Map of sampling sites within each region (upper panel) aligned with cross-section of terrain characteristics of the four study regions (middle panel) depicted in photos (lower panel): (a) Richardson Mountains, (b) Peel Plateau, (c) Mackenzie Lowlands, and (d) Travailant Uplands. In upper panel, site numbers are shown within or adjacent to symbols, and letters and arrows correspond to approximate locations and directions of photos in lower panel. Image of Mackenzie Lowlands from Google Earth. Laurentide Ice Sheet western limit from the literature (Duk-Rodkin & Hughes, 1992a, 1992b). Base map from ESRI ArcGIS Online.

glacial tills of the Peel Plateau; (c) the organic-rich till plains of the Mackenzie Lowlands; and (d) the rolling till plains of the Travailant Uplands. This transect of glacial history and topography-driven variation in hydrology and organic carbon accumulation (Table 1) provides an ideal setting to determine how variation in permafrost landscape type gives rise to regional patterns in modern-day fluvial chemistry, carbon cycling, and ecosystem

**Table 1**  
*Physiographic Conditions of the Study Regions*

Parameter	Units	Richardson Mountains	Peel Plateau	Mackenzie Lowlands	Travaillant Uplands
<i>Ecoregion characteristics and meteorological conditions</i>					
Ecoregion correlation	–	British-Richardson Mountains	Tundra Cordillera high subarctic ecoregion	Arctic Red Plain high subarctic ecoregion	Travaillant Upland high subarctic ecoregion
Ecoregion area	km <sup>2</sup>	26,690	7,828	22,907	26,389
Elevation	masl	450–900	100–750	25–350	50–450
MSAT	°C	11.8	12.8	14.5	13.2
TSP	mm	74	238	–	112
<i>Watershed characteristics</i>					
Slope	°	14.8 (2.1)	5.7 (1.4)	0.8 (0.1)	1.2 (0.2)
Elevation	m	815 (35)	503 (68)	88 (12)	156 (14)
Area	km <sup>2</sup>	28 (16)	6 (5)	62 (24)	102 (74)
Carbonate	%	60 (18)	0	0	0
Silicate	%	40 (18)	100 (0)	100 (0)	100 (0)
Colluvial	%	93 (3)	40 (18)	0.4 (0.4)	0.2 (0.2)
Fluvial	%	6 (3)	0	0	0
Moraine	%	0	60 (18)	60 (9)	92 (4)
Organic	%	1 (1)	0	39 (9)	7 (4)
Lakes/ponds	%	0	0.2 (0.1)	18 (7)	7 (2)
SOC	kgC m <sup>-2</sup>	16.3 (3.9)	21.4 (0.2)	70.5 (2.1)	29.8 (5.2)
GPP	gC m <sup>-2</sup> d <sup>-1</sup>	3.3 (0.2)	5.5 (0.2)	5.7 (0.3)	5.8 (0.2)
NEE	gC m <sup>-2</sup> d <sup>-1</sup>	–0.65 (0.02)	–0.70 (0.03)	–0.82 (0.02)	–0.60 (0.09)

*Note.* Ecoregion correlations and areas from the literature (Ecosystem Classification Group, 2009, 2010; Smith et al., 2004). MSAT = mean summer (June–August) air temperature. TSP = total summer precipitation. Elevation, Slope, and Area = mean watershed elevation, slope, and area. Carbonate and Silicate = distribution of carbonate and silicate bedrock, respectively (sum = ~100) (Norris, 1985). Colluvial, Fluvial, Moraine, Organic = distribution of surficial geology deposits (sum = ~100) (Côté et al., 2013; Lipovsky & Bond, 2014). Distribution of lakes and ponds from Natural Resources Canada (<https://open.canada.ca>). SOC = soil organic carbon content from 0 to 100 cm (Hugelius et al., 2013). GPP = gross primary productivity (Running et al., 2015). NEE = net ecosystem exchange (Kimball et al., 2018).

carbon balance, and dictates potential trajectories of future change. We tested three hypotheses. First, that stream water chemistry and carbon species would show systematic variation reflective of the divergent physiographic conditions among the four ecoregions. Second, that total fluvial carbon yields (i.e., flux divided by watershed area) would be highest in unglaciated uplands, where greater terrain relief, streamflow, and exposed bedrock enhances weathering and lateral inorganic carbon fluxes. Third, that lateral fluxes would be larger relative to NEE on the ice-rich till Peel Plateau, in particular where recent acceleration in hillslope thermokarst activity is known to mobilize carbon into fluvial networks. We sampled the outlets of 33 watersheds (0.1–610 km<sup>2</sup>) across these four regions (Figure 1) from June through August 2016 and combined measurements of stream chemistry, CO<sub>2</sub> and CH<sub>4</sub> efflux, and hydrology with geospatial landscape characteristics and modeled estimates of growing season NEE derived from remotely sensed data. Our findings reveal how physiography shapes variation in biogeochemical cycling and fluvial contributions to ecosystem carbon balance.

## 2. Methods

### 2.1. Study Regions

Across the circumpolar North, a range of physiographic conditions (e.g., geology, glacial history, and hydrology) together with Holocene climate change have given rise to regional variation in ecosystems, the composition of soils and permafrost, and hydrology. This is exemplified in the western Canadian Arctic, where we focus on four adjacent ecoregions that span a transect of continental glaciation (Figure 1). In contrast to ecosystems west of the Richardson Mountains, the three previously glaciated terrains located to the east, within the Mackenzie

River delta region, represent variation in topography, permafrost ground ice and soil conditions, and mass wasting intensity. This gives rise to large regional differences in the distribution of organic soils and thaw-driven mobilization of permafrost substrate into contemporary biogeochemical cycles (Hugelius et al., 2014; Kokelj, Tunnicliffe, et al., 2017).

The previously unglaciated Richardson Mountains (ecoregion 1) demarcates the western limit of the former Laurentide Ice Sheet (LIS) during the LGM (Clark et al., 2009; Ehlers et al., 2011) and was shaped by mass wasting, colluviation, and weathering of shale, carbonate, and sandstone bedrock outcrops through the Pleistocene (Norris, 1985; Smith et al., 2004). Mountain peaks reach 1,600 masl and upper slopes are veneered by mostly unvegetated colluvium, which transitions into tussock- and shrub-tundra on pediment surfaces at lower elevations, with stands of white spruce in sheltered valleys of larger rivers. Thaw-driven landslides are not common in the Richardson Mountains, where watersheds are dominated by exposed bedrock and colluvium. Regional observations of icings indicate potential contributions from groundwater to fluvial networks in mountainous terrains west of the LIS limit (Crites et al., 2020). A structural and topographic depression separates uplifted shales in the northern Richardson Mountain watersheds (sites RM-6 to RM-8) from folded and exposed limestone and sandstone in the southern watersheds (RM-1 to RM-5) (Norris, 1985; Smith et al., 2004) (Figure 1).

Western headwaters of the Peel Plateau (ecoregion 2) region are sparsely vegetated mountain slopes which consist mainly of colluvium from exposed marine shale and sandstone bedrock (Duk-Rodkin & Hughes, 1992b; Norris, 1985) and transition into tussock- and shrub-tundra on the plateau and open spruce forest at lower elevations (Kokelj, Tunnicliffe, et al., 2017). The plateau is a fluvially incised hillslope plateau within a glacial margin depositional environment hosting ice-rich landslide-susceptible tills that are mantled by deposits hosting modern organic carbon (Kokelj, Tunnicliffe, et al., 2017). Expansion of the LIS eroded regional Mesozoic and Paleozoic shales, sandstones, and limestones, and its retreat ~18 kybp (Lacelle et al., 2013) emplaced carbonate, sulfide, and silicate bearing tills on the Peel Plateau (Zolkos & Tank, 2020) via burial and preservation of basal glacier ice and development of segregated ground ice (Kokelj, Tunnicliffe, et al., 2017). The modern-day Peel Plateau contains ice-rich hummocky moraine, glaciofluvial, glaciolacustrine, and colluvial deposits with permafrost up to 50 m in thickness (Kokelj, Tunnicliffe, et al., 2017). Rapid warming and intensifying precipitation are accelerating thaw-induced mass wasting in the form of retrogressive thaw slump (RTS) thermokarst features along the Peel Plateau and in glacial margins elsewhere across northwestern Canada (Kokelj, Lantz, et al., 2017; Segal et al., 2016). Valleys in fluvial network headwaters promote development of RTS hillslope thermokarst features (Segal et al., 2016) and associated downslope wasting of tens to millions of cubic meters of thawed sediments (van der Sluijs et al., 2018). These sediments now exceed the transport capacity of streams by orders of magnitude and are altering geochemical fluxes and ecosystem function across watershed scales (Kokelj et al., 2021). RTS activity covers only a small areal proportion of watersheds, yet propagates a sediment- and solute-rich slurry containing thawed permafrost substrate that is dominated by particulates and cascades across watershed scales via fluvial processes (Bröder et al., 2021; Kokelj et al., 2013; Malone et al., 2013; Shakil et al., 2020; Zolkos et al., 2020).

