High biodegradability of riverine dissolved organic carbon in late winter in Hudson Bay, Canada

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Hudson Bay, at the southern margin of the Arctic Ocean, receives nearly one-third of Canada’s river discharge and approximately 5.5 Tg of riverine dissolved organic carbon (DOC) annually. Riverine DOC fluxes to Hudson Bay are expected to increase with climate change, but how this increase will influence the biogeochemistry of the coastal waters is largely unknown. In particular, the fate of riverine DOC that enters Hudson Bay during the dark, frozen winter period (roughly January to April) is poorly known despite high discharge from the large, regulated rivers of Hudson and James Bays at that time. Few studies have assessed the degradability of riverine DOC transported in winter anywhere across the Arctic, leaving unanswered questions regarding the impact of riverine DOC on the Arctic carbon budget, CO2 fluxes, and local food webs. Here, we assessed the biodegradability of DOC in riverine and coastal waters of southern Hudson Bay in late winter using 45-day incubation experiments. We found 24%–60% of the DOC in the rivers and on average 21% of the DOC in the immediate coastal waters to be biodegradable. Differences in biodegradability appeared to depend on properties of the rivers/watersheds and physical and biochemical processes in the aquatic environments. DOC biodegradability correlated strongly with DOC concentration, which was higher during winter than summer in all studied rivers and higher in the Nelson and Hayes Rivers, draining the Hudson Bay Lowlands than in most previously studied large rivers of the Arctic watershed. The Nelson River, regulated for hydropower production, had the highest winter DOC concentrations and most degradable DOC. The high biodegradability of Hudson Bay riverine DOC in late winter and high concentrations and fluxes of riverine DOC at that time imply strong leverage for future increases in DOC fluxes to impact the carbon cycle of these coastal waters.

Keywords: Carbon cycle, Remineralization, Freshwater, Arctic, Permafrost, Climate change

1. Introduction

Arctic rivers deliver a large amount of organic carbon to Arctic coastal waters each year. The Arctic Ocean receives approximately 11% of global river discharge (Lammers et al., 2001) and 33 Tg y⁻¹ of riverine dissolved organic carbon (DOC; McGuire et al., 2009), resulting in an Arctic “Riverine Coastal Domain” (Carmack et al., 2015) that contains the highest concentrations of land-derived DOC among the world’s oceans (Benner et al., 2005). In recent decades, climate change and human activity have led to increased river discharge (McClelland et al., 2006; McGuire et al., 2009; Dery et al., 2011), accelerated coastal erosion (Mars and Houssaknech, 2007), and permafrost thaw (Yvon et al., 2015), all leading to increased release and transport of riverine DOC to Arctic coastal waters. Amon et al. (2012) predict that DOC fluxes from Arctic rivers could increase in a warmer climate even if conditions are otherwise undisturbed.

The implications of the recent increase in riverine DOC transport to the Arctic Ocean for the carbon cycle and coastal marine environments are uncertain. For example, greater remineralization of riverine DOC may increase CO2 emission from arctic watersheds and coastal waters (Else et al., 2008, and references therein; Lapierre et al., 2013), thus decreasing the extent to which the Arctic Ocean acts as an atmospheric CO2 sink (McGuire et al., 2009; MacGilchrist et al., 2014; Yasunaka et al., 2018). On the other hand, riverine DOC may be an important source of energy for local food webs (Benner, 2005; Guillemette et al., 2017; Müller et al., 2018). Another possibility is that the biogeochemical changes associated with increased DOC loads will be minor. While most marine DOC is recycled efficiently by heterotrophic bacteria in the surface ocean (Bauer et al., 2013; Bendtsen et al., 2015), riverine DOC may be less biodegradable as it is mostly of terrestrial origin (i.e., tDOC), sourced from vascular plant materials that contain high concentrations of recalcitrant nitrogen-
free biomacromolecules (Ertel et al., 1986; Ittekott, 1988; Hedges et al., 1997). Moreover, DOC cycled and transported by inland waters undergoes varying degrees of mineralization in streams, rivers, and lakes before discharging to oceans (Tranvik et al., 2018; Hutchins et al., 2019), which may render the organic matter deposited to the coastal ocean even more recalcitrant. Indeed, Arctic riverine DOC traditionally has been considered refractory, given its apparent conservative behavior across the Eurasian continental shelf (Cauwet and Sidorov, 1996; Amon and Meon, 2004). This view was also somewhat supported by the results of a few river water incubation experiments demonstrating poor photodegradability (e.g., Osburn et al., 2009) and biodegradability (e.g., Kohler et al., 2003) of riverine DOC. However, Bianchi (2011) proposed a “new paradigm” based on the fact that only a small fraction of the organic matter dissolved in seawater or preserved in marine sediments appears to be land-derived despite massive amounts of terrestrial organic carbon entering the world’s oceans through rivers (referred to as “missing carbon”). Indeed, photo- and especially biodegradation of riverine DOC may occur to a much greater extent than proposed previously (cf. Hernes and Benner, 2002). Recent results indicate that biodegradation of riverine DOC by heterotrophic microbes is a more important remineralization mechanism (67%–94% of the total degradation) compared to photodegradation (Fichot and Benner, 2014; Lu et al., 2016). Biodegradation is thought to be an especially important removal mechanism in polar watersheds and the Arctic Ocean due to low insolation and long periods of ice cover, which limit photodegradation (Benner et al., 2005; Bélanger et al., 2006). Recent data also show that Arctic river DOC varies in composition between high and low flow conditions (Amon et al., 2012), implying that spring or summer observations of biodegradation potential ought not to be extrapolated to other seasons.

In this study, we conducted 45-day incubation experiments to examine the biodegradation of DOC during late winter (prefreshet) conditions in riverine and coastal waters of Hudson Bay. Located at the southern margin of the Canadian Arctic, Hudson Bay is even more strongly river-influenced than the Arctic Ocean, with an annual runoff yield of approximately 0.9 m (Granskog et al., 2011). Winter river discharge to Hudson Bay is a significant fraction of the annual total (ca. one-fifth) and increasing during recent decades in part to ongoing climate change and river regulation for hydropower production (Déry et al., 2016). We use the results of the incubation experiments to assess the biodegradation potential of DOC in late winter and to compare two contrasting Hudson Bay riverine coastal areas differing in amount and composition of DOC and in marine characteristics (e.g., salinity, stratification). The results provide some of the first information regarding biodegradability of wintertime riverine DOC within the Arctic watershed and point to basin properties including river regulation and dissolved nutrient concentrations as variables warranting further exploration in terms of their influence on the biodegradability of arctic riverine DOC.

2. Method

2.1. Study area

Hudson Bay (including James Bay) is a large (approximately 1.2 × 10^6 km^2) shelf sea that receives and processes Arctic Ocean outflow and then discharges it via Hudson Strait (Figure 1) to the Labrador Sea. Hudson Bay is ice-covered for up to 9 months of each year, with the exception of leads and polynyas, and the surrounding watershed contains the most southerly extent of permafrost in Canada (Figure 1). The location of Hudson Bay at the southern margin of the Arctic makes it more vulnerable to climate change including shortening of the season of sea ice cover (Hochheim and Barber, 2014) and hydrologic changes in the watershed (see also Macdonald and Kuzyk, 2011; Déry et al., 2016). Hudson Bay has a drainage basin of about 3.9 × 10^6 km^2 (Figure 1) and receives river inflow totaling more than 760 km^3 yr^-1 or about 30% of the total Canadian river runoff (Déry et al., 2011). Winter river discharge to southwestern Hudson and James Bays increased significantly between 1964 and 2013 due in part to hydroelectric development on several large rivers, which has altered natural hydrological cycles so that river flow rates remain high in winter when demand for hydropower production peaks (Déry et al., 2016).

