



# Global Biogeochemical Cycles

## RESEARCH ARTICLE

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### Key Points:

- Ground ice in permafrost coasts contains only low amounts of DOC and thus fluxes through erosion are low with  $54.9 \pm 0.9 \text{ Mg yr}^{-1}$
- Particulate organic carbon (POC) dominates the organic carbon fluxes from coastal erosion with a DOC to POC ratio of 1:900
- DOC fluxes from ground ice possibly play a greater role in late summer, when dominating river discharge is low

### Supporting Information:

- Supporting Information S1
- Data Set S1
- Data Set S2

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## Eroding permafrost coasts release low amounts of dissolved organic carbon (DOC) from ground ice into the nearshore zone of the Arctic Ocean

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**Abstract** Ice-rich permafrost coasts in the Arctic are highly sensitive to climate warming and erode at a pace that exceeds the global average. Permafrost coasts deliver vast amounts of organic carbon into the nearshore zone of the Arctic Ocean. Numbers on flux exist for particulate organic carbon (POC) and total or soil organic carbon (TOC, SOC). However, they do not exist for dissolved organic carbon (DOC), which is known to be highly bioavailable. This study aims to estimate DOC stocks in coastal permafrost as well as the annual flux into the ocean. DOC concentrations in ground ice were analyzed along the ice-rich Yukon coast (YC) in the western Canadian Arctic. The annual DOC flux was estimated using available numbers for coast length, cliff height, annual erosion rate, and volumetric ice content in different stratigraphic horizons. Our results showed that DOC concentrations in ground ice range between 0.3 and 347.0 mg L<sup>-1</sup> with an estimated stock of 13.6 ± 3.0 g m<sup>-3</sup> along the YC. An annual DOC flux of 54.9 ± 0.9 Mg yr<sup>-1</sup> was computed. These DOC fluxes are low compared to POC and SOC fluxes from coastal erosion or POC and DOC fluxes from Arctic rivers. We conclude that DOC fluxes from permafrost coasts play a secondary role in the Arctic carbon budget. However, this DOC is assumed to be highly bioavailable. We hypothesize that DOC from coastal erosion is important for ecosystems in the Arctic nearshore zones, particularly in summer when river discharge is low, and in areas where rivers are absent.

### 1. Introduction

The Arctic is subject to changing climate conditions more than any other region on Earth. Climate models project that temperatures in the Arctic will increase more rapidly than the global mean, with projected warming over land between 1°C (RCP 2.6) and 8°C (RCP 8.5) by the end of the 21st century [*Intergovernmental Panel on Climate Change*, 2013]. One of the key components of the Arctic cryosphere is permafrost, which stores 1035 ± 150 Pg organic carbon (OC) [*Hugelius et al.*, 2014] and regulates the release of greenhouse gases and thus is able to alter global climate conditions [*Callaghan et al.*, 2011]. Warmer air and ground temperatures will strongly impact permafrost, which is already thawing in many parts of the Northern Hemisphere [*Romanovsky et al.*, 2010; *Arctic Monitoring and Assessment Programme (AMAP)*, 2011; *United Nations Environment Programme (UNEP)*, 2012]. This could result in a loss of 30 to 85% of the near-surface permafrost by 2100 [*UNEP*, 2012; *Schaefer et al.*, 2014].

Permafrost coasts are particularly vulnerable to changing environmental conditions because they are directly exposed to both atmospheric and marine forcing [*Rachold et al.*, 2005a; *Lantuit et al.*, 2013]. Recent environmental change has led to extensive erosion [e.g., *Shaw et al.*, 1998; *Solomon*, 2005; *Jorgenson and Brown*, 2005; *Mars and Houseknecht*, 2007; *Günther et al.*, 2015; *Obu et al.*, 2016], especially along coastlines consisting of unconsolidated material, which make up 65% of the Arctic coasts [*Lantuit et al.*, 2012]. In winter, which generally lasts from 7 to 9 months, persistent sea-ice cover protects the coastline from waves and currents. In the ice-free season, permafrost coasts rapidly erode at rates of up to several meters per year [*Lantuit et al.*, 2009, 2012]. High ground ice contents in permafrost are known to facilitate erosion [*Aré*, 1988; *Dallimore et al.*, 1996; *Lantuit and Pollard*, 2008; *Günther et al.*, 2015].