In the Mackenzie Lowlands (ecoregion 3) and Travaillant Uplands (ecoregion 4), and in permafrost peatlands elsewhere across western Canada, relatively large stores of organic carbon are increasingly susceptible to thaw (Hugelius et al., 2020). The geology of the Mackenzie Lowlands and Travaillant Uplands is similar: both regions contain LIS-derived tills of variable thicknesses atop Devonian and Cretaceous age sandstone and shale bedrock (Norris, 1985). Organic carbon-rich Holocene permafrost peatlands are widespread in the low-relief, poorly drained Mackenzie Lowlands (Burn & Kokelj, 2009), where streams connect thousands of small thermokarst lakes and ponds (Duk-Rodkin & Hughes, 1992a, 1992b) among black spruce-dominated forest, and willow fens (Ecosystem Classification Group, 2009). In the Travaillant Uplands, lake-fed streams have developed across an elevational gradient and flow through relatively organic-rich peatlands (Duk-Rodkin & Hughes, 1992a) and across hummocky plains and open spruce forest (Ecosystem Classification Group, 2009; Norris, 1985).

## 2.2. Stream Sampling

We sampled streams at 33 sites along a 300 km transect accessed by the Dempster Highway from near Rock River, Yukon Territory, to near Inuvik in the Northwest Territories (Figure 1). Streams in most regions spanned Strahler orders 1–5 and were chosen to reflect the varied environmental conditions within and among regions. Sites were visited three times each from June to August 2016 (Table S1 in Supporting Information S1). During each site

visit, water temperature, specific conductance, dissolved oxygen, and pH were measured using a pre-calibrated YSI Professional-Plus water quality meter, and samples were collected to determine concentrations of DIC, DOC, CO<sub>2</sub>, and CH<sub>4</sub>. Samples for dissolved CO<sub>2</sub> and CH<sub>4</sub> concentrations were collected following the headspace equilibration method (Hesslein et al., 1991). We also sampled for cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) and anions (SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>) to constrain sources of mineral weathering; chromophoric dissolved organic matter, to characterize organic matter (specific UV absorbance at 254 nm [SUVA<sub>254</sub>] and spectral slope ratio [*S<sub>R</sub>*]); and for dissolved iron (dFe), to correct SUVA<sub>254</sub> measurements. To further constrain the carbon balance, we collected total suspended solids in a subset of streams to determine total PC concentrations. This subset was also sampled for total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (DIN = Σ[NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>]) to characterize inorganic nutrient status among regions, and stable isotopes of DIC (δ<sup>13</sup>C-DIC) and DOC (δ<sup>13</sup>C-DOC) to constrain dissolved carbon sources. At each site at the end of the summer, we sampled streams for stable water isotopes (δ<sup>18</sup>O-H<sub>2</sub>O and δ<sup>2</sup>H-H<sub>2</sub>O). During each site visit, we measured stream velocity (Lurry & Kolbe, 2000) and cross-sectional area (Gordon et al., 2004) to calculate discharge. Laboratory analyses of geochemical constituents followed standard methodologies. Full methods on water sample collection and analysis, QA/QC, and details about instrument manufacturers are provided in Supporting Information S1.

The efflux (*J*) of CO<sub>2</sub> (μmol m<sup>-2</sup> s<sup>-1</sup>) was measured in triplicate using an EGM-4 (PP Systems) connected to a stationary streamlined transparent chamber (Crawford et al., 2013). Discrete CH<sub>4</sub> samples were collected every 5 min for a single 20-min period from a port in the Bev-a-line tubing, stored, and later analyzed in the same fashion as dissolved CH<sub>4</sub> samples to determine *J*<sub>CH<sub>4</sub></sub> (nmol m<sup>-2</sup> s<sup>-1</sup>) (Methods S2 in Supporting Information S1). Measurements were made at each site at the beginning and end of the summer, and *J*<sub>CO<sub>2</sub></sub> and *J*<sub>CH<sub>4</sub></sub> were calculated as  $J = PH\Delta C/RT\Delta t \times c$  (Duc et al., 2013), where *P* is atmospheric pressure (atm); *H* is flux chamber height (m); Δ*C* is the change in headspace gas (ppmv); *R* is the ideal gas constant (82.0562 mL atm K<sup>-1</sup> mol<sup>-1</sup>); *T* is air temperature (°K); Δ*t* is measurement duration (s); and *c* converts from mol to μmol (CO<sub>2</sub>) or nmol (CH<sub>4</sub>). CO<sub>2</sub> and CH<sub>4</sub> efflux data were quality-checked and 11 measurements of CH<sub>4</sub> efflux were omitted, owing to poor linearity due to variability in the data (*n* = 6) and CH<sub>4</sub> loss from the chamber (*n* = 5) (Table S2 in Supporting Information S1). Gas transfer velocities (*k*, m d<sup>-1</sup>) of CO<sub>2</sub> and CH<sub>4</sub> were calculated for comparison to other studies, using *J* and the concentrations of dissolved gas (mol m<sup>-3</sup>) in the stream (*c*<sub>water</sub>) and in equilibrium with the atmosphere (*c*<sub>sat</sub>) (Cole & Caraco, 2001). Excess carbon gas, calculated as a proportion (*c*<sub>water</sub>: *c*<sub>sat</sub>), was used to evaluate whether stream gas concentrations were oversaturated (*c*<sub>excess</sub> > 1, indicating gas loss to the atmosphere), undersaturated (*c*<sub>excess</sub> < 1), or in equilibrium (*c*<sub>excess</sub> = 1) with the atmosphere (Striegl et al., 2012). Additional details on gas efflux measurements are provided in Supporting Information S1.

### 2.3. Fluvial Carbon Fluxes and Yields

Lateral constituent fluxes were calculated as the product of constituent concentration and instantaneous stream discharge. To estimate CO<sub>2</sub> and CH<sub>4</sub> efflux at the watershed scale, we summed the product of *J*<sub>CO<sub>2</sub></sub> or *J*<sub>CH<sub>4</sub></sub> and fluvial surface area for each stream order in each watershed (Campeau et al., 2014; Zolkos et al., 2019). Fluvial surface area in each watershed, estimated as the product of mean stream width from field measurements and total stream length for each stream order (Methods S3 in Supporting Information S1). To constrain the effects of varying *J*<sub>CO<sub>2</sub></sub>, *J*<sub>CH<sub>4</sub></sub>, and stream width on upscaled efflux, we report the mean and range of upscaled fluvial *J*<sub>CO<sub>2</sub></sub> and *J*<sub>CH<sub>4</sub></sub>. These estimates do not capture fine-scale heterogeneity in aquatic gas efflux within individual stream reaches (e.g., Crawford et al., 2017), yet our sampling across stream orders attempts to capture variability in gas concentrations across scales (e.g., Hutchins et al., 2021) and allows for a first estimate of watershed-scale CO<sub>2</sub> and CH<sub>4</sub> efflux in western Arctic Canada. To assess how the types of carbon comprising fluvial fluxes varied among sites and regions, we calculated fluxes of individual carbon species relative to the total carbon flux at each site, henceforth termed proportional flux: *p* = species flux/total flux, where total flux equals the sum of efflux (*J*<sub>CO<sub>2</sub></sub> and *J*<sub>CH<sub>4</sub></sub>) and lateral fluxes of DIC, DOC, PIC, and POC.

To control for potential effects of watershed area on discharge and constituent concentration, constituent fluxes and stream discharge were normalized to watershed area to estimate daily constituent yields (μmol m<sup>-2</sup> d<sup>-1</sup>) and water yield (runoff; mm d<sup>-1</sup>). The relationship between carbon yield and runoff is useful for comparing watershed carbon sources and export, and reflects the degree to which carbon export may be limited by availabilities of carbon versus water (e.g., Striegl et al., 2005). The fluvial fluxes and yields that we estimate represent carbon export during the summer growing season. Varied environmental conditions during the year would likely



impart seasonal variability if we had extended our observations beyond the summertime. We focus on spatial instead of temporal variability in our data due to low sampling frequency ( $n \leq 3$  per site) (Table S1 in Supporting Information S1).

#### 2.4. Net Ecosystem Exchange and Fluvial Contributions to Ecosystem Carbon Balance

To assess the relative magnitudes of summertime fluvial and terrestrial carbon fluxes among the study regions, we compared our estimates of total fluvial carbon flux for each watershed with collocated estimates of mean NEE from June through August 2016. For this, we used the NASA Soil Moisture Active Passive Level 4 product (SPL4CMDL) (Kimball et al., 2018), which provides global gridded (9 km) daily estimates of NEE ( $\text{CO}_2$ ) using a satellite data-based terrestrial carbon flux model informed by satellite measurements of ecosystem properties including soil moisture, land cover, and vegetation, and the NASA Goddard Earth Observing System Model, version five (GEOS-5) land model assimilation system. For comparison with fluvial carbon fluxes in our study regions, we converted NEE estimates for each watershed to  $\text{kgC d}^{-1}$ , first subtracting the surface area covered by freshwaters (streams, lakes/ponds) from the total watershed area to obtain terrestrial area. To determine relative contributions of fluvial and terrestrial carbon fluxes to ecosystem carbon balance, we normalized our daily estimates of lateral fluxes ( $\Sigma[\text{DIC}, \text{DOC}, \text{PIC}, \text{and POC}]$ ) and total efflux ( $\Sigma[J_{\text{CO}_2}, J_{\text{CH}_4}]$ ) to NEE. Additional information is available in Supporting Information S1.

#### 2.5. Geospatial Analyses

We used ArcHydro tools in ArcGIS 10.5 software to delineate watersheds from the Canadian Digital Elevation Model, which we reconditioned using satellite imagery-adjusted stream vectors from the Natural Resources Canada National Hydro Network (NHN; <https://open.canada.ca>). To constrain the varied potential landscape controls on carbon cycling and balance, we used published geospatial data to characterize the distributions of surficial and bedrock geology (Côté et al., 2013; Lipovsky & Bond, 2014; Norris, 1985), lakes and ponds (NHN), soil organic carbon content (SOC) in the upper 1 m of soil (Hugelius et al., 2013), and vegetation GPP (Running et al., 2015). Mean summer air temperature ( $^{\circ}\text{C}$ ) and total summer precipitation (mm) of the study regions were calculated from daily data collected by Environment and Climate Change Canada meteorological stations in Inuvik, Fort McPherson, and Rock River (<http://climate.weather.gc.ca/>), and a Government of Northwest Territories meteorological station located on the Peel Plateau. Full methods for deriving watershed topography, geology, and estimates of vegetation productivity can be found in Supporting Information S1.