With an abundance of wetlands, peatlands, and soil carbon in the Hudson Bay watershed (Godin et al., 2017), riverine inputs of DOC to Hudson Bay are very high relative to the surface area of the bay or its seawater volume (Granskog et al., 2011). James Bay and Hudson Bay river waters have been sampled opportunistically during ArcticNet-funded CCGS Amundsen expeditions and during irregular monitoring programs involving industry, government, and community partners. DOC concentrations in the sampled river waters range between 0.24 and 116 mg L^-1 (Granskog et al., 2007, 2014; Kirk and St. Louis, 2009; Rosa et al., 2012; Godin et al., 2017), with DOC fluxes and composition varying among individual watersheds in relation to climate, vegetation, permafrost distribution, and hydrology (Rosa et al., 2012; Godin et al., 2017). The annual riverine DOC inputs are estimated from the scarce data at approximately 5.5 Tg C (Mundy et al., 2010), which is an order of magnitude more than the inputs of particulate organic carbon (POC, 0.46 ± 0.33 Tg C; Kuzyk et al., 2009). Domiance of DOC over its particulate counterpart in river discharge is expected as many of the large rivers drain the massive permafrost-bound wetland/peatland of the Hudson Bay Lowlands (Godin et al., 2017). Within Hudson Bay, river runoff is introduced to a strong, anticlockwise, surface coastal current system that largely confines the river water to a coastal corridor approximately 100 km wide (Granskog et al., 2009, 2011; St-Laurent et al., 2011).

This study focuses on two subareas within the Hudson Bay riverine coastal domain: the southwestern Hudson Bay (SWHB) and southeastern Hudson Bay (SEHB) study areas (Figure 1). The coastal waters of SWHB receive discharge from the Nelson and Hayes Rivers. These rivers drain mainly flat-lying sedimentary rocks covered by unconsolidated Quaternary sediments (Rosa et al., 2012). The Nelson River has an extensive watershed (>1.1 × 10^6 km^2; Figure 1) that
contains many dams and other control structures. Its flow is augmented by partial diversion of the Churchill River resulting in a mean annual discharge of 109 km$^3$ yr$^{-1}$ (2004–2013) or one-seventh of the total discharge to Hudson Bay and the single largest river discharging to Hudson Bay (Déry et al., 2016). The regulation of the Nelson River results in a relatively flat hydrograph with high winter flows compared to unregulated rivers (Figure 2A). Most of the Nelson River basin is covered by boreal forest (Boreal Shield and Boreal Plains), but Prairies with agricultural land lie in the southwestern part of the basin (Godin et al., 2017; Figure 1). The lower 150 km of the Nelson River crosses the Hudson Plains in a deep valley incised into the flat Hudson Bay Lowlands, with near-vertical, permanently frozen river banks (Rosenberg et al., 2005; see inset photo in Figure 1). The annual DOC flux of the Nelson River represents more than one-fifth of the Bay’s total input at approximately 1.2 Tg C yr$^{-1}$ (Rosa et al., 2012). DOC concentrations in Nelson River water remain relatively high throughout winter, possibly because of abundant large lakes and wetlands in the catchment that continue to supply DOC when soils are frozen (Rosa et al., 2012). The Hayes River, which contributes to the same estuary as the Nelson River, is a smaller, unregulated river with a mean annual discharge of 21.3 km$^3$ yr$^{-1}$ (2004–2013; Dery et al., 2016). Its basin is relatively small and, similar to the neighboring Nelson River basin, spans the Boreal Shield and Hudson Plain eco-zones, with continuous and discontinuous permafrost covering the whole basin and boreal forest being the dominant type of vegetation (Godin et al., 2017; Figure 1).

The Nelson and Hayes Rivers discharge together into a large, mostly shallow (approximately 6 m), funnel-shaped estuary, which subsequently discharges onto a shallow, gently sloping marine shelf. The tide in the estuary is semidiurnal and the tidal range varies from 2 to 5 m for neap and spring tides, respectively (Wang et al., 2012).
Winter ice cover reduces tidal amplitude and range due to under-ice friction while increasing tidal velocity due to reduced channel cross-section (Wang et al., 2012). Hydraulic residence times for the estuary were estimated by Manitoba Hydro utilizing a calibrated MIKE3 HD model (RSW-Environnement Illimité Inc., 2014) coupled with a 3D transport module from the Danish Hydraulic Institute. The model results indicate that under an average flow of 3,500 m³ s⁻¹, the mean length of time a parcel spends in the estuary varies from <2 days at the Nelson River mouth to 40 days in the outer portion of the estuary (K Sydor, Manitoba Hydro, personal communication, 2019).

The watershed and coastal morphology of SEHB differs markedly from SWHB. Precambrian rocks create a more rolling topography, and small nearshore basins reach water depths of 100 m or more (Hudon et al., 1996). SEHB receives discharge directly from the Great Whale River, which is unregulated and similar in size to the Hayes River, having mean annual discharge of 19 km² yr⁻¹ for the period of 2004–2013 (Dery et al., 2016). SEHB is also in the path of James Bay outflow (Figure 1), which remains relatively fresh (salinity < 26) throughout the year, due to river inflow, and causes shallow stratification to be maintained throughout winter in SEHB (Eastwood et al., 2020). Tidal amplitudes are smaller in SEHB than in SWHB averaging <2 m. The Great Whale River drains a transitioning mixed forest-tundra zone (Taiga Shield; Figure 1), and the basin is covered by patchy and sporadic discontinuous permafrost (Godin et al., 2017). The annual DOC flux of the Great Whale River is approximately 0.12 Tg C yr⁻¹, an order of magnitude lower than the Nelson River (Rosa et al., 2012).

2.2. Sampling locations and environmental conditions during sampling

Water sample collection and measurement of temperature and salinity for this study were conducted from the river ice and landfast ice (approximately 1 m thick) in SWHB and SEHB between April 9 and April 13, 2017 (Table 1), prior to the start of spring freshet (Figure 2). The discharge of the Nelson River was about 3,500 m³ s⁻¹ during the sampling period (Figure 2). The Nelson River was partially ice-covered between Split Lake and the coast (Sentinel-1 hosted on SIKU.org: not shown), and the last 40 km stretch of river was completely ice-covered (Figure 3A). The Hayes River, which was flowing at approximately 400 m³ s⁻¹ (Figure 2), was ice-covered throughout its whole length (Figure 3A). Due to logistical constraints, surface samples were collected near the mouth of the Nelson and Hayes Rivers (Figure 3A). The Nelson/Hayes Estuary was ice-covered at the time of sampling except for an intermittent area of open water (flaw lead; Figure 3A), which is typical of this estuary throughout winter (Wang et al., 2012). The SWHB coastal sampling sites were evenly distributed over a distance of about 80 km along the landfast ice, paralleling the shoreline in an E-NE direction, and within 5 km of shore (Figure 3A). The water depth at these sampling sites varied from 3 to 5.5 m (Table 1). At the time of sampling, SWHB was receiving only approximately 1,400 µmol m⁻² s⁻¹ of photosynthetically active radiation, of which less than 4% was transmitted through the snow and ice cover at our sampling sites (L Dalman, personal communication, 2020). This small fraction implies that at the ice-covered portion of SWHB, riverine and coastal waters were receiving little light and had low photobleaching potential.