Permafrost contains the largest OC pool on Earth [*Tarnocai et al.*, 2009; *Hugelius et al.*, 2014]. Given the high erosion rates affecting permafrost coasts, the fluxes of OC into the Arctic Ocean are substantial [*Arctic Climate Impact Assessment*, 2005; *McGuire et al.*, 2009; *AMAP*, 2011; *Lantuit et al.*, 2013; *Wegner et al.*, 2015]. The POC and DOC inputs from Arctic rivers into the ocean are well studied, but for coasts only

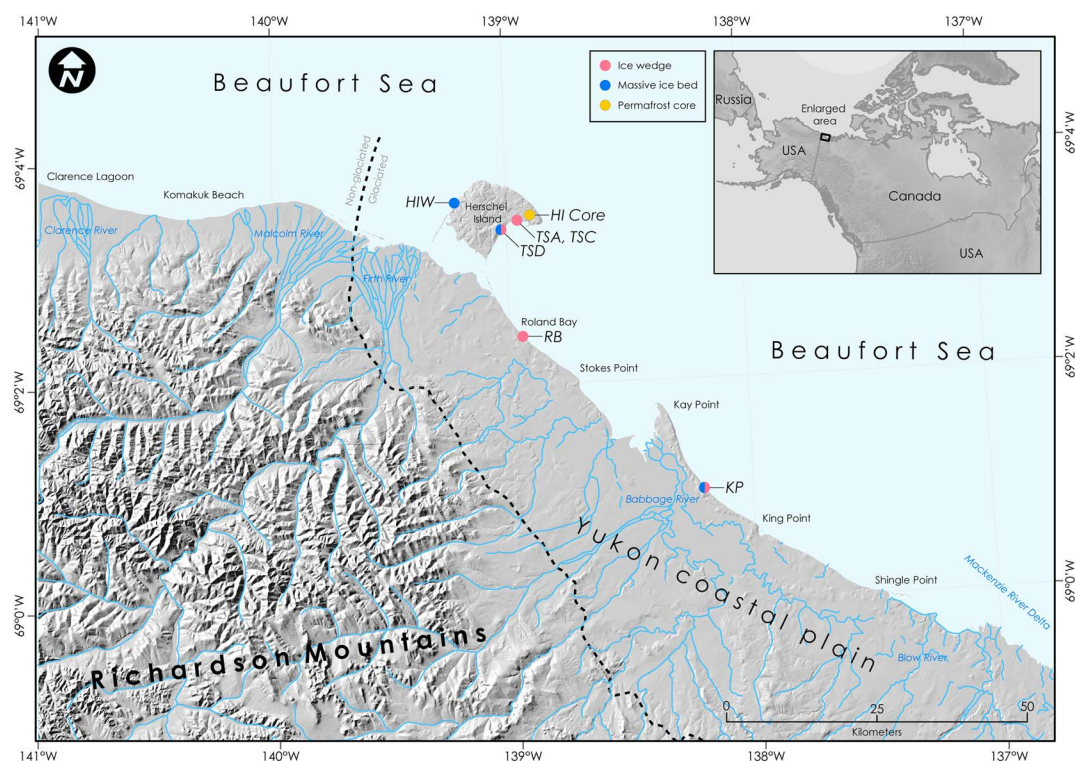
POC and SOC fluxes have been estimated [Macdonald *et al.*, 1998; Rachold *et al.*, 2004; Raymond *et al.*, 2007; McGuire *et al.*, 2009; Vonk *et al.*, 2012; Macdonald *et al.*, 2015]. However, DOC that is stored in ground ice has not yet been considered separately in OC fluxes, although ground ice makes up on average nearly 20 vol % of coastal cliffs around the Arctic rim [Lantuit *et al.*, 2012]. DOC fluxes play an essential role in terrestrial and marine ecosystems, since DOC is generally more bioavailable than POC and can affect marine elemental cycles, primary production, and the food web [Neff and Asner, 2001; Dittmar and Kattner, 2003; Cleveland *et al.*, 2004; Dunton *et al.*, 2006]. With its release from permafrost and ice it could have a major impact on ecosystems and climate as it is biochemically highly labile [Dou *et al.*, 2008; Vonk *et al.*, 2013a; Mann *et al.*, 2015] and can be rapidly mineralized by microbial activity or photochemical processes [Battin *et al.*, 2008; Cory *et al.*, 2013; Vonk *et al.*, 2013a].