#### 2.6. Statistics

Statistics were performed using R software v.3.4.4 (R Core Team, 2018). To test for variation in hydrochemical and environmental variables during the summer sampling period (Table S1 in Supporting Information S1), we used the analysis of variance (ANOVA) function *aov* in the R software package *stats*. We included the interaction between sampling period and region as the independent variable, to account for environmental variability among regions while testing for temporal variation in dependent variables. We used redundancy analysis (RDA) to characterize environmental controls on carbon cycling across our study regions. Dependent variables in the RDA included measurements of gas efflux ( $J_{\text{CO}_2}$  and  $J_{\text{CH}_4}$ ) and carbon yields (DIC, PIC, DOC, and POC). Explanatory (environmental) variables included water quality and chemistry (water temperature, specific conductance, dissolved oxygen, pH, d-excess, and TDN yield) and landscape conditions (terrain slope, GPP, SOC 0–100 cm), percent distribution of surficial geology units (carbonate, colluvial, moraine, and organic), and lake coverage. The RDA used mean summertime values from the 18 of 33 sites for which all carbon species were measured. Prior to performing the RDA, values were log or square root transformed to achieve normality. To simplify the RDA, we performed automated stepwise model selection using the *ordistep* function from the R package *vegan* (Oksanen et al., 2018). To determine potential contributions from pluvial events to variation in stream chemistry and constituent export (Beel et al., 2021; Kokelj et al., 2015), we tested correlations between rainfall, stream chemistry, and total carbon export. Using data from the meteorological station nearest each region (Figure 1), we calculated total rainfall at 0, 12, 24, 48, 72, and 96 hr prior to sample collection at each site to test for immediate and delayed effects from rainfall on stream flow and constituent transport. Unless noted, values for individual sites are reported as summertime mean  $\pm$  standard error, values for study regions ( $n = 4$ ) are reported as the

means of individual sites  $\pm$  standard error, and values across all sites ( $n = 33$ ) as mean  $\pm$  one standard deviation ( $1\sigma$ ). Additional information is available in Supporting Information S1.

### 3. Results

#### 3.1. Physiographic and Meteorological Conditions Underlying Regional Ecosystem Variation

Physiographic and meteorological characteristics varied considerably among study regions (Table 1). These varied conditions in part underlie regional variation in hydrology. Runoff was highest on the Peel Plateau ( $4.5 \text{ mm d}^{-1}$ ), where total summertime precipitation was highest (238 mm), intermediate in the Richardson Mountains ( $2.6 \text{ mm d}^{-1}$ ), and lowest in the low-relief Mackenzie Lowlands and Travaillant Uplands (both  $\sim 0.5 \text{ mm d}^{-1}$ ). In the Mackenzie Lowlands and Travaillant Uplands, where lakes and ponds covered 7%–18% of the study watersheds (Table S3 in Supporting Information S1), lower d-excess values represented deviation from the global meteoric water line and stronger effects from evaporation on regional hydrology (Table S3 in Supporting Information S1).

#### 3.2. Stream Water Quality and Chemistry

Specific conductance was higher in streams in the previously unglaciated Richardson Mountains (mean =  $225 \mu\text{S cm}^{-1}$ ) than those in the ice-rich moraine Peel Plateau ( $149 \mu\text{S cm}^{-1}$ ), poorly drained Mackenzie Lowlands ( $95 \mu\text{S cm}^{-1}$ ), and rolling till plains of the Travaillant Uplands ( $82 \mu\text{S cm}^{-1}$ ). Temperatures were lower and dissolved oxygen levels higher in streams of the Richardson Mountains ( $5.6^\circ\text{C}$ ,  $11.0 \text{ mg L}^{-1}$ ) and Peel Plateau ( $7.1^\circ\text{C}$ ,  $11.1 \text{ mg L}^{-1}$ ) than in those of the Travaillant Uplands ( $11.6^\circ\text{C}$ ,  $8.6 \text{ mg L}^{-1}$ ) and Mackenzie Lowlands ( $13.0^\circ\text{C}$ ,  $9.9 \text{ mg L}^{-1}$ ). On average, pH was lower on the Peel Plateau (5.31) than in the other regions (6.65–6.86) (Table 2). Weathering ions plotted using a Piper diagram showed that all streams were characterized by  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$  type waters, with varying contributions from  $\text{H}_2\text{CO}_3$  versus sulfuric acid ( $\text{H}_2\text{SO}_4$ ) driven carbonate weathering (Figure 2).

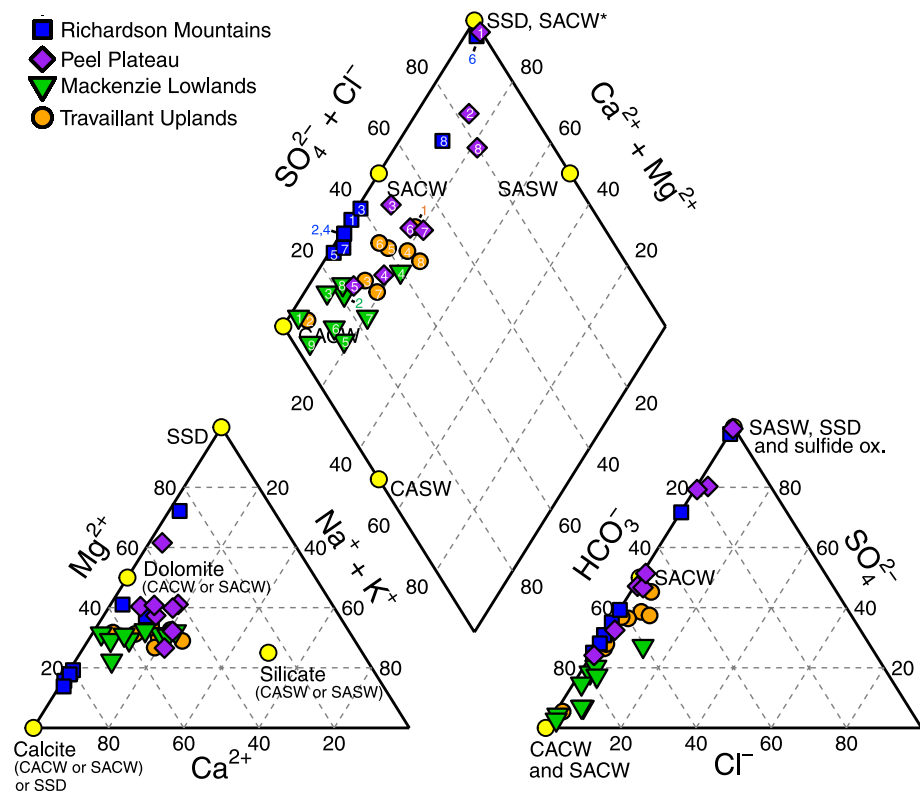
DOC was the primary carbon species in the Mackenzie Lowlands ( $1,900 \mu\text{M}$ ) and Travaillant Uplands ( $1,510 \mu\text{M}$ ), where organic surficial deposits were abundant (Table S3 in Supporting Information S1), and SOC and GPP were higher (Table 1). Across sites, DOC concentrations were strongly anticorrelated with mean watershed elevation ( $p_{31} < 0.001$ ,  $R^2 = 0.79$ ). DIC concentrations in streams of the Richardson Mountains ( $1,816 \mu\text{M}$ ) were two to six times higher than in the other regions and comprised primarily of  $\text{HCO}_3^-$  ( $1,730 \mu\text{M}$ ). Because pH among all sites was circumneutral to acidic,  $\text{CO}_3^{2-}$  was a minor component of DIC ( $\leq 0.3\%$ ). Concentrations of POC were relatively low for most regions ( $24$ – $99 \mu\text{M}$ ) except the Peel Plateau ( $2,483 \mu\text{M}$ ), where the highest POC concentrations were observed in with streams affected by hillslope RTS activity. Our analysis of 36 total PC samples from the Peel Plateau allowed for an estimate of a mean PIC:POC ratio of 0.15. We acknowledge that this ratio developed using suspended solids from Peel Plateau streams may vary in other regions due to, for instance, particulate composition. However, use of these ratios enables first-order estimates of total carbon and the carbon balance in a region where this has not been previously examined (Methods S4 in Supporting Information S1). Total dissolved and PC concentrations ( $\Sigma[\text{DIC}, \text{PIC}, \text{DOC}, \text{and POC}]$ ) were highest and most variable in streams of the Peel Plateau ( $4,400 \mu\text{M}$ ) (Table 2). Excluding RTS-affected streams, however, mean concentrations were slightly lower on the Peel Plateau ( $1,360 \mu\text{M}$ ) (Table S4 in Supporting Information S1) than in the other regions ( $1,770$ – $4,210 \mu\text{M}$ ).