In SEHB, the river was completely ice-covered throughout its entire length in April 2017 and the Great Whale River estuary had a continuous cover of landfast sea ice (Figure 3B). Sampling sites S-1, S-2, and S-3 were close to the river mouth (Figure 3B), where previous work shows the river plume spreading out in a thin layer under the landfast ice (Ingram and Larouche, 1987). The water depth at these sampling sites ranged from 41 to 61 m (Table 1). The remaining SEHB sampling sites (S-4 and S-5) were located approximately 25 km away in a NE direction within 5 km of shore with water depths of 36.5 and 31 m, respectively (Table 1; Figure 3B).

2.3. Temperature and salinity measurements

Water samples were collected from depths of 1–6 m in SWHB and 1–50 m in SEHB using a Kemmerer sampler lowered through a hole cut in the landfast ice. The water was placed into an acid-cleaned amber Nalgene bottle and stored in a cooler to avoid freezing during transport by snowmobile back to the field lab. Subsequently, samples for salinity analysis were subsampled into precleaned glass bottles rinsed three times with sample water before filling. The in situ temperature and salinity measurements were performed using an Idronaut Ocean Seven CTD sensor with the temperature accuracy of ± 0.002 °C, conductivity accuracy of 0.003 mS cm⁻¹, and pressure (depth) accuracy of ± 0.05% full scale.

Water samples were shipped to the University of Manitoba for analyses. Salinity was measured on bottle samples using a Guildline Autosal 8400 salinometer with a precision of 0.002 or greater. Samples were standardized against the International Association for the Physical Sciences of the Ocean Standard Seawater. The salinity sample from the Great Whale River was lost, so that in this work we assume a near-zero salinity (0.05) as previously reported for Great Whale River water near the river mouth (Granskog et al., 2011).

2.4. Incubation experiments

DOC biodegradability and lability were assessed using incubation experiments that were started directly after sample collection and followed an incubation protocol modified from Vonk et al. (2015). Within a few hours of field sampling, samples were filtered through precombusted (4 h, 450 °C) 0.7-µm glass fiber filters. The filtrate was decanted into duplicate incubation sets of eight precleaned glass vials (20 mL volume). In total, there were 54 incubation sets: 11 duplicate incubation sets for samples collected in SWHB and 16 duplicate incubation sets for samples collected in SEHB. About 2 mL of headspace was left in each vial in order to avoid oxygen depletion and allow CO₂ outgassing during DOC degradation. The vials were tightly sealed and stored in the dark at 4 °C and shaken daily throughout the incubation period. The vials were acidified (200 µL of 2 M of hydrochloric acid (HCl) added) at different time points (T = 0, T = 0.3, T = 1,
Table 1. Stations sampled in the two study areas, southwestern Hudson Bay and southeastern Hudson Bay, as shown in Figure 3. DOI: https://doi.org/10.1525/elementa.2020.00123.t1

| Station | Latitude | Longitude | Bottom Depth (m) | Depth Sampled (m) | Date Sampled (2017) |
|---------|----------|-----------|------------------|-------------------|---------------------|
| NR      | 57.033   | −92.521   | N/A              | 1.0               | April 9             |
| HR      | 57.008   | −92.260   | N/A              | 1.0               | April 9             |
| W-1     | 57.098   | −91.972   | 5.0              | 1.0               | April 9             |
| W-1     | 57.098   | −91.972   | 5.0              | 3.0               | April 9             |
| W-2     | 57.158   | −91.711   | 4.0              | 1.0               | April 12            |
| W-3     | 57.162   | −91.714   | 4.5              | 1.0               | April 12            |
| W-3     | 57.162   | −91.714   | 4.5              | 2.0               | April 12            |
| W-4     | 57.223   | −91.402   | 3.0              | 1.0               | April 9             |
| W-4     | 57.223   | −91.402   | 3.0              | 3.0               | April 9             |
| W-5     | 57.246   | −91.405   | 5.5              | 1.0               | April 9             |
| W-5     | 57.246   | −91.405   | 5.5              | 6.0               | April 9             |
| GWR     | 55.280   | −77.642   | N/A              | 1.0               | April 12            |
| S-1     | 55.288   | −77.808   | 41.0             | 1.0               | April 11            |
| S-1     | 55.288   | −77.808   | 41.0             | 5.0               | April 11            |
| S-1     | 55.288   | −77.808   | 41.0             | 10.0              | April 11            |
| S-1     | 55.288   | −77.808   | 41.0             | 40.0              | April 11            |
| S-2     | 55.294   | −77.821   | 61.0             | 1.0               | April 12            |
| S-3     | 55.303   | −77.824   | 60.0             | 1.0               | April 12            |
| S-3     | 55.303   | −77.824   | 60.0             | 5.0               | April 12            |
| S-3     | 55.303   | −77.824   | 60.0             | 20.0              | April 12            |
| S-3     | 55.303   | −77.824   | 60.0             | 50.0              | April 12            |
| S-4     | 55.430   | −77.504   | 36.5             | 1.0               | April 13            |
| S-4     | 55.430   | −77.504   | 36.5             | 10.0              | April 13            |
| S-4     | 55.430   | −77.504   | 36.5             | 35.0              | April 13            |
| S-5     | 55.475   | −77.595   | 31.0             | 1.0               | April 13            |
| S-5     | 55.475   | −77.595   | 31.0             | 5.0               | April 13            |
| S-5     | 55.475   | −77.595   | 31.0             | 30.0              | April 13            |

NR = Nelson River; HR = Hayes River; W series = coastal waters near HR outflow; GWR = Great Whale River; S series = coastal waters near GWR outflow; N/A = not available.

\(T = 3, T = 8, T = 15, T = 25, \text{ and } T = 45 \text{ days}) \) in order to terminate microbial activity and lower pH of the water to remove inorganic carbon. The time series was designed to capture the dynamics of both rapid DOC degradation in the first few days and slower DOC degradation over a span of a few weeks to few months.

All plastic equipment used in the experiment, such as syringes, forceps, filter holders, and vial caps, were rinsed with 10% HCl, while glass equipment, such as vials, were precombusted at 550 °C for 6–12 h. Special care was taken at all times to avoid organic carbon contamination.

2.5. Analysis of DOC content

DOC analysis was conducted using a Thermalox™ TOC-TN analyzer employing the thermal catalytic oxidation technique. Each incubation set was analyzed fully during the same DOC analysis session so that the same calibration curve could be applied to the whole set. Because DOC concentrations spanned a wide range between the river and marine samples, a new calibration curve specific for the expected DOC range of the samples to be analyzed was generated for each DOC analysis session. Deep seawater reference material from the Hansell Laboratory (Rosenstiel School of Marine and Atmospheric Science, University of Miami) with a DOC range of 0.492–0.528 mg L⁻¹ was used as an additional calibration point when generating calibration curves for the low-DOC SEHB samples.

Five to eight injections were used for each sample depending on the coefficient of variation, which was considered valid when the coefficient was \(\leq 2%\). The lower the DOC concentration, the greater the number of injections.
that were needed to achieve a valid coefficient of variation. Coefficients of variation among duplicate samples were typically ≤5%.

2.6. Biodegradability and lability calculations

The DOC degraded during the total length of the incubation experiment was defined as biodegradable DOC (BDOC). The results of the incubation experiment were reported primarily as %BDOC (fraction of total DOC that was biodegraded) at time point x according to the following equation:

\[
\text{%BDOC} = \left( \frac{[\text{DOC}_{T=x} - \text{DOC}_{T=0}]}{\text{DOC}_{T=0}} \right) \times 100, \tag{1}
\]

where \( \text{DOC}_{T=0} \) is the initial DOC concentration, and \( \text{DOC}_{T=x} \) is the DOC concentration at time \( x \) days.