Ground ice is ubiquitous in permafrost coasts and stores DOC [Lantuit *et al.*, 2012; Fritz *et al.*, 2015]. Most studies only capture DOC in the combined pool of TOC or SOC and do not investigate it separately. To clarify, DOC refers to all OC  $<0.7 \mu\text{m}$ . SOC and TOC are used interchangeably in this study and include all OC, dissolved as well as particulate. DOC is composed of various organic molecules, including humic substances (polymeric organic acids), hydrophilic acids, and neutral compounds, like sugars, alcohols, and ketones [Thurman, 1985]. Other erosion studies focus on the particulate fraction only and routinely exclude the volume of ground ice from OC flux estimations. However, this is important because DOC is assumed to be more labile than the POC in the sedimentary fraction and ground ice makes up large volumes of coastal cliffs [Vonk *et al.*, 2013a; Fritz *et al.*, 2015; Vonk *et al.*, 2015]. The magnitude of DOC fluxes from the coast could increase with permafrost thaw and increasing coastal erosion and have the potential to considerably affect the biogeochemistry of the nearshore zone. Recent studies have provided first numbers on DOC concentrations in ground ice, ranging from 1.6 to 68.5  $\text{mg L}^{-1}$  in ice wedges [Douglas *et al.*, 2011; Vonk *et al.*, 2013b; Fritz *et al.*, 2015], from 0.3 to 5.2  $\text{mg L}^{-1}$  in massive ground ice beds [Fritz *et al.*, 2015], from 8.7 to 613.6  $\text{mg L}^{-1}$  in cave ice [Douglas *et al.*, 2011], and  $14.6 \pm 5.0 \text{ mg L}^{-1}$  in ice within permafrost exposures [Abbott *et al.*, 2015].

It is the objective of this study to quantify DOC concentrations in massive and non-massive ground ice and to calculate DOC fluxes from eroding permafrost coasts to provide first estimates of their contribution to the Arctic carbon budget and nearshore ecosystems of the ocean.

## 2. Study Area

The Yukon coast (YC) in the western Canadian Arctic is the landward extension of the Beaufort Shelf, stretching approximately 200 km from the Mackenzie Delta in the east to the Alaskan boarder in the west (Figure 1). It is characterized by a polar tundra climate and is situated in an area of continuous permafrost that is several hundred meters thick [Rampton, 1982]. Sea ice is present for nearly three quarters of the year, with a brief open-water period lasting 3–4 months in summer. In the vicinity of the Mackenzie Delta, warmer river headwaters cause a longer open-water period beginning of spring [Dunton *et al.*, 2006]. Most of the YC was glaciated by the Laurentide Ice Sheet during the Late Wisconsin (MIS 2), although the western part was not glaciated [Fritz *et al.*, 2012]. The YC is composed of five major surficial geologic units; these include fluvial, lacustrine, glaciofluvial, morainal, and marine deposits [Rampton, 1982]. The top layer of the sediments is generally rich in OC with highest concentrations found in fluvial and lacustrine sediments. In morainal parts OC concentrations are lower but assumed to be underestimated because organic-rich layers have been subducted into deeper parts through glaciotectionic processes [Couture, 2010]. Recent air temperatures are  $\sim 2.5^\circ\text{C}$  higher than at the beginning of the twentieth century, and over the last century mean permafrost temperatures increased by 1.9 to  $2.6^\circ\text{C}$  [Burn and Zhang, 2009]. Ground ice, which is defined as all types of ice formed in freezing and frozen ground [Harris *et al.*, 1988], comprises up to 50% by volume of the near-surface permafrost and can be found as massive ice in the form of ice wedges and ice beds, as well as non-massive ice in the form of pore ice and intrasedimental ice [Harry *et al.*, 1988]. Massive ground ice can occupy volumes as high as 90% [Mackay, 1971; Pollard, 1990; Fritz *et al.*, 2011, 2012]. Massive ice is all ground ice with a gravimetric ice content exceeding 250% [Harris *et al.*, 1988, and references therein]. Ice-rich coastal slopes are subject to intense thermokarst and thermoerosional activity [Lantuit and Pollard, 2008]. The land deformation process resulting from thawing ice-rich permafrost and melting massive ice is defined as thermokarst [van Everdingen, 2005].