Across all study sites,  $\delta^{13}\text{C}$ -DIC ( $-13.0\text{‰} \pm 4.4\text{‰}$ ) showed relatively greater variation than  $\delta^{13}\text{C}$ -DOC ( $-27.3\text{‰} \pm 0.3\text{‰}$ ),  $S_R$  ( $0.85 \pm 0.05$ ), and  $\text{SUVA}_{254}$  ( $3.77 \pm 0.58 \text{ L mgC}^{-1} \text{ m}^{-1}$ ), and thus provided more utility in discerning carbon sources and cycling. The span of  $\delta^{13}\text{C}$ -DIC values occurred across a large pH gradient, with paired values reflective of fractionation more strongly coupled to biotic production and atmospheric exchange of  $\text{CO}_2$  at lower pH, and increasing contributions from primarily  $\text{H}_2\text{CO}_3$  and/or  $\text{H}_2\text{SO}_4$  carbonate weathering at higher pH (Figure 3). On the Peel Plateau,  $\delta^{13}\text{C}$ -DIC was generally lower in non-RTS affected headwaters (PP-7 =  $-23.4\text{‰}$ ) than in larger RTS-affected watersheds (PP-8 =  $-5.9\text{‰}$ ). In the high pH streams of the Richardson Mountains, relatively constrained  $\delta^{13}\text{C}$ -DIC values ( $-8.3\text{‰}$  to  $-11.7\text{‰}$ ) aligned with DIC sourced primarily from carbonate weathering, whereas lower values in the Mackenzie Lowlands ( $-9.5\text{‰}$  to  $-17.5\text{‰}$ ) and Travaillant Uplands ( $-6.1\text{‰}$  to  $-18.4\text{‰}$ ) were indicative of biotic  $\text{CO}_2$  comprising a larger portion of DIC (Figure 3). Stronger biotic  $\text{CO}_2$  production in the Mackenzie Lowlands was also evidenced by  $p\text{CO}_2$  and  $p\text{CH}_4$  that were, on average, more than 30% higher than in the other regions (Table 2).

**Table 2**  
*Water Quality, Chemistry, and Carbon Fluxes in Streams of the Western Canadian Arctic*

Parameter	Units	Richardson Mountains	Peel Plateau	Mackenzie Lowlands	Travaillant Uplands
<i>Water quality and chemistry</i>					
Temperature	°C	5.6 (0.6)	7.1 (0.7)	13.0 (0.6)	11.6 (0.6)
Sp. conductance	μS cm <sup>-1</sup>	255 (51)	149 (76)	95 (13)	82 (7)
Dissolved oxygen	mg L <sup>-1</sup>	11.0 (0.3)	11.1 (0.4)	8.6 (0.7)	9.9 (0.7)
pH	pH units	6.86 (0.4)	5.31 (0.4)	6.68 (0.2)	6.65 (0.2)
DOC	μM	325 (75)	1,051 (198)	1,899 (303)	1,507 (104)
DIC	μM	1,816 (456)	298 (102)	776 (85)	578 (39)
POC	μM	24 (8)	2,483 (1,654)	56 (16)	99 (62)
PIC	μM	4 (1)	382 (255)	9 (2)	15 (10)
TC	μM	3,268 (174)	4,389 (1,973)	2,948 (383)	2,171 (244)
pCO <sub>2</sub>	μatm	1,300 (202)	1,537 (326)	2,700 (681)	1,592 (381)
pCH <sub>4</sub>	μatm	102 (55)	309 (93)	341 (56)	243 (97)
CO <sub>2</sub> excess	–	3.5 (0.3)	4.1 (0.5)	6.7 (1.1)	3.3 (0.5)
CH <sub>4</sub> excess	–	106 (73)	178 (52)	216 (35)	135 (55)
TDN	μM	18.4 (1.4)	29.4 (5.1)	52.4 (5.8)	37.0 (4.4)
DIN	μM	6.2 (1.7)	6.9 (3.3)	1.3 (0.2)	2.8 (1.2)
NH <sub>4</sub> <sup>+</sup>	μM	0.1 (0.02)	4.2 (1.2)	0.9 (0.1)	2.2 (0.8)
NO <sub>3</sub> <sup>-</sup>	μM	6.1 (1.3)	1.8 (0.6)	0.3 (0.2)	0.7 (0.2)
δ <sup>13</sup> C-DIC	‰ VPDB	–9.8 (0.9)	–14.8 (2.4)	–13.4 (1.4)	–13.7 (1.9)
δ <sup>13</sup> C-DOC	‰ VPDB	–27.3 (0.0)	–27.1 (0.1)	–27.5 (0.1)	–27.4 (0.0)
d-excess	–	7.0 (0.3)	8.7 (0.1)	–1.3 (1.6)	1.4 (1.7)
<i>Water and carbon fluxes</i>					
DOC flux	mmol s <sup>-1</sup>	104 (55)	139 (105)	463 (180)	695 (445)
DIC flux	mmol s <sup>-1</sup>	1,219 (735)	100 (98)	296 (167)	289 (189)
POC flux	mmol s <sup>-1</sup>	7.7 (3.1)	1,127 (908)	18.3 (6.2)	52 (40)
PIC flux	mmol s <sup>-1</sup>	1.2 (0.5)	174 (131)	2.8 (1.0)	8.0 (6.2)
TC flux	mmol s <sup>-1</sup>	1,070 (630)	1,643 (1,544)	1,037 (620)	1,321 (881)
DOC yield	μmol m <sup>-2</sup> d <sup>-1</sup>	949 (327)	4,812 (1,672)	1,040 (355)	754 (123)
DIC yield	μmol m <sup>-2</sup> d <sup>-1</sup>	3,453 (865)	984 (186)	408 (105)	275 (39)
POC yield	μmol m <sup>-2</sup> d <sup>-1</sup>	38 (9)	5,801 (3,515)	37 (9)	43 (22)
PIC yield	μmol m <sup>-2</sup> d <sup>-1</sup>	5.9 (1.5)	893 (541)	5.7 (1.4)	6.6 (3.4)
TC yield	μmol m <sup>-2</sup> d <sup>-1</sup>	5,777 (1,465)	12,715 (4,178)	2,068 (636)	1,188 (187)
J <sub>CO<sub>2</sub></sub>	μmol m <sup>-2</sup> s <sup>-1</sup>	4.3 (0.6)	3.7 (1.0)	5.6 (0.8)	4.2 (1.4)
J <sub>CH<sub>4</sub></sub>	nmol m <sup>-2</sup> s <sup>-1</sup>	32.4 (18.2)	46.0 (14.4)	24.7 (4.3)	19.0 (4.4)
k <sub>CO<sub>2</sub></sub>	m d <sup>-1</sup>	7.8 (0.9)	5.6 (0.7)	6.0 (0.9)	6.5 (1.1)
k <sub>CH<sub>4</sub></sub>	m d <sup>-1</sup>	172 (151)	15.1 (5.3)	8.7 (2.7)	9.9 (2.3)
Q	m <sup>3</sup> s <sup>-1</sup>	0.52 (0.31)	0.16 (0.10)	0.33 (0.16)	0.53 (0.35)
Runoff	mm d <sup>-1</sup>	2.6 (0.5)	4.5 (0.9)	0.5 (0.1)	0.5 (0.1)

*Note.* Values are regional mean ± standard error during the summertime study period. See Table S4 in Supporting Information S1 for mean ± standard error for each site. TC = total carbon (Σ[IC, OC]).



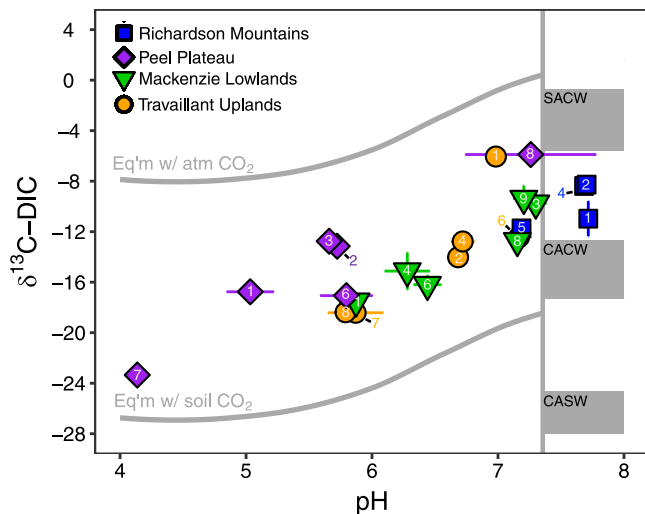
**Figure 2.** Piper diagram showing stream geochemistry as proportions of ion equivalent concentrations for the four study regions: Richardson Mountains (previously unglaciated), Peel Plateau (ice-rich tills), Mackenzie Lowlands (organic-rich), and Travaillant Uplands (rolling till plains). CACW =  $\text{H}_2\text{CO}_3$  carbonate weathering, SACW =  $\text{H}_2\text{SO}_4$  carbonate weathering, CASW =  $\text{H}_2\text{CO}_3$  silicate weathering, SASW =  $\text{H}_2\text{SO}_4$  silicate weathering, and SSD = sulfate salt (gypsum) dissolution. End members determined from equations in the text. Site numbers shown within symbols of upper diamond plot.

TDN was lowest in the Richardson Mountains (18  $\mu\text{M}$ ), intermediate on the Peel Plateau (29  $\mu\text{M}$ ) and in the Travaillant Uplands (37  $\mu\text{M}$ ), and highest in the Mackenzie Lowlands (52  $\mu\text{M}$ ) and, on average, comprised of 85% DON. Similar to DOC, SOC, and GPP, TDN was anticorrelated with mean watershed elevation ( $p_{18} < 0.001$ ,  $R^2 = 0.85$ ). DIN was highest on the Peel Plateau (6.9  $\mu\text{M}$ ) and in the Richardson Mountains (6.2  $\mu\text{M}$ ), and lower in the Travaillant Uplands (2.8  $\mu\text{M}$ ) and Mackenzie Lowlands (1.3  $\mu\text{M}$ ). DIN was primarily  $\text{NH}_4^+$  except in the Richardson Mountains, where DIN was primarily  $\text{NO}_3^-$  (Table 2).