The lability of BDOC describes how fast the degradation of DOC is happening. In accordance with Kirchman et al. (1993), the BDOC degraded by Day 3 was defined as labile (L-BDOC) and the BDOC degraded from Day 3 to Day 45 was defined as semilabile (SL-BDOC). Hence, %L-BDOC is the fraction of the total DOC degraded by Day 3.

Additionally, the results of the incubation experiment were reported with biodegradation rate constants, \( k' \) and \( k'' \), which were computed from the following equations describing the microbial degradation rates of L-BDOC and SL-BDOC, respectively:

\[
\text{DOC}_{T=x} = \text{DOC}_{T=0} \times e^{-k't_x} \text{ for } 0 \leq x \leq 3, \tag{2.1}
\]

\[
\text{DOC}_{T=x} = \text{DOC}_{T=3} \times e^{-k''t_x} \text{ for } 3 \leq x \leq 45, \tag{2.2}
\]

where \( \text{DOC}_{T=0} \) is the initial DOC concentration, and \( \text{DOC}_{T-x} \) is the DOC concentration at time \( x \) days.

3. Results

3.1. Physical characteristics of the riverine and coastal waters

The temperatures of the riverine and coastal waters were close to their respective freezing points in mid-April 2017,
except for subsurface waters below depths of 15–25 m in SEHB, which were slightly warmer (−0.8 °C; Figure 4). In SWHB, the shallow water column (<6 m) was well mixed (W-2) to weakly stratified (remaining stations) with surface salinity ranging from 1 to 12 and bottom salinity ranging from 1 to 17 (Figure 4A). Surface salinity in SWHB

Figure 3. The two riverine coastal study areas on April 11, 2017, with locations of sampling sites. The southwestern Hudson Bay area (A) and southeastern Hudson Bay area (B) are shown by satellite imagery (Sentinel-1, Google Earth, and SIKU.org by Arctic Eider Society). In Panel A, the dark area is open water, which is surrounded by mobile pack ice, and the landfast ice is the band that lies parallel to shore with an irregular outer edge. The landfast ice is ridged near the shoreline because it goes up and down with the large tides and interacts with the seabed. In Panel B, the snow-covered land is light-toned and the landfast sea ice is darker. DOI: https://doi.org/10.1525/elementa.2020.00123.f3
increased with increased distance from the river mouths (compare stations W-2 and W-3, located approximately 35 km northeast of the Hayes River mouth, to stations W-4 and W-5, located about 60 km northeast of the Hayes River mouth). However, Site W-1, closest to the Hayes River mouth, had a surface salinity of approximately 10, likely because the sample was collected at high tide and the discharge from the Hayes is relatively weak at this time of year. Overall, the range of salinity in SWHB samples (0.06–16.51) was much narrower than that in SEHB samples (0.11–29.3) with the latter group having mostly very low or very high salinities (Figure 4C). The vertical profiles of salinity and temperature in SEHB (Figure 4B) indicate a highly stratified under-ice plume, which is associated with the Great Whale River (Ingram and Larouche, 1987). Low-salinity (<4) river plume waters extend to a depth of 3–5 m and overlie cold, saline waters (25–29) at intermediate depths (Figure 4C). Warmer, slightly saltier waters underlie the cold, saline waters extending from depths of 20–30 m to the bottom (Figure 4B). A warm, salty subsurface water mass has been seen previously in southeast Hudson Bay, presumably a remnant from the previous summer (Petrusevich et al., 2018; Eastwood et al., 2020). Despite this regional feature, a strong linear relationship exists between temperature and salinity ($p << .001, R^2 = .86$) across all the collected samples, which indicates mixing between fresh, cold (approximately 0 °C) river waters and a common salty (approximately 26), colder (approximately –1.3 °C) marine water mass (Figure 4C).

### 3.2. In situ concentrations of DOC

In situ DOC concentrations in the Nelson and Hayes Rivers and in SWHB were higher than in the Great Whale River and SEHB (Figure 5). The Nelson, Hayes, and Great Whale Rivers had DOC concentrations of 23.6, 14.2, and 8.2 mg L$^{-1}$, respectively. SWHB coastal samples had DOC concentrations ranging between 10.2 and 17.3 mg L$^{-1}$, and SEHB coastal samples had DOC concentrations ranging between 1.9 and 6.9 mg L$^{-1}$.

In SWHB, there was no statistically significant, linear relationship between DOC concentration and salinity, reflecting nonconservative behavior of riverine DOC across the Nelson/Hayes Estuary and/or influence of both high-DOC (Nelson) and low-DOC (Hayes) riverine sources (Figure 5). After a drop in DOC concentrations as salinity increased from 0 to 3, DOC concentrations increased slightly around a salinity of 10 (Figure 5). In SEHB, the data distribution appeared to be bimodal in terms of salinity, which may be attributed to the high stratification of the coastal waters. If, however, we assume a linear relationship between DOC and salinity ($R^2 = .54$, but the assumption of data normality is not met), then DOC concentration decreased by 0.12 mg L$^{-1}$ per unit of salinity increase (Figure 5).

### 3.3. DOC biodegradation

Table 2 summarizes the results of the microbial degradation experiments. The Nelson, Hayes, and Great Whale rivers contained 60%, 33%, and 24% BDOC, respectively, while BDQC in coastal waters was 16%–65% (averaging 23% with standard error of the mean, SEM, ± 4%). The $k'$ values for the Nelson, Hayes, and Great Whale rivers calculated according to Equation 2.1 were 0.236 d$^{-1}$ ($R^2 = .75$), 0.059 d$^{-1}$ ($R^2 = .99$), and 0.027 d$^{-1}$ ($R^2 = .67$), respectively, while the $k'$ values (Equation 2.2) ranged between 0.003 and 0.005 d$^{-1}$ ($R^2 > .55$). The $k'$ values for the coastal ocean reached 0.262 d$^{-1}$ with the mean = 0.049 (SEM ± 0.014; each $R^2 > .50$), while the $k'$ values...
for the coastal ocean reached 0.008 d\(^{-1}\) with the mean = 0.002 (SEM ± 0.001; each \(R^2 > .55\)).

The DOC concentrations measured at intervals over the incubation period (45 days) are shown in Figure 6. For both SWHB and SEHB samples, DOC concentrations declined within the first 3 days. For SWHB, DOC concentrations continued to decline more slowly throughout the first one-third (15 days) of the experiment (Figure 6). For SEHB, little change occurred between 3 and 15 days. Despite the large early decreases in SWHB DOC concentrations, they remained well above SEHB DOC concentrations throughout the incubation period.

Figure 7 expresses the results for each river and estuary in terms of the proportion of DOC that was biodegradable overall (\(\%\)BDOC) and the relative proportions of L-BDOC and SL-BDOC to that BDOC total. Approximately one-half of the BDOC in SWHB coastal waters and about three-quarters of the BDOC in SEHB coastal waters was degraded by Day 3 (by definition L-BDOC; Figure 7). The BDOC in Nelson River water was dominated by L-BDOC, whereas the Hayes River water and the SWHB coastal water had equivalent contributions of L-BDOC and SL-BDOC. Interestingly, the Great Whale River BDOC was mostly semilabile, but the SEHB coastal waters contained an even representation of L-BDOC and SL-BDOC. In other words, the relative contribution of L-BDOC to total BDOC increased from the Great Whale River to the SEHB coastal waters (Figure 7). The relative contribution of L-BDOC in SEHB coastal waters was nearly on par with that of the Nelson River.