**Figure 1.** The study sites along the Yukon coast with the sampling sites indicated by dots. HIW = Herschel Island West; TSA = Thaw slump A; TSC = Thaw slump C; TSD = Thaw slump D; PG = Herschel Island permafrost cores; RB = Roland Bay; and KP = Kay Point.

### 3. Methods

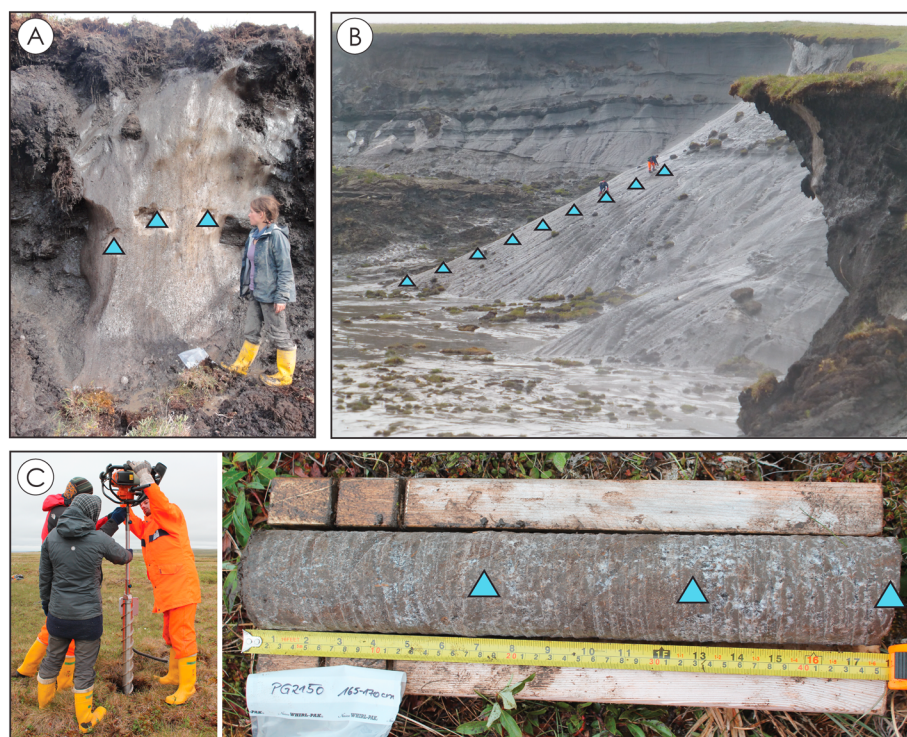
#### 3.1. Field Work

Forty-one massive ice samples were taken from coastal exposures and 69 non-massive ice samples were taken from nine permafrost cores on the mainland of the YC and on Herschel Island in 2012 and 2013 ( $n = 110$ ) (Figure 2). Massive ice bodies were sampled on the westside and eastside of Herschel Island and at Kay Point on the mainland coast ( $n = 19$ ). Five ice wedges were also sampled on Herschel Island and on the mainland coast at Roland Bay and Kay Point ( $n = 22$ ). In order to sample non-massive intrasedimental ice, nine permafrost cores were drilled on Herschel Island, targeting the ice-rich upper permafrost layer. The drilling locations were characterized by different ecological zones and had active layer thicknesses between 15 and 77 cm. The core depths ranged from 59 to 235 cm below the ground surface, and subsamples of 5 cm thickness were taken every 10 cm to be representative.