### 3.3. Fluvial Carbon Fluxes in Total and by Species

Lateral fluvial carbon fluxes ( $\Sigma[\text{DIC}, \text{PIC}, \text{DOC}, \text{and POC}]$ ) were largest and most variable on the Peel Plateau ( $1,643 \pm 1,544 \text{ mmol s}^{-1}$ ), and smallest and least variable in the Mackenzie Lowlands ( $1,037 \pm 620 \text{ mmol s}^{-1}$ ) (Table 2). The ANOVA revealed no temporal variation in constituent concentrations or lateral fluxes during the summer sampling period (Table S5 in Supporting Information S1). Excess  $\text{CO}_2$  (range = 3.3–6.7) and  $\text{CH}_4$  (106–216) substantially greater than one indicated  $\text{CO}_2$  and  $\text{CH}_4$  efflux to the atmosphere, which was corroborated and quantified by direct measurements (Table 2, Table S4 in Supporting Information S1). Broadly,  $\text{CO}_2$  efflux trended opposite elevation and relief. Mean  $J_{\text{CO}_2}$  was highest in the low-relief, organic-rich Mackenzie Lowlands ( $5.6 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) and lowest on the Peel Plateau ( $3.7 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ). Rates of  $\text{CO}_2$  transfer were, on average, higher in the Richardson Mountains ( $k_{\text{CO}_2} = 7.8 \text{ m d}^{-1}$ ) than in the other regions (5.6–6.4).  $J_{\text{CH}_4}$  was higher and more variable in the relatively high-velocity streams on the Peel Plateau ( $46.0 \text{ nmol m}^{-2} \text{ s}^{-1}$ ) and Richardson Mountains ( $32.4 \text{ nmol m}^{-2} \text{ s}^{-1}$ ), where  $k_{\text{CH}_4}$  was also high and variable (mean for both regions =  $93.6 \text{ m d}^{-1}$ ) (Table 2).

The proportional fluxes of individual carbon species ( $p$ ) illustrate how the types of carbon comprising total fluvial carbon flux (lateral plus efflux) varied among regions. Mean proportional fluxes were generally highest



**Figure 3.** Composition of stable dissolved inorganic carbon isotopes ( $\delta^{13}\text{C-DIC}$ ) versus pH among the four study regions: Richardson Mountains (previously unglaciated), Peel Plateau (ice-rich tills), Mackenzie Lowlands (organic-rich), and Travaillant Uplands (rolling till plains). Mean values are shown with error bars representing range. In some cases, error bars are smaller than the symbol ( $n = 2$  for most points). Curvilinear reference lines depict theoretical end-members for equilibrium reactions with atmospheric and biogenic  $\text{CO}_2$ . Gray areas span theoretical end-member values for kinetically controlled mineral weathering reactions with atmospheric and biogenic  $\text{CO}_2$ . SACW =  $\text{H}_2\text{SO}_4$  carbonate weathering; CACW =  $\text{H}_2\text{CO}_3$  carbonate weathering; CASW =  $\text{H}_2\text{CO}_3$  silicate weathering. Site numbers shown within symbols. The vertical lines assist in visually distinguishing the pH at which  $<10\%$  of DIC is comprised of  $\text{CO}_2$  and thus kinetic reactions (weathering end-members) are inferred to have greater effects on stable isotope values than equilibrium reactions.  $\delta^{13}\text{C-DIC}$  values are reflective of isotope fractionation more strongly coupled to biotic production and atmospheric exchange of  $\text{CO}_2$  at lower pH, and increasing contributions from primarily  $\text{H}_2\text{CO}_3$  and/or  $\text{H}_2\text{SO}_4$  carbonate weathering at higher pH.

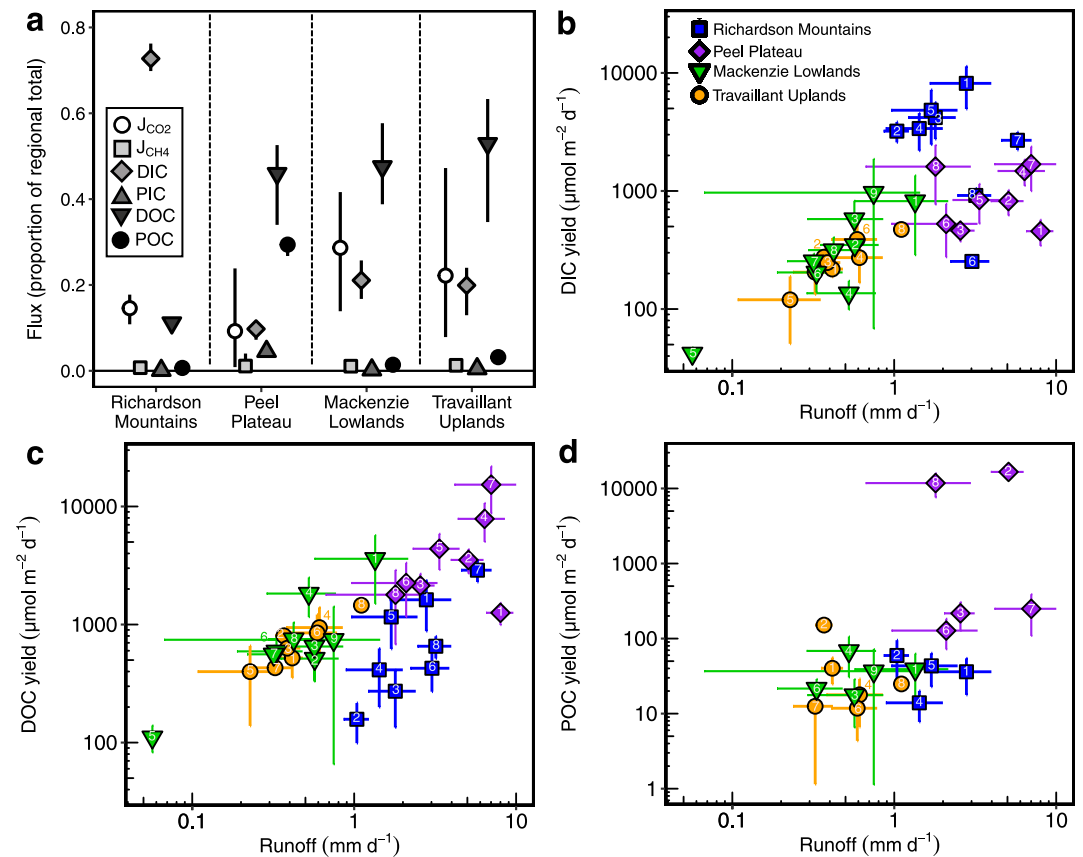
for DOC ( $\text{DOC}_p = 0.11\text{--}0.51$ ), DIC ( $0.10\text{--}0.74$ ), and  $J_{\text{CO}_2}$  ( $0.10\text{--}0.29$ ) (Figure 4a, Table S6 in Supporting Information S1). In the colluviated Richardson Mountains, DIC comprised the largest proportion of total carbon flux ( $0.74$ ), whereas carbon fluxes on the Peel Plateau were mostly DOC ( $0.46$ ) and POC ( $0.29$ ). On the Peel Plateau, lateral fluxes of POC in RTS-affected streams were roughly 10 times larger than in pristine streams and comprised  $66\%\text{--}69\%$  of the total fluvial carbon flux. DOC was the largest flux component in the organic-rich Mackenzie Lowlands ( $0.48$ ) and Travaillant Uplands ( $0.51$ ), followed by  $J_{\text{CO}_2}$  ( $\sim 0.26$ ) and DIC ( $\sim 0.20$ ). These proportional fluxes together with daily lateral fluvial carbon yields reinforced patterns in carbon cycling coupled to physiographic variation across study regions. In the Richardson Mountains, lateral yields across sites were moderate ( $5,800 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) and almost entirely comprised of DIC ( $66\%$ ) and DOC ( $13\%$ ). DIC yields were lower relative to runoff where silicate lithologies predominated (RM-6–8, PP-1–7), and higher where carbonate bedrock (RM-1–5) and RTS-activity (PP-8) were widespread (Figure 4b). On average, lateral yields for two RTS-affected watersheds (PP-2 and PP-8) on the Peel Plateau ( $20,300 \mu\text{mol m}^{-2} \text{d}^{-1}$ ) were more than five times higher than at all other sites (Table S4 in Supporting Information S1). This was primarily due to POC release, yet among all sites there were no clear trends between POC yield and runoff because disturbance effects overwhelmed other sources of between-catchment conditions (Figure 4d). In the Mackenzie Lowlands and Travaillant Uplands, organic carbon comprised more than  $75\%$  of the lateral yields. The relationship between dissolved carbon yields and runoff was similar for these two regions. Specific conductance, but not total carbon export, showed moderate albeit significant correlation with prior rainfall at several intervals for sites in the Richardson Mountains and Travaillant Uplands (Figures S1 and S2 in Supporting Information S1).