The \(\%\)BDOC in relation to the initial DOC concentration and salinity is presented in Figure 8. Overall, \(\%\)BDOC increased with DOC concentration, but at different rates depending on the location and salinity. In SEHB, \(\%\)BDOC and DOC concentrations were related linearly to the high salinity (14.6–29.2) and low DOC waters (\(p < .001, R^2 = .94\)), and the increase in \(\%\)BDOC with increasing DOC is so steep that \(\%\)BDOC reaches >50\% for DOC concentrations ≥5 mg L\(^{-1}\) (Figure 8). In low-salinity SEHB waters (0.05–2.93), the \(\%\)BDOC-DOC relationship has a very similar slope to that of the high salinity waters at low DOC concentrations but levels off at DOC concentrations above 7 mg L\(^{-1}\) and BDOC of approximately 23\%. In SWHB, which has only low-salinity waters, \(\%\)BDOC increases with initial DOC concentrations but at a much slower rate than in SEHB. The \(\%\)BDOC-DOC relationship in SWHB waters seems to level off when \(\%\)BDOC reaches 60\% (Figure 8).

4. Discussion

4.1. DOC concentrations

4.1.1. DOC concentrations in rivers

The Nelson and Hayes Rivers had higher DOC concentrations than the Great Whale River in late winter, consistent with previous reports that the Nelson and Hayes Rivers on average contain two to six times greater DOC concentration than other Hudson Bay rivers (Mundy et al., 2010). The boreal forest, wetlands/peatlands, and thawing permafrost covering the Nelson and Hayes River drainage basins (Smith et al., 2015; Godin et al., 2017) are expected to leach a large amount of DOC to the rivers (Benner et al., 2004; Rontani et al., 2014). The much higher DOC of the Nelson River (23.6 mg L\(^{-1}\)) versus Hayes River (14.2 mg L\(^{-1}\)) in April was unexpected, given that similar concentrations are found in the two rivers during summer (Granskog et al., 2011; Godin et al., 2017). The higher DOC concentrations in the Nelson have been noted as remaining high during winter (Rosa et al., 2012), perhaps due to sustained supplies from lakes, reservoirs, and wetlands throughout the winter period when soils are frozen. To our knowledge, there are no previous winter DOC data for the Hayes.

Little is known about the sources of DOC in the Nelson River. Kirk and St. Louis (2009) found wide variation in
DOC concentrations (15.1 ± 19.7 mg L⁻¹, n = 66) when they conducted biweekly sampling in the northern part of the Nelson River at the Limestone Generating Station (120 km from the river mouth). Particularly high concentrations (>20 mg L⁻¹) occurred irregularly but always during periods of relatively high flow (>3,000 m³ s⁻¹; see Figure S1 in Kirk and St. Louis, 2009). Manitoba Hydro’s monitoring data associated with the Keeyask development (https://keeyask.com/wp-content/uploads/2020/06/PEMP-2020-01-Physical-Environment-Monitoring.pdf) indicate a typical DOC concentration of 8–10 mg L⁻¹ for the open-water season. However, DOC concentrations in the Nelson River also vary from place to place. Data (n = 851 samples) collected throughout the Nelson River watershed as part of the Coordinated Aquatic Monitoring Program (2014) show clustering of high DOC concentrations in the northern part of the basin (Figure 9). Small tributaries and backbays monitored during the open-water period have high concentrations of DOC (>20 mg L⁻¹; T Papakyriakou, personal communication, 2020).

In comparison to other major northern rivers (Holmes et al., 2018), the Nelson clearly emerges as a DOC-rich river (Figure 10). DOC concentrations measured across this and previous studies (Kirk and St. Louis, 2009; Rosa et al., 2012; Godin et al., 2017) place the Nelson River at the upper end of the range for major northern rivers, particularly during winter (Figure 10). Presumably, DOC supply from the Nelson watershed is stronger especially

### Table 2. Results of the microbial degradation experiments performed for the two study areas: southwestern Hudson Bay and southeastern Hudson Bay. DOI: https://doi.org/10.1525/elementa.2020.00123.t2

| Station | Depth (m) | Salinity | Temperature (°C) | DOC (mg L⁻¹) | BDOC* (%) | L-BDOC* (%) | k' (d⁻¹) | k* (d⁻¹) |
|---------|-----------|----------|-----------------|--------------|------------|-------------|----------|----------|
| NR      | 1         | 0.15     | 0               | 23.6         | 60         | 53          | 0.236    | 0.003    |
| HR      | 1         | 0.06     | 0.05            | 14.2         | 33         | 16          | 0.059    | 0.005    |
| W-1     | 1         | 10.9     | −0.61           | 16.6         | 25         | 15          | 0.038    | 0.003    |
| W-1     | 3         | 11.4     | −0.64           | 14.2         | 24         | 15          | 0.041    | 0.002    |
| W-2     | 1         | 0.97     | −0.03           | 12.3         | 16         | 9           | 0.023    | 0.002    |
| W-3     | 1         | 2.94     | −0.16           | 17.3         | 40         | 35          | 0.099    | 0.001    |
| W-3     | 2         | 3.05     | −0.16           | 10.2         | 0          | 0           | 0        | 0        |
| W-4     | 1         | 8.46     | −0.46           | 13.0         | 22         | 16          | 0.052    | 0.002    |
| W-4     | 3         | 9.37     | −0.52           | 13.4         | 26         | 8           | 0.022    | 0.004    |
| W-5     | 1         | 11.76    | −0.62           | 15.1         | 37         | 5           | 0.017    | 0.008    |
| W-5     | 6         | 16.51    | −0.86           | 12.5         | 42         | 20          | 0.061    | 0.007    |
| GWR     | 1         | N/A      | 0.05            | 8.2          | 24         | 8           | 0.027    | 0.005    |
| S-1     | 1         | 0.11     | 0.05            | 6.0          | 16         | 16          | 0.043    | 0        |
| S-1     | 5         | 14.75    | −0.59           | 2.4          | 0          | 0           | 0        | 0        |
| S-1     | 10        | 26.28    | −1.33           | 5.0          | 55         | 51          | 0.244    | 0.002    |
| S-1     | 40        | 28.84    | −0.91           | 1.9          | 0          | 0           | 0        | 0        |
| S-2     | 1         | 0.72     | −0.04           | 5.2          | 0          | 0           | 0        | 0        |
| S-3     | 1         | 2.93     | 0.06            | 6.9          | 21         | 10          | 0.028    | 0.003    |
| S-3     | 5         | 23.64    | −1.10           | 3.2          | 16         | 7           | 0.026    | 0.002    |
| S-3     | 20        | 26.89    | −1.38           | 3.3          | 28         | 15          | 0.043    | 0.004    |
| S-3     | 50        | 29.30    | −0.73           | 2.0          | 0          | 0           | 0        | 0        |
| S-4     | 1         | 1.35     | −0.06           | 6.6          | 23         | 23          | 0.052    | 0        |
| S-4     | 10        | 25.57    | −1.22           | 5.7          | 59         | 35          | 0.133    | 0.008    |
| S-4     | 35        | 27.71    | −0.83           | 2.9          | 0          | 0           | 0        | 0        |
| S-5     | 1         | 24.60    | −1.33           | 2.5          | 0          | 0           | 0        | 0        |
| S-5     | 5         | 25.61    | −1.36           | 2.3          | 0          | 0           | 0        | 0        |
| S-5     | 30        | 27.04    | −1.34           | 5.4          | 65         | 57          | 0.262    | 0.004    |

NR = Nelson River; HR = Hayes River; W series = coastal waters near HR outflow; GWR = Great Whale River; S series = coastal waters near GWR outflow; N/A = not available; DOC = dissolved organic carbon.

*aFraction of total DOC that is biodegraded (BDOC); L-BDOC is the fraction of BDOC degraded by Day 3.*
during winter due to its sub-Arctic setting and more extensive wetlands. With these high DOC concentrations and relatively high flows maintained during winter by regulation, the Nelson River winter DOC fluxes would likely exceed those of the Mackenzie, Yenisei, and Ob Rivers despite their larger size.