#### 3.2. DOC Concentration

The samples were processed at  $-20^{\circ}\text{C}$  in the cold lab of the German Research Centre for Geosciences (GFZ Potsdam, Germany) and prepared for hydrochemical and sedimentological analysis by removing the partially melted or thawed margins of the ice samples. After controlled thawing, samples were filtered with a glass microfiber filter ( $0.7\ \mu\text{m}$  Whatman GF/F) and acidified to  $\text{pH} < 2$  with hydrochloric acid (HCl 30% suprapur) to prevent microbial alteration. The DOC concentration was measured with a Shimadzu TOC-V<sub>CPH</sub> TOC analyzer. Inorganic carbon compounds were transformed into carbon dioxide ( $\text{CO}_2$ ) by internal acidification and purged out of the solution. Nonpurgeable OC was transformed by high-temperature catalytic combustion at  $680^{\circ}\text{C}$  into  $\text{CO}_2$  and measured by a nondispersive infrared detector. Blank samples (ultrapure water with DOC concentrations  $< 0.25\ \text{mg L}^{-1}$  provided by a Milli-Q<sup>®</sup> water treatment system) and certified standard reference material were used to validate the quality of the measurements (see Data Set S1 in the supporting information). For massive ground ice samples with low DOC concentrations, the device-specific measurement error can range between  $\pm 15$  and 20% for concentrations between 0 and  $10\ \text{mg L}^{-1}$  and  $\pm 15\%$  for 0 to  $100\ \text{mg L}^{-1}$ . For ground ice with higher concentrations, i.e., non-massive intrasedimental ice, an error of  $\pm 10\%$  is possible.





**Figure 2.** Examples of each of the three investigated ground ice types: (A) ice wedges, (B) massive ice beds, and (C) non-massive intrasedimental ice. Blue triangles indicate sampling locations.

### 3.3. DOC Flux Estimation

In order to calculate the DOC flux from ground ice along the YC, the coast was divided into 44 segments based on a morphological model developed by Couture [2010] to assess the ice content along the entire YC. The segments were defined by homogeneous characteristics including predominant landforms, surficial material, ground ice conditions, and coastal processes [Rampton, 1982; Rachold *et al.*, 2005b; Overduin and Couture, 2006]. For each segment, the volume of ice wedges (IW), massive ice beds (MIB), and non-massive intrasedimental ice (NMI) was determined according to Couture and Pollard [2015] by direct measurements and extrapolation. This segmentation on a landscape scale is associated with potential error sources, because of the low density of ground ice sampling, the simplifying nature of the model used to quantify ground ice stratigraphically, and the use of different data sources that were already characterized by error margins. Therefore, a precise error description of the data set is not possible. However, Couture and Pollard [2015] report that any result should be considered as representative with a possible error not exceeding 10%.

In this study, we use the term “non-massive intrasedimental ice” instead of “pore ice and thin segregated ice lenses” to account for all non-massive ice. DOC stocks and annual fluxes were calculated for each coastal segment. The calculation is based on an equation provided by Lantuit *et al.* [2009]. This equation was originally used for the estimation of TOC fluxes, but it excluded massive ground ice. In this study, the calculation was modified and expanded to include all ground ice. In order to calculate the annual DOC fluxes, the DOC stocks were estimated first.

The estimation of DOC stocks is based on the results of the DOC concentration measurements in this study and the volumetric ground ice calculation by Couture and Pollard [2015]. With the known median DOC concentration ( $DOC_{conc,j}$ ) and volumetric ice content for each ice type ( $\theta_j$ ) in each coastal segment ( $n=44$ ), the DOC stock (in  $g\ m^{-3}$ ) was estimated for the entire YC following equation (1), where  $\rho$  is  $0.92\ g\ cm^{-3}$ , the density of pure ice at  $-10^\circ C$  [Lide *et al.*, 2009]. The estimation was done for each ice type separately, ice wedges ( $DOC_{stock\ IW}$ ), massive ice bodies ( $DOC_{stock\ MIB}$ ), and non-massive intrasedimental ice ( $DOC_{stock\ NMI}$ ), and then summed up for all ground ice ( $DOC_{stock}$ ; equation (2)). The extrapolation of DOC concentrations to entire coast segments necessarily leads to some error as samples were taken only from the formerly glaciated

zone and not from the formerly non-glaciated zone. The total DOC stock is the weighted average of DOC stocks within the individual coast segments. Error bounds with a confidence level of 95% were added to report error.