### 3.4. Multivariate Indicators of Regional Patterns in Carbon Cycling

Simultaneously evaluating carbon yields and geospatial metrics of physiographic conditions refined understanding of the associations between carbon cycling and regional environmental characteristics. The trimmed RDA retained significant variables for water quality, nutrients, and landscape factors (Table 3). The ANOVA revealed no temporal variation in these variables during the summer sampling period, except for GPP (Table S5 in Supporting Information S1), which decreased from June to August. RDA axis one (RDA1) and two (RDA2) were both significant. Broadly, RDA1 separated carbon export among gaseous, dissolved, and PC species. Most sites in the lake- and organic-rich Mackenzie Lowlands and rolling till plains of the Travaillant Uplands plotted in a cluster of negative values along RDA1, and were associated with more organic carbon (SOC), higher vegetation productivity (GPP), and higher  $\text{CO}_2$  and  $\text{CH}_4$  efflux (Figure 5). On the Peel Plateau, RTS-affected sites two and eight plotted with high RDA1 values and were associated with PC export. While RDA1 separated among carbon species, RDA2 was associated with regional differences in terrain relief and carbon accumulation. Along RDA2, sites in the southern Richardson Mountains were associated with higher DIC yields, specific conductance, and carbonate coverage, reflecting more intense physical erosion and chemical weathering of carbonate bedrock.

### 3.5. Fluvial Carbon Fluxes Relative to Net Ecosystem Exchange

Modeled estimates of NEE from SPL4CMDL ranged from  $-0.60 \text{ gC m}^{-2} \text{d}^{-1}$  in the Travaillant Uplands to  $-0.82 \text{ gC m}^{-2} \text{d}^{-1}$  in the Mackenzie Lowlands (Table 1). Estimated for the entire fluvial network in each watershed, upscaled fluvial effluxes of  $\text{CO}_2$  and  $\text{CH}_4$  were, on average, equivalent to  $2\%$  of NEE and total lateral carbon fluxes were, on average,  $15\%$  of NEE (Figure 6, Table S6 in Supporting Information S1). Considering all carbon species, total fluvial carbon flux ( $\Sigma[J_{\text{CO}_2}, J_{\text{CH}_4}, \text{DIC}, \text{DOC}, \text{PIC}, \text{and POC}]$ ) across regions was equivalent to  $17\%$  of NEE (range =  $4\%\text{--}59\%$ ). Among regions, total fluvial carbon flux relative to NEE was lowest in the Travaillant



**Figure 4.** Carbon fluxes and yields among the four study regions: Richardson Mountains (previously unglaciated), Peel Plateau (ice-rich tills), Mackenzie Lowlands (organic-rich), and Travaillant Uplands (rolling till plains). (a) Fluxes (mean  $\pm$  range) of carbon species in each region, shown as a proportion of the total in each region. Yields versus runoff for (b) dissolved inorganic carbon (DIC), (c) dissolved organic carbon (DOC), and (d) particulate organic carbon (POC). For panels (b–d), error bars represent mean  $\pm$  standard error.

Uplands (4%–13%) and Mackenzie Lowlands (5%–15%), where streamflow velocity was lower and GPP was higher, and higher in the Richardson Mountains (11%–25%). Total fluvial carbon fluxes relative to NEE were highest and most variable on the Peel Plateau (8%–59%), due to a first-order watershed with relatively high DOC flux (PP-7) and two RTS-affected watersheds with high lateral carbon fluxes relative to NEE (PP-2 = 52% and PP-8 = 57%) (Table S6 in Supporting Information S1).

## 4. Discussion

### 4.1. Stream Chemistry and Carbon Cycling Are Coupled to Varied Landscape Histories

In the western Canadian Arctic, regional variation in stream water chemistry reveals how geology and climate history since the LGM have shaped the evolution of landscapes along varied trajectories, giving rise to diverse contemporary ecosystems and modes of carbon cycling and defining potential trajectories of future change.

The high-relief Richardson Mountain study sites are beyond the westernmost limit of the LIS and are comprised of ice-poor colluvial slopes and exposed bedrock, resulting in enhanced erosion and chemical weathering. DIC yields in the Richardson Mountain sites alone were double the summed dissolved and PC yields in the Mackenzie Lowlands and Travaillant Uplands. Relatively high pH and stream water specific conductance, trends in major ions (Figure 2), and  $\delta^{13}\text{C}$ -DIC values (Figure 3) indicate that DIC in the southern Richardson Mountains sites derives mainly from carbonate weathering by  $\text{H}_2\text{CO}_3$ , likely from atmospheric  $\text{CO}_2$  dissolved within summertime rainfall and from minor contributions of organic acids from GPP within this relatively sparsely vegetated landscape. Sulfide oxidation and/or sulfate salt dissolution were most strongly indicated in the subset

**Table 3**  
Summary of the Significance of Landscape Covariates and Axes From the Redundancy Analysis (RDA) of Carbon Export, Stream Chemistry, and Landscape Characteristics

	df	<i>p</i>	<i>F</i>	Variance
<i>Covariate</i>				
pH	1	<0.01	52.1	4.61
Carbonate (%)	1	<0.01	27.2	2.41
Dissolved oxygen (%)	1	<0.01	14.3	1.27
Sp. conductance	1	<0.01	14.0	1.24
d-excess	1	0.01	7.7	0.68
TDN yield	1	0.02	6.4	0.57
Lakes/ponds (%)	1	0.02	5.5	0.49
SOC	1	0.02	5.3	0.47
Organic (%)	1	0.03	4.7	0.42
Slope	1	0.07	3.3	0.29
GPP	1	0.25	1.5	0.13
Residual	6	–	–	0.53
<i>RDA axis</i>				
RDA1	1	<0.01	206.0	9.12
RDA2	1	<0.01	43.5	1.93
RDA3	1	0.05	17.6	0.78
RDA4	1	0.34	14.9	0.66
RDA5	1	0.99	2.0	0.09
Residual	12	–	–	0.53

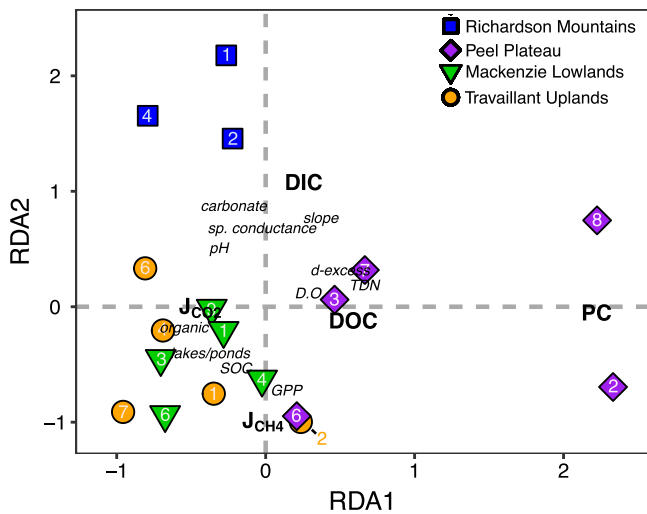
of watersheds in the Richardson Mountains containing shale lithologies (RM-6 and RM-8). High DIC yields and low DOC yields relative to runoff (Figures 4b and 4c) further emphasize relatively stronger contributions from mineral weathering to carbon cycling in the southern Richardson Mountains than in the other regions. While climate warming and permafrost thaw may not manifest in the Richardson Mountains as thaw-induced mass wasting as occurring on the ice-rich Peel Plateau, biogeochemical effects may be stark nonetheless: an increase in atmospheric CO<sub>2</sub> from 355 to 560 ppm is predicted to increase CO<sub>2</sub> drawdown by 50% via enhanced H<sub>2</sub>CO<sub>3</sub> carbonate and silicate weathering in the Richardson Mountains and elsewhere across the Mackenzie River Basin (Beaulieu et al., 2012). This enhanced weathering would contribute to a 18% increase in HCO<sub>3</sub><sup>-</sup> export from the Mackenzie River to the coastal Arctic Ocean, which could help to counterbalance future increases in ocean acidification associated with increasing riverine organic carbon export (Tank et al., 2012; Terhaar et al., 2019). This estimate does not account for thermokarst in watersheds of major tributaries like the Peel, where intensifying hillslope thermokarst is driving increased carbonate alkalinity concentrations and export through fluvial networks (Tank et al., 2016; Zolkos et al., 2020).

In contrast to the colluviated Richardson Mountains, intensifying thaw-driven mass wasting of ice-rich moraine deposits on the Peel Plateau enhances chemical weathering of carbonates, and fluvial fluxes of HCO<sub>3</sub><sup>-</sup> and particulates relative to non-RTS affected streams. Indeed, relatively high specific conductance and total carbon yields in streams on the Peel Plateau were driven by hillslope RTS-affected sites PP-2 and PP-8. Major ions and δ<sup>13</sup>C-DIC show that fluvial DIC in Peel Plateau streams originates mainly from H<sub>2</sub>SO<sub>4</sub> carbonate weathering—which is a CO<sub>2</sub> source over geological timescales (Calmels et al., 2007)—with some biotic CO<sub>2</sub> indicated by relatively depleted δ<sup>13</sup>C-DIC values. The signal of H<sub>2</sub>SO<sub>4</sub> carbonate weathering was strongest for site PP-8, which integrates biogeochemical effects of multi-

ple large hillslope RTSs. This aligns with the understanding that growth of RTSs on the Peel Plateau can mobilize increasingly greater quantities of deeper carbonate- and sulfide-bearing permafrost till to chemical weathering fronts (Kokelj et al., 2021; Zolkos et al., 2018). Our RDA further reveals that RTS activity shifts fluvial networks from conveyors of primarily dissolved carbon to PC (sites PP-2 and PP-8 in Figure 5) (Littlefair et al., 2017; Shakil et al., 2020). RTS-enhanced sediment and PC export on the Peel Plateau, observed in this and other studies (Kokelj et al., 2013; Shakil et al., 2020), is reflected in the orders of magnitude higher PC yields in RTS-affected sites PP-2 and PP-8 (Figure 4d).