4.1.2. DOC concentrations in the coastal waters
The high DOC flux from the Nelson River in April (6,730 t day⁻¹, assuming 3,300 m³ s⁻¹ and DOC concentration of 23.6 mg L⁻¹), together with the flux from the Hayes (440 t day⁻¹, assuming 360 m³ s⁻¹ and 14.2 mg L⁻¹, respectively), produces a low-salinity, high-DOC estuarine environment in SWHB coastal waters (Figure 5). These conditions are not unusual in the Arctic, where high concentrations of DOC in surface coastal waters are sourced from river discharge containing higher concentrations of terrigenous DOC (Amon and Benner, 2003), but they are rarely described in winter. In contrast, SEHB coastal waters are characterized in April by very fresh

Figure 6. Change in DOC concentration with time during 45-day incubation experiments. The blue and red borders separate labile (L) and semilabile (SL) fractions of BDOC based on degradation time. Data from the Nelson and Hayes Rivers pertain to the southwestern Hudson Bay (SWHB) coastal samples; data from the Great Whale River pertain to the southeastern Hudson Bay (SEHB) coastal samples. DOC = dissolved organic carbon; BDOC = biodegradable DOC. DOI: https://doi.org/10.1525/elementa.2020.00123.f6

Figure 7. Biodegradable fraction of total DOC with labile and semilabile proportions in riverine and coastal samples. Labile (L-BDOC) versus semilabile (SL-BDOC) proportions of the biodegradable fraction of total DOC (%BDOC) are shown for river samples and coastal samples from southwestern Hudson Bay (SWHB) and southeastern Hudson Bay (SEHB). Error bars indicate standard error of the mean (n = 9 for SWHB; n = 15 for SEHB). DOC = dissolved organic carbon. DOI: https://doi.org/10.1525/elementa.2020.00123.f7
(approximately 0) river plume waters overlying salty (25–30) waters with DOC concentrations nowhere exceeding 7 mg L\(^{-1}\) (Table 1; Figure 5). In both environments, DOC concentrations show a tendency to decrease with increasing salinity (Figure 5), as expected from the low DOC concentrations (1.3 mg L\(^{-1}\)) in marine waters of Hudson Bay (Mundy et al., 2010). Conservative mixing of riverine and marine water masses would yield a linear salinity–DOC relationship with a steeper slope for the SWHB coastal area where DOC concentrations in river water were higher (cf. Hansell et al., 2004). The nonlinear salinity–DOC relationship that we observed in SWHB (Figure 5) thus provides a first indication that the DOC supplied by the Nelson and Hayes Rivers is more labile and/or degradable than that supplied by the Great Whale River.

### 4.2. DOC biodegradation

#### 4.2.1. %BDOC and lability in rivers

Comparison of %BDOC values for the three Hudson Bay rivers and other Arctic rivers (Table 3) indicates relatively high biodegradability of Hudson Bay riverine DOC in late winter. The values in the table vary widely but in general fall within the range of 10%–40% BDOC after 1–3 months of incubation; the available data are biased...
toward the summer season and incubation temperatures of 15 °C and 20 °C. In view of the low incubation temperature, we used 4 °C, which might be expected to limit microbial degradation, the %BDOC results for the Hayes and Great Whale Rivers are notable for their comparability to those reported for other Arctic rivers. The 60% BDOC of the Nelson River is exceptional (Table 3). We speculate that continued DOC supply during winter (e.g., from reservoirs, wetlands/peatlands, and thawing permafrost) together with better preservation during transport compared to open-water conditions account for the high biodegradability of the Hudson Bay riverine DOC and the Nelson River DOC, specifically.

Permafrost is extensive near the mouth of the Nelson and Hayes Rivers, and its degradation is associated with increasing river bank instability (Stainton, 2019; K Skaftefeld, personal communication, 2020). Permafrost DOC is not only biodegradable but also degraded relatively rapidly (approximately 50% within 1 week) once released into streams (Drake et al., 2015; Mann et al., 2015; Spencer et al., 2015; Ward and Cory, 2015; Müller et al., 2018). Both the Nelson and Hayes had relatively large proportions of L-BDOC (DOC degraded within 3 days; Figure 7), consistent with expectations for permafrost DOC. We do not know the transport time from DOC source to the river mouths where sampling occurred, but faster transport in the Nelson River with its high (regulated) winter flows perhaps contributed to its higher BDOC and L-BDOC compared to the Hayes.

Another potential source of degradable DOC along the Nelson is the series of lakes and reservoirs formed by damming, which support primary production during summer yet have limited storage relative to the larger and deeper reservoirs of, for example, La Grande Rivière system. The possible transport of labile aquatic DOC from the reservoirs during winter might explain the measured L-BDOC (Figure 7). Water residence times in the Nelson reservoirs are too short for DOC buildup in deep waters, but labile DOC could be sourced from reservoir sediments. Higher preservation of riverine DOC during winter versus summer transport certainly may be expected because of the darkness (under the snow and ice cover), which limits photodegradation, and low temperatures, which limit microbial degradation. The small areas of open water

Figure 10. DOC concentrations in the major Arctic rivers compared to those measured in Hudson Bay rivers. Mean monthly DOC concentrations for the major Arctic rivers (PARTNERS rivers; Holmes et al., 2018) and April DOC concentrations for the Nelson, Hayes, and Great Whale Rivers of Hudson Bay (A), with a more detailed comparison of April discharge versus DOC concentrations for the same set of rivers (B). Error bars represent standard error of the mean; n values for means in Panels A and B are provided in Table S1 and Table S2, respectively. DOI: https://doi.org/10.1525/elementa.2020.00123.f10
below each dam may have allowed some minor photo-bleaching that, while not affecting DOC concentrations, facilitated photo-enhanced biomineralization of DOC (Fichot and Benner, 2014). Gue´guen et al. (2016) found that during summer, photobleaching rates for Nelson River dissolved organic matter (DOM; i.e., decrease in DOM signal resulting from exposure to solar radiation) ranged from 0.005 to 0.030 h–1, corresponding to half-lives of 4.9–9.9 days. However, there was so little open water during April along the lower Nelson River that we may assume photobleaching had negligible effects on our results, at least until the riverine DOC arrived at the Nelson/Hayes Estuary and may have been recirculated in the area of the flaw lead (Figure 3A).

Previous work suggests that %BDOC in northern rivers is strongly related to nutrient availability (cf. Wickland et al. 2012). Indeed, Wickland et al. (2012) found that the molar ratio between DOC and dissolved inorganic nitrogen (DIN; typically NO₃⁻ + NH₄⁺) was a good predictor of %BDOC in the Yukon River and tributaries and speculated that higher %BDOC in winter arose from greater nutrient availability at that time. The Nelson River does appear to be a nitrate-rich river relative to other Hudson Bay rivers (see Table 1 in Kuzyk et al., 2010). Lacking ammonium data for our samples, our best estimates for the DIN concentrations in late winter are previously collected Coordinated Aquatic Monitoring Program data for the Nelson and Hayes Rivers in February to March (8.8 and 6.3 µM, Table 3.