$$\text{DOC}_{\text{stock IW, MIB, NMI}} = \sum_{j=1}^n \theta_j * \rho * \text{DOC}_{\text{conc},j} \quad (1)$$

$$\text{DOC}_{\text{stock}} = \text{DOC}_{\text{stock IW}} + \text{DOC}_{\text{stock MIB}} + \text{DOC}_{\text{stock NMI}} \quad (2)$$

In order to calculate an annual DOC flux ( $\text{DOC}_{\text{flux}}$ ) for the YC, which is the sum of each ( $j$ ) of the 44 segments (see Data Set S2 in the supporting information), the following input variables were used: length of the coastline ( $L_j$ ), cliff height ( $H_j$ ), annual erosion rate ( $R_j$ ), and DOC stock in each ice type ( $\text{DOC}_{\text{stock},j}$ ). The coastline length ( $L_j$ ) of all segments was provided by Couture [2010], who used a shoreline produced by the Geological Survey of Canada (GSC) based on digitized air photos, Landsat imagery, and 1:50,000 topographic maps. The cliff height ( $H_j$ ) originated from a variety of literature sources and was controlled for consistency with a digital elevation model at 30 m pixel resolution compiled by the Yukon government [Couture, 2010, and references therein]. The erosion rates ( $R_j$ ) for all units were derived from McDonald and Lewis [1973], Harper et al. [1985], Harper [1990], Forbes et al. [1995], and Lantuit and Pollard [2008]. Although these data date back to the 1980s, their use is appropriate because they are the best available data sets for the area and because rates of erosion have not substantially changed since then (A. M. Konopczak, personal communication, 2015). The DOC flux in  $\text{Mg yr}^{-1}$  was first calculated according to equation (3) separately for each ground ice type and was then summed up (equation (4)). Error bounds with a confidence level of 95% were added to the total DOC flux, i.e., the sum of fluxes from all coastal segments.

The cliff height (i.e., backshore elevation) is defined as “the upper part of the active beach above the normal reach of the tides, but affected by large waves occurring during a high water event” [Overduin and Couture, 2006; Lantuit et al., 2012]. The cliff heights used in this study originate from a variety of sources, including Couture [2010]; Forbes [1997]; McDonald and Lewis [1973]; Lewis and Forbes [1974]; Harry et al. [1985]; Rampton [1982]; Harry et al. [1988], and Gillie [1987]. In a few cases, where no heights were available for coast segments, cliff heights were derived from the Coastal Information System database (CIS) of the GSC, which is based on visual estimates from low-level helicopter surveys. All of the cited studies have been conducted by or in cooperation with the GSC using standard techniques, i.e., level and rod, theodolite, hand level and measure tape, or differential GPS and total station. The measurements were normally taken at the cliff top, cliff base, and the wet-dry line and have an accuracy of  $\leq 0.1$  m. Heights were generally determined in relation to mean sea level or local water level at the time of the surveys. As the tidal range is small between high and low water mark in this region (usually less than 0.5 m) there would not be a significant difference. All cliff heights given for a single coast segments in this study are considered as representative for the entire coast segment, so any error in measurement would probably be lower than the range of heights of the coast segment. As there is no highly detailed bathymetry and information on the subsurface below sea level available, we decided to exclude the subaqueous part of the coastal profile from this study.