Despite striking mobilization of permafrost carbon via hillslope thermokarst, the high rates of CH<sub>4</sub> efflux for three sites (PP-4, 5, 6; Table S4 in Supporting Information S1) in low-relief (mean slope = 2.8°) and relatively organic-rich watersheds (mean DOC = 1,200 μM) on the Peel Plateau highlights variation in carbon cycling even within the varied regions along our transect. Similar observations on the Peel Plateau and elsewhere indicate that spatial variability in the accumulation of organics is a primary driver of CH<sub>4</sub> production and efflux (Crawford et al., 2017; Zolkos et al., 2019). The negative correlation between *p*CH<sub>4</sub> and NO<sub>3</sub><sup>-</sup> (*p*<sub>18</sub> < 0.001, *R*<sup>2</sup> = 0.52), as well as *p*CH<sub>4</sub> and SO<sub>4</sub><sup>2-</sup> (*p*<sub>31</sub> < 0.001, *R*<sup>2</sup> = 0.68), indicates suppression of methanogenesis across regions, due to the presence of alternative electron acceptors that microbes use preferentially (Bridgman et al., 2013; Schädel et al., 2016).

In contrast to the Richardson Mountains and Peel Plateau, the Mackenzie Lowlands and Travaillant Uplands displayed starkly different aquatic environments and modes of fluvial carbon cycling. Stream temperatures and dissolved oxygen levels reflected warmer, less oxygenated conditions across these peatland-dominated and relatively lake-rich low-relief landscapes. Ions indicate that carbonate weathering also generated DIC in the Mackenzie Lowlands, but lower δ<sup>13</sup>C-DIC values suggest this weathering was more strongly coupled to H<sub>2</sub>CO<sub>3</sub> production from soil organic matter oxidation within the abundant peatlands and plant root respiration (Berner, 1992)



**Figure 5.** Ordination plot of redundancy analysis of mean summertime carbon yields (bold text) and landscape and water chemistry variables (italicized) among the four study regions: Richardson Mountains (previously unglaciated), Peel Plateau (ice-rich tills), Mackenzie Lowlands (organic-rich), and Travaillant Uplands (rolling till plains). Site numbers shown within points (Figure 1, Table S1 in Supporting Information S1). Peel Plateau sites 2 and 8 were downstream of active retrogressive thaw slump thermokarst features. DOC = dissolved organic carbon. PC = particulate organic and inorganic carbon.  $J_{CO_2}$  and  $J_{CH_4}$  =  $CO_2$  and  $CH_4$  efflux. D.O. = dissolved oxygen. TDN = total dissolved nitrogen yield. Sp. conductance = specific conductance. GPP = mean watershed gross primary productivity. SOC = mean watershed soil organic carbon content at 1 m depth. Slope = mean watershed percent coverage of landscape surface types. See units and details in text and Table 1.

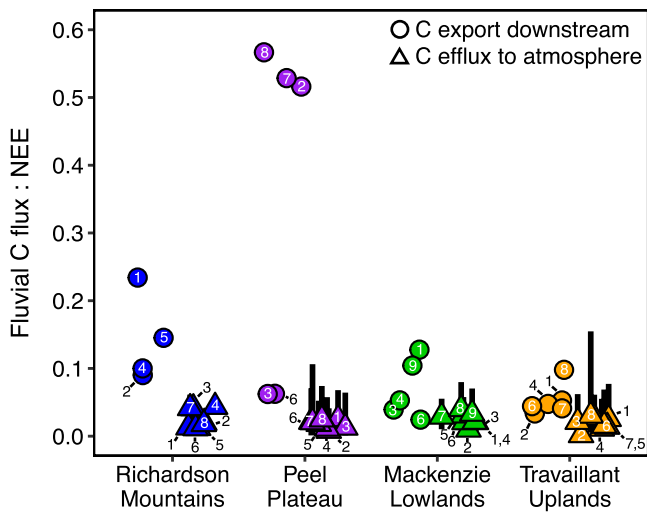
associated with relatively high vegetation productivity (i.e., GPP). Biotic contributions to the DIC pool were also indicated by high concentrations of DOC,  $pCO_2$ , TDN, and SOC, and also by  $\delta^{13}C$ -DOC values (Table 1) similar to  $\delta^{13}C$  of organic carbon in boreal and tundra soils (e.g., Bird et al., 2002; Hicks Pries et al., 2013), which together indicate that soil-stream linkages (e.g., Campeau et al., 2018) drive summertime carbon cycling in the poorly drained, organic-rich Mackenzie Lowlands. Lower  $Q$  and more negative  $d$ -excess values (reflecting greater evaporation) in the Mackenzie Lowlands are reflective of slower-moving water with longer residence times than in the high-relief fluvial networks of the Richardson Mountains and on the Peel Plateau. Longer water residence times in this relatively organic- and lake-rich wetland terrain likely enhanced carbon degradation, contributing to  $pCO_2$  and  $pCH_4$  supersaturation and a diffusion gradient supportive of the high aquatic  $CO_2$  and  $CH_4$  efflux we observed (e.g., Rocher-Ros et al., 2019).

Similar to the Mackenzie Lowlands, stream chemistry in the relatively lake- and organic carbon-rich Travaillant Uplands indicated that carbon cycling was driven by biotic processes. However, compared with the Mackenzie Lowlands, the lower SOC and low abundance of carbonate lithologies coupled with low runoff suggest that interactions between terrestrial carbon and flowing waters are relatively more limited in this terrain, as also reflected by the lower sum of dissolved plus PC concentrations (Table 1) and yields (Table S4 in Supporting Information S1). Over millennia, low topographic gradients within these poorly drained permafrost landscapes has favored the accumulation of organics, leading to the development of organic- and nutrient-rich soils and freshwaters that may become a net source of carbon to the atmosphere as the climate warms at northern high latitudes (Hugelius et al., 2020).

#### 4.2. Regional Fluvial Carbon Export and Contributions to Ecosystem Carbon Balance

The distinct ecosystems and associated modes of summertime carbon cycling that have emerged during the Holocene in the western Canadian Arctic (Section 4.1) underlie regional variation in aquatic carbon export and contributions to ecosystem carbon balance. In the Mackenzie Lowlands and Travaillant Uplands, our finding that lateral transport of DOC and biogenic  $CO_2$  efflux accounted for most of the fluvial carbon flux supports our hypothesis that carbon export would be dominated by organic species in these relatively low-relief, organic- and lake-rich terrains (Figure 4a). In these regions, SOC accumulation and microbial oxidation of organic carbon appear to drive carbon cycling and linkages across the terrestrial aquatic interface (Campeau et al., 2019). Despite this, lower runoff imposed by a shallow terrain gradient (Figure 1) reduces lateral export in these lowland regions compared with the Peel Plateau, where higher runoff mobilizes more organic substrate into fluvial networks (Figures 4c and 4d). While rainfall is known to significantly increase constituent export on the Peel Plateau (Kokelj et al., 2015) and in other permafrost terrains (Beel et al., 2021), we found no strong or consistent effects on stream chemistry or constituent export from rainfall prior to our stream sampling, perhaps because our sampling did not target the largest rainfall events (Figures S1 and S2 in Supporting Information S1). Thus, our estimates of constituent export are likely more conservative than if we had captured rainfall effects with targeted high-frequency sampling. Increased future rainfall at northern high latitudes (Bintanja & Andry, 2017) may partly alleviate hydrologic limitations to carbon export in regions where thaw does not temporarily enhance runoff (Connon et al., 2021), and prompt further divergence in summertime carbon cycling by enhancing PC export on the Peel Plateau (Kokelj et al., 2015). In the previously unglaciated, sparsely vegetated Richardson Mountains, lower DOC yields at comparable levels of runoff reflect source limitation imposed by sparser terrestrial organic carbon stores. Predominance of DIC yields (mainly as  $HCO_3^-$ ) in the Richardson Mountains emphasizes a primarily mineral weathering-driven pathway of atmospheric  $CO_2$  uptake, transfer into fluvial networks, and export to downstream environments. From a climate





**Figure 6.** The proportion of fluvial carbon flux relative to net ecosystem exchange (NEE) for sites among the four study regions: Richardson Mountains (previously unglaciated), Peel Plateau (ice-rich tills), Mackenzie Lowlands (organic-rich), and Travaillant Uplands (rolling till plains). Values are shown separately for lateral export (circles) and efflux to the atmosphere (triangles). Lateral export represents summed dissolved and particulate inorganic and organic carbon. Efflux to the atmosphere represents summed  $\text{CO}_2$  and  $\text{CH}_4$  efflux. Efflux was measured at every site in each region, whereas lateral export presented here is limited by the subset of sites at which particulate carbon was measured. Error bars for efflux span the estimated range of fluvial surface area. Error bars for lateral export are smaller than the data points.

perspective, DIC export throughout our study regions and the circumpolar north will continue to represent a  $\text{CO}_2$  sink or neutrality where  $\text{H}_2\text{CO}_3$  rather than  $\text{H}_2\text{SO}_4$  drives silicate and carbonate weathering (Zolkos et al., 2018).