| Reference                      | Study Site                  | Sampling Time       | Initial DOC (mg L⁻¹) | Incubation Time (Days) | Incubation Temperature (°C) | Parameter Analyzed | %BDOC* |
|--------------------------------|------------------------------|---------------------|----------------------|------------------------|-----------------------------|-------------------|--------|
| Kawahigashi et al. (2004)      | Yenisei River               | August              | 4–30                 | 97                     | 20                          | CO₂               | 4–28   |
| Holmes et al. (2008)           | Alaskan rivers              | Spring freshet      | 2–15                 | 90                     | 20                          | DOC               | 14–33  |
|                                |                              | July                | 2–8                  | 90                     | 20                          | DOC               | Up to 9 |
| Balcarczyk et al. (2009)       | Alaska streams              | June                | 2–7                  | 40                     | 4                           | DOC               | 4–17   |
|                                |                              |                     |                      |                        | 20                          | DOC               | 4–35   |
| Mann et al. (2012)             | Kolyma River                | Preflush (May)      | 2–3                  | 28                     | 20                          | DOC               | Up to 10 |
|                                |                              | Freshet (May to June)| 8–14                 | 28                     | 20                          | DOC               | 1–20   |
| Wickland et al. (2012)         | Yukon River and its tributaries | Winter          | 3                     | 28                     | 5                           | CO₂               | 27–35  |
|                                |                              | Spring freshet      | 3–17                 | 28                     | 5                           | CO₂               | 2–29   |
|                                | Yukon River                  | Summer              | 3–7                  | 28                     | 5                           | CO₂               | 4–19   |
|                                |                              | Winter              | 2–4                  | 28                     | 15                          | CO₂               | 9–53   |
|                                |                              | Spring freshet      | 2–17                 | 28                     | 15                          | CO₂               | 5–47   |
| Herlemann et al. (2014)        | Kalix River                 | June                | 5                    | 28                     | 10                          | DOC               | 6–8    |
| Shirokova et al. (2017)        | Severnaya Dvina River        | June (spring flood) | 10–15                | Approximately 25        | 20                          | DOC               | Negligible |
|                                |                              | August              | 12–15                | Approximately 25        | 20                          | DOC               | 15–20  |
| This study                     | Nelson River                | April               | 24                   | 45                     | 4                           | DOC               | 60     |
|                                | Hayes River                 | April               | 14                   | 45                     | 4                           | DOC               | 33     |
|                                | Great Whale River           | April               | 8                    | 45                     | 4                           | DOC               | 24     |

DOC = dissolved organic carbon.

*Percentage of total DOC that is biodegradable.
respectively) and previously published April DIN concentrations for the Great Whale River (4 μM; Hudon et al., 1996). Substituting these values with our DOC data into the Wickland et al.’s (2012) equation yields predictions of %BDOC no more than 10% for any of the samples. The Wickland et al.’s (2012) equation may underestimate the late winter %BDOC in the Hudson Bay rivers, particularly the Nelson, because we are underestimating DIN or the differences in DOM composition or microbial community among rivers may significantly alter the relationship.

4.2.2. %BDOC and lability in the coastal waters
A marked decline in %BDOC, and especially the proportion of labile DOC, was observed between the Nelson River and SWHB coastal waters (Figure 7), which we attribute to the dynamics of the Nelson/Hayes Estuary and specifically the accumulation of older, semilabile DOC along the southern shore where winter sampling was conducted. Manitoba Hydro’s MIKE model simulates river water residence times of 30–40 days for that portion of the estuary (K Sydor, Manitoba Hydro, personal communication, 2019). Presumably, the long residence times mean that the in situ DOC was not all freshly introduced riverine DOC, but a mixture including older residual, much less labile DOC. If the entire estuary had been covered with landfast ice allowing sampling in the central (thalweg) area, where the residence time is much shorter, presumably we would have seen higher biodegradability and lability of the DOC. During summer, Guéguen et al. (2016) found a strong, negative linear correlation between salinity and DOC (i.e., conservative behavior) throughout the estuary even in the thalweg area. However, the low lability of DOC in the coastal waters in summer might simply reflect poor preservation of labile Nelson River DOC during transport to the estuary. During open-water conditions, DOC may be degraded upstream, closer to its point of release, whereas during the cold, dark season, the conditions, DOC may be degraded upstream, closer to its source. Remnant old(er) marine DOC or disintegrated POC produced in the previous summer may account for some or all of the observed %BDOC.

In terms of nutrients, very low nitrate concentrations are characteristic of Hudson Bay surface waters, while river waters are notoriously low in phosphate. Thus, %BDOC may have increased in the more saline estuary waters due to better nutrient availability, possibly resulting from the release of adsorbed NH₄⁺ from riverine sediments as they encountered the saline conditions of the estuary (cf. Bysgaard et al., 1999) combined with seawater supply of phosphate, which has 5–6-fold higher phosphate concentrations than river water (Z. Kazmiruk, personal communication, 2020). The %BDOC in the very fresh plume waters of the SEHB coast increased in direct relation to concentrations of DOC, but the apparent “leveling off” at DOC concentrations above 7 mg L⁻¹ (Figure 8) is consistent with the notion of nutrient limitation in that water mass. The under-ice plume of the Great Whale River apparently also retains river water (and associated DOC) for months at a time (Ingram and Larouche, 1987), which may mean that the plume becomes increasingly phosphate-poor over time as river-derived phosphate is consumed and little crosses the sharp halocline from the deep marine waters. Thus, we speculate that the river plume waters lacked the nutrients for efficient biodegradation of DOC, whereas the more saline coastal surface waters provided a more favorable environment for degradation.

Interestingly, the only saline SEHB samples showing no biodegradation were those drawn from the warmer water mass below 30 m depth (Table 2). The cold saline waters found between depths of 0 and 20 m at stations S1–S4 were the waters that showed high %BDOC (16%–59%; Table 2). Presumably, the warm water mass, which has been isolated from the surface and thus riverine DOC inputs since the previous summer (Petruievich et al., 2018; Eastwood et al., 2020), contained only residual recalcitrant DOC.

4.2.3. Biodegradation rate constants
Biodegradation rate constants complement %BDOC results as they provide additional insight regarding biodegradation dynamics. However, methodological differences in how L-BDOC and SL-BDOC are defined and in curve-fitting approaches make directly comparing results difficult in most cases. For example, Kawahigashi et al. (2004) reported k' values for the Yenisei River (1.833–2.514 d⁻¹), nearly an order of magnitude greater than the k' values for Hudson Bay rivers (0.027–0.236 d⁻¹) and k values that were much lower (<0.001 d⁻¹) than the k' values in our study (0.003–0.005 d⁻¹). These differences arise from Kawahigashi et al. (2004) having defined the degradation of L-BDOC as the first 15–90 min of the incubation period (rather than 3 days), having used a model that forced the best fit of both L-BDOC and SL-BDOC simultaneously, and
having a longer total incubation time. These sorts of methodological differences are what motivated Vonk et al. (2015) to propose a standardized BDOC protocol, which we adopted with few modifications for the present work.

A potential limitation in our incubation protocol due to the remote setting and lack of facilities at our field stations is that samples were shaken only once per day rather than constantly agitated (e.g., in a rotating chamber). Ward et al. (2019) suggested that DOC biodegradation rate in rivers may depend on water mixing as a result of interactions among suspended particles, dissolved constituents, and free-living and particle-bound microbes. Had we been able to implement constant mixing of our river waters, we expect it would have increased the biodegradation rates observed.