The backshore elevation was also controlled for consistency with a digital elevation model at 30 m pixel resolution compiled by the Yukon government [Environment Canada et al., 2014; Beaulieu and Clavet, 2009]. To sum up, there is a range in the accuracy of cliff height measurement because of the range of methods used. However, the measurements have been averaged over a coast segment, so even for really accurate cliff height measurement there is an error in the extrapolation to the entire coast segment. Taking all error sources into account, we assume the error for the cliff height is about 20%.

The length of the coast used in equation (1) depends strongly on the scale at which it was digitized. This problem is well known and termed the fractal dimension of coastlines [Mandelbrot, 1967; Håkanson, 1978]. Lantuit et al. [2009] showed that scale related errors could amount to 30% in some extreme cases. In order to take the fractal dimension of the coastline into account, we refer to the error values measured by Lantuit et al. [2009], who reported an error of  $\pm 3.4\%$  for the neighboring Herschel Island.

$$\text{DOC}_{\text{flux IW, MIB, NMI}} = \sum_{j=1}^n L_j * H_j * R_j * \text{DOC}_{\text{stock},j} \quad (3)$$

$$\text{DOC}_{\text{flux}} = \text{DOC}_{\text{flux IW}} + \text{DOC}_{\text{flux MIB}} + \text{DOC}_{\text{flux NMI}} \quad (4)$$

**Table 1.** Classification and Morphological Characteristics of the Yukon Coast (YC) Segments<sup>a</sup>

Glaciation and Geology	%YC	<i>L</i> (km)	<i>H</i> (m)	<i>R</i> (m yr <sup>-1</sup> )	<i>θ</i> (vol%)
Non-glaciated	33.2	101.7	2.0	0.7	17.1
Glaciated	66.8	205.5	19.3	0.6	39.9
Lacustrine plain	18.0	55.0	7.9	1.0	54.8
Marine beach, bar, or spit	20.2	61.8	1.2	0.8	3.0
Stream terrace	4.2	13.1	21.7	0.7	36.2
Alluvial fan	13.8	42.1	1.0	0.4	0
Floodplain or delta	3.5	10.7	3.0	0	27.5
Ice-thrust moraine ridge	22.1	67.7	34.3	0.7	49.4
Rolling moraine	12.9	39.4	23.0	0.3	47.8
Outwash plain/Valley train	4.5	13.9	2.6	0.3	44.4
Outwash fan	0.9	2.7	7.0	2.7	41.8
Total	100	306.2			
Weighted average			11.3	0.8	33.9

<sup>a</sup>Classification into formerly glaciated and non-glaciated segments and after Quaternary geology according to *Rampton* [1982]; for each part the table gives an overview of the percent coverage of the whole Yukon coast (%YC), coastline length (*L*), the average cliff height (*H*), annual erosion rate (*R*), and volumetric ice content (*θ*); data are based on *Couture* [2010, and references therein] and *Couture and Pollard* [2015]; a weighted average was used for *H*, *R*, and *θ* to account for the different lengths of coastal segments.

## 4. Results

### 4.1. Segmentation of the Coast—Literature Synthesis

#### 4.1.1. Cliff Height

The cliff height along the YC averages 11.3 m and varies substantially (Table 1). In the formerly glaciated region, cliff heights are nearly 10 times higher than in the formerly non-glaciated region. With regard to the geologic units, cliff heights are lower in alluvial fans, marine beaches, bars, and spits. Higher cliffs are found in ice-thrust moraine ridges, rolling moraines, stream terraces, and lacustrine plains.

#### 4.1.2. Coastal Erosion

Erosion rates along the YC average 0.8 m yr<sup>-1</sup>, with similar erosion rates along the formerly non-glaciated and glaciated parts (Table 1). Virtually no erosion or low erosion rates occur along floodplains or deltas, rolling moraines, and outwash plains or valley trains. Higher erosion rates were detected along lacustrine plains, followed by marine beaches, bars or spits, and alluvial fans.

#### 4.1.3. Ground Ice Content

Ice contents are much lower in non-glaciated regions than in formerly glaciated ones (Table 1). There is no or very little ice in marine beaches, bars, spits, and alluvial fans. The highest ground ice contents occur in lacustrine plains, ice-thrust moraine ridges, and rolling moraines.

### 4.2. DOC Concentration