Contributions from fluvial  $\text{CO}_2$  and  $\text{CH}_4$  efflux to total fluvial carbon fluxes in the Travaillant Uplands ( $26 \pm 4\%$ , mean  $\pm$  SE) and Mackenzie Lowlands ( $30 \pm 5\%$ ) were larger than in the Richardson Mountains ( $11 \pm 5\%$ ) and on the Peel Plateau ( $13 \pm 5\%$ ). However, we find that  $\text{CO}_2$  and  $\text{CH}_4$  efflux in the western Canadian Arctic accounts for a smaller proportion of total fluvial carbon fluxes than in the Yukon River basin ( $\sim 50\%$ ) (Striegl et al., 2007, 2012) and in Sweden (58%) (Humborg et al., 2010). Lakes cover 7%–18% of the landscape in the Mackenzie Lowlands and Travaillant Uplands (Table 1). Recent measurements of summertime lacustrine total  $\text{CH}_4$  efflux (diffusive plus ebullitive) made in the Mackenzie Lowlands were, on average,  $24.7 \text{ mgC m}^{-2} \text{ d}^{-1}$  (Kuhn et al., 2021). Assuming similar rates of  $\text{CH}_4$  efflux from lakes in the Mackenzie Lowlands and Travaillant Uplands during our study period, we estimate that fluvial and lacustrine effluxes would be 32% in the Travaillant Uplands and 48% in the Mackenzie Lowlands. Net  $\text{CO}_2$  and  $\text{CH}_4$  exchange between lakes and the atmosphere is expected to vary across the northern permafrost region in response to climate warming (Bogard et al., 2019; Walter Anthony et al., 2016) and should be included in future efforts to refine estimates of ecosystem carbon balance.

Our measurements of fluvial carbon flux combined with remote sensing estimates of NEE show that terrestrial productivity in all watersheds assimilated more carbon during the growing season than was lost via efflux and lateral fluxes within fluvial networks. During the shoulder seasons and winter, terrestrial photosynthesis ceases and summertime  $\text{CO}_2$  uptake is counterbalanced by  $\text{CO}_2$  emissions from ecosystem respiration (Natali

et al., 2019). While not captured by our observations, enhanced terrestrial carbon loss together with aquatic export outside of the growing-season may result in positive NECB annually. Our estimate that total fluvial carbon flux (lateral + efflux) was, on average, equivalent to 6%–38% of carbon uptake by terrestrial vegetation encompasses estimates for the Yukon River basin (14%) (Striegl et al., 2007, 2012), all of Alaska (16%–17%) (McGuire et al., 2018; Stackpoole et al., 2017), and all of Sweden (22%) (Humborg et al., 2010). However, we note that SPL4CMDL NEE, and thus the terrestrial component of our carbon balance assessment, does not include  $\text{CH}_4$  exchange, which is typically a net annual source of carbon from northern high latitude terrestrial ecosystems to the atmosphere (Kuhn et al., 2021; Natali et al., 2019). For future studies, we also note that SPL4CMDL estimates of NEE may be more representative of terrestrial  $\text{CO}_2$  exchange at multi-kilometer spatial scales similar to the area of the watersheds in this study (mean =  $50 \text{ km}^2$ ), as indicated by comparison between mean summertime NEE from SPL4CMDL and NEE observed within relatively small footprints of flux towers in boreal and tundra environments (Figure S3 and Table S7 in Supporting Information S1). Importantly, as indicated by this first step toward integrating terrestrial and aquatic carbon fluxes in the western Canadian Arctic presented here, permafrost thaw that manifests as hillslope mass wasting may have significant implications for both aquatic ecosystem function (Chin et al., 2016; Levenstein et al., 2018; Shakil et al., 2021) and ecosystem carbon balance (Song & Wang, 2021).

### 4.3. Intensifying Thaw-Induced Mass Wasting Defines New Trajectories of Permafrost Region Ecosystem Carbon Balance

Regional patterns in fluvial carbon cycling (Section 4.1) and contributions to ecosystem carbon balance (Section 4.2) observed in this study are primarily controlled by ecosystem conditions coupled to variation in geology and topography (RDA2 in Figure 5). These trends are skewed by the distribution of ice-rich till deposits, which are particularly susceptible to climate-driven mass wasting (Kokelj et al., 2021). Although terrains that may be susceptible to thaw-induced mass wasting like hillslope RTSs represent less than 5% of the northern permafrost region (Olefelt et al., 2016), these thaw features propagate and re-sequester terrestrial carbon across

increasing watershed scales (Kokelj et al., 2021; Shakil et al., 2020). On the Peel Plateau, RTSs cover <1% of the landscape, but may increase sediment and solute transport by several orders of magnitude (Kokelj et al., 2013; Malone et al., 2013; Zolkos et al., 2020) and enable up to a seven-fold increase in fluvial carbon flux where they occur (see also Shakil et al., 2020). Our measurements of fluvial carbon export on the Peel Plateau offer a striking glimpse of a shifting carbon balance that may come to typify pan-Arctic terrains susceptible to thaw-induced mass wasting. In watersheds directly affected by hillslope RTS, the magnitude of PC export approached 60% of net CO<sub>2</sub> uptake by vegetation (Figure 6 and Table S6 in Supporting Information S1). At a bulk level, POC mobilized by RTS on the Peel Plateau mainly consists of organic matter that is recalcitrant to biotic transformation, including petrogenic organic carbon (Bröder et al., 2021; Keskitalo et al., 2021; Shakil et al., 2021). While erosion of POC and its deposition along the freshwater-to-marine continuum is considered to be an effective mode of carbon sequestration for thousands of years (Goñi et al., 2005; Hilton et al., 2015), the balance between petrogenic oxidation and burial of biogenic organic carbon is important in determining whether the Mackenzie River basin is a net source or sink of carbon to the atmosphere (Horan et al., 2019).

Thermokarst also mobilizes elements other than carbon, as indicated by the elevated concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> observed in this study and elsewhere across the northern permafrost zone (Abbott et al., 2015; Lamhonwah et al., 2017). Complex interactions between carbon and other elemental cycles exist (e.g., Shaver et al., 1992), such as suppression of methanogenesis through the presence of alternate electron acceptors (Bridgham et al., 2013; Schädel et al., 2016), coupling between methanotrophy and nitrogen availability (e.g., Bodelier & Laanbroek, 2004; King, 1997; Liebner & Svenning, 2013), or a general lifting of nutrient limitations leading to stimulation of microbial growth and decomposition even of recalcitrant carbon (Abbott et al., 2015; Voigt et al., 2017; Wild et al., 2014). These linkages between carbon and nutrient cycles are not well studied in Arctic watersheds, but may become increasingly important, especially where intensifying thermokarst activity strengthens land-freshwater linkages (Kokelj et al., 2021).

As thermokarst activity like hillslope RTSs intensify in northwestern Canada (Segal et al., 2016), sediment transport and deposition within fluvial networks (Keskitalo et al., 2021) will likely emerge as a key process of regional ecosystem carbon balance. Our results emphasize that this trajectory of ecosystem carbon balance appears to typify thaw-driven renewal of post-glacial landscape evolution and is therefore likely to emerge in other ice-rich moraine deposits across the circumpolar north (Kokelj, Lantz, et al., 2017). The degree to which this mobilized carbon represents a source of CO<sub>2</sub>—and thus its susceptibility to biogeochemical transformation at a pan-Arctic scale—will influence the strength of the northern high latitude terrestrial carbon sink (Virkkala et al., 2021; Watts et al., 2021) and feedbacks to climate change (Turetsky et al., 2020). Future research priorities should include efforts to: constrain the sources, transformation, and fate of permafrost carbon along the terrestrial-freshwater-marine continuum, particularly in areas susceptible to thaw-induced mass wasting (Keskitalo et al., 2022; Shakil et al., 2022), and integrate terrestrial and aquatic carbon fluxes across permafrost terrains which exhibit varied modes of thaw (e.g., hillslope mass wasting, thermokarst lakes, and active layer deepening), to reduce uncertainty in northern ecosystem carbon balance and the implications for global climate.

## 5. Conclusion

In this study, we investigated how geology together with climate and ecosystem history gave rise to regional variation in present-day fluvial carbon cycling and ecosystem carbon balance in the western Canadian Arctic. We found significant variability in fluvial chemistry and ecosystem carbon balance coupled to diverse biophysical conditions reflected among unglaciated mountains, ice-rich moraine with thaw-driven mass wasting, and organic rich lowlands underlain by glacial tills. In the Richardson Mountains and RTS-affected tributaries of the Peel Plateau, where the exposure of mineral substrate was greatest, mineral weathering was enhanced and abiotic carbon cycling predominated. In the Mackenzie Lowlands and Travaillant Uplands, where low relief has enabled the accumulation of organic matter, hydrochemistry revealed that biotic processes dominated carbon cycling. Across ecoregions, fluvial carbon fluxes in watersheds not affected by thaw-induced wasting were, on average, equivalent to 6%–16% of NEE, and nearly 60% of NEE in watersheds affected by hillslope RTS activity due to amplified lateral carbon export. These results demonstrate that northern permafrost terrains susceptible to thaw-induced mass wasting (Kokelj, Lantz, et al., 2017) may drive emerging trajectories of ecosystem carbon balance, in which the quantity of thawed permafrost carbon mobilized into fluvial networks may be similar in magnitude to carbon uptake by terrestrial vegetation (Plaza et al., 2019). Permafrost thaw and strengthening

terrestrial-freshwater-marine connectivity across the pan-Arctic (Kokelj et al., 2021; Vonk et al., 2019) highlight the need for additional studies which integrate aquatic and terrestrial carbon and nutrient cycling to better constrain ecosystem carbon balance and potential climate feedbacks (Turetsky et al., 2020).

### Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

### Data Availability Statement

Data used in this study are publicly accessible via Zolkos et al. (2022). Code is available at <https://zenodo.org/badge/latestdoi/509124741>.

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