Compared to rivers, coastal ocean biodegradation rate constants have been reported much more frequently and compiled in some recent review articles (e.g., Lonborg and Álvarez-Salgado, 2012; Kaiser et al., 2017). DOC biodegradation rate constants for the Hudson Bay coastal waters ($k^r = 0.049 \pm 0.014 \text{ d}^{-1}$, $n = 24$; mean $k^r = 0.002 \pm 0.001 \text{ d}^{-1}$, $n = 24$) are comparable to the global biodegradation rate constants ($k$ combining $k^r$ and $k^w$, incubation time $> 40$ days) reported for the global coastal ocean (0.066 ± 0.065 d$^{-1}$, $n = 127$; Lonborg and Álvarez-Salgado, 2012). This agreement is not surprising as the coastal ocean DOC is supplied mostly by rivers. Moreover, if we apply the formula for the correlation of tDOC decay constants with temperature ($\frac{k}{k_n} = 0.049 + 0.014 \text{ d}^{-1}$) and the formula for the correlation of tDOC decay constants with incubation time ($n = 8$) derived in the review study of Kaiser et al. (2017), the resulting 3-day biodegradation rate ($k$) of 0.053 ± 0.024 d$^{-1}$ and 45-day biodegradation rate ($k$ combining $k$ and $k^w$) of 0.008 ± 0.002 d$^{-1}$ are very similar to our findings for the Hudson Bay coastal waters.

### 4.2.4. Implications of DOC degradation for carbon cycling in Hudson Bay coastal waters

For more than a decade, coastal waters of Hudson Bay have been recognized as supersaturated in CO$_2$ with respect to the atmosphere during late summer, while off-shore waters are undersaturated, and the distribution of CO$_2$ has been recognized as strongly related to river discharge (Eise et al., 2008). A recent carbon budget integrating inorganic and organic forms of carbon demonstrated that on an annual basis, the remineralization of terrestrial DOC is the main driver of CO$_2$ accumulation in the bay’s coastal surface waters (Capelle et al., 2020). During the month of July, Burt et al. (2016) observed elevated dissolved inorganic carbon (DIC) concentrations in the Nelson/Hayes Estuary (approximately 100 µM excess DIC; see Figure 6B in Burt et al., 2016, and associated discussion) as compared to the remaining coastal waters of Hudson Bay, which implied that biodegradation of the DOC delivered by these rivers plays a disproportionate role in the CO$_2$ patterns.

Our biodegradation results may be used to provide a first test of the hypothesis of Burt et al. (2016) that the Nelson/Hayes Estuary contains approximately 100 µM excess DIC relative to the remaining riverine coastal domain of Hudson Bay. Our DOC concentrations and %BDOC values for the Nelson and Hayes Rivers (Table 2), in combination with the April river discharge data (Figure 2), imply that 1,105 µM DIC is produced as a result of biodegradation of the riverine DOC: $\frac{(\text{Riverine DOC} \times \% \text{BDOC} \times \text{Discharge}_{\text{Nelson}} + \text{Riverine DOC} \times \% \text{BDOC} \times \text{Discharge}_{\text{Hayes}})}{(\text{Combined discharge of the Nelson and Hayes Rivers})} = [(1,963 \text{ µM} \times 0.600 \times 3,646 \text{ m}^3 \text{s}^{-1}) + (1,183 \text{ µM} \times 0.325 \times 366 \text{ m}^3 \text{s}^{-1})] / 4,012 \text{ m}^3 \text{s}^{-1} = 1,105 \text{ µM of DIC}$. Assuming a 40-day residence time of river water in the Nelson/Hayes Estuary (based on Manitoba Hydro’s MIKE model), the addition of river water with the 1,105 µM DIC excess concentration would result in about 1.5 × 10$^{16}$ µmol DIC added to the estuary in excess, yielding a DIC excess concentration of 136 µmol L$^{-1}$ in the estuary (assuming a total volume of water in the estuary is 1.13 × 10$^{17}$ m$^3$ based on 4,500 km$^2$ with an average depth of 25 m). Thus, the DIC excess of approximately 100 µM observed by Burt et al. (2016) in the Nelson/Hayes Estuary is reasonable or even low in comparison to what appears to be the potential DIC enrichment in the Nelson/Hayes Estuary resulting from the biodegradation of riverine DOC. A 30-day residence time would yield a DIC excess concentration of 102 µM, in near-perfect agreement with the observations of Burt et al. (2016). Also likely is that some of the excess DIC produced by biodegradation during April and the subsequent ice-covered months (May and part of June) would be lost from the estuary by CO$_2$ evasion prior to an observation period in July. The only other estimate of Nelson/Hayes freshwater residence time that we can find is the one given by Granskog et al. (2009), which was in the order of months. Our biodegradation results imply that a DIC buildup much stronger than 100 µM would be expected if this longer residence time is accurate.

### 5. Summary and conclusions

The Arctic Ocean receives the greatest riverine DOC input in the global ocean on a per volume basis, and much progress has been made in recent years on quantifying this input (Holmes et al., 2011; Tank et al., 2012). The purpose of this study was to contribute to the scarce but accumulating knowledge of DOC degradation in Arctic rivers and the Arctic riverine coastal domain in winter, which has been mostly ignored because of the assumption that low base flow and low DOC concentration result in insignificant DOC supply. However, recent observations show an increase in winter freshwater discharge in the Arctic (Déry et al., 2016; St. Jacques et al., 2009; Walvoord and Striegl, 2007), and this study reports relatively high DOC concentrations for the Nelson, Hayes, and Great Whale rivers and adjacent Hudson Bay coastal waters during winter.

The winter DOC concentration in the Nelson River is high relative to other major Arctic rivers, probably due to relatively high water levels mobilizing DOC from permafrost in river banks or from wetlands, lakes, or reservoirs. The Nelson River winter DOC is also highly biodegradable. The high biodegradability and lability of the Nelson River DOC may relate to high contributions of fresh permafrost DOC leaching from sources along the lower Nelson River and its tributaries and/or DOC production in the system’s
reservoirs. The composition of Nelson River DOC warrants further study.

The receiving coastal waters of SWHB have lower %BDOC than the source rivers due to DOC degradation. In each study area, %BDOC increased with DOC concentration, which is likely due to heterotrophic microbial communities performing better at a higher concentration of organic matter that includes more biodegradable components. Likely, in the estuarine settings, there were differences in the extent of DOC degradation that had occurred prior to the sampling and lowered both %BDOC and DOC concentration. The long residence time of the river water in the Nelson/Hayes Estuary (ca. 40 days) causes an accumulation of less degradable DOC in the estuary, which, in turn, leads to a decrease in DOC lability and a decrease in the slope of the %BDOC-DOC relationship in the SWHB coastal waters (Figure 7). In the SEHB coastal waters, the lability of the DOC is higher in the salty waters than in the source river, presumably due to the priming effect and higher phosphate concentrations in the coastal ocean.

We acknowledge that the explanations for the biodegradability and lability dynamics described above are mostly hypothetical and need to be verified by analyzing heterotrophic bacterial communities and assessing DOC chemical structure/properties. Thus, future studies need to complement biodegradation experiments with such measurements as well as expand on the types of rivers and seasons studied. Models of organic carbon budget, water–atmosphere CO2 exchange, and food web dynamics in the Arctic watersheds and the Arctic Ocean would greatly benefit from this research.

Data accessibility statement
Data sets used within this study have been archived on the Canadian Watershed Information Network (CanWIN; http://lwbin-datahub.ad.umanitoba.ca). River discharge data for the Nelson, Hayes, and Great Whale rivers can be accessed at the website of Environment and Natural Resources, Government of Canada (https://wateroffice.ec.gc.ca). DOC concentration and discharge data for the major Arctic rivers (PARTNERS) can be accessed at the website of the Arctic Great Rivers Observatory (https://arcticgreatrivers.org/data/).

Supplemental files
The supplemental files for this article can be found as follows:
Table S1. Number of samples (n) used to produce Figure 10A.
Table S2. Number of samples (n) used to produce Figure 10B.

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The authors declare that they have no conflict of interest.

Author contributions
Contributed to the conception and design: ZVK, ZAK, TP.
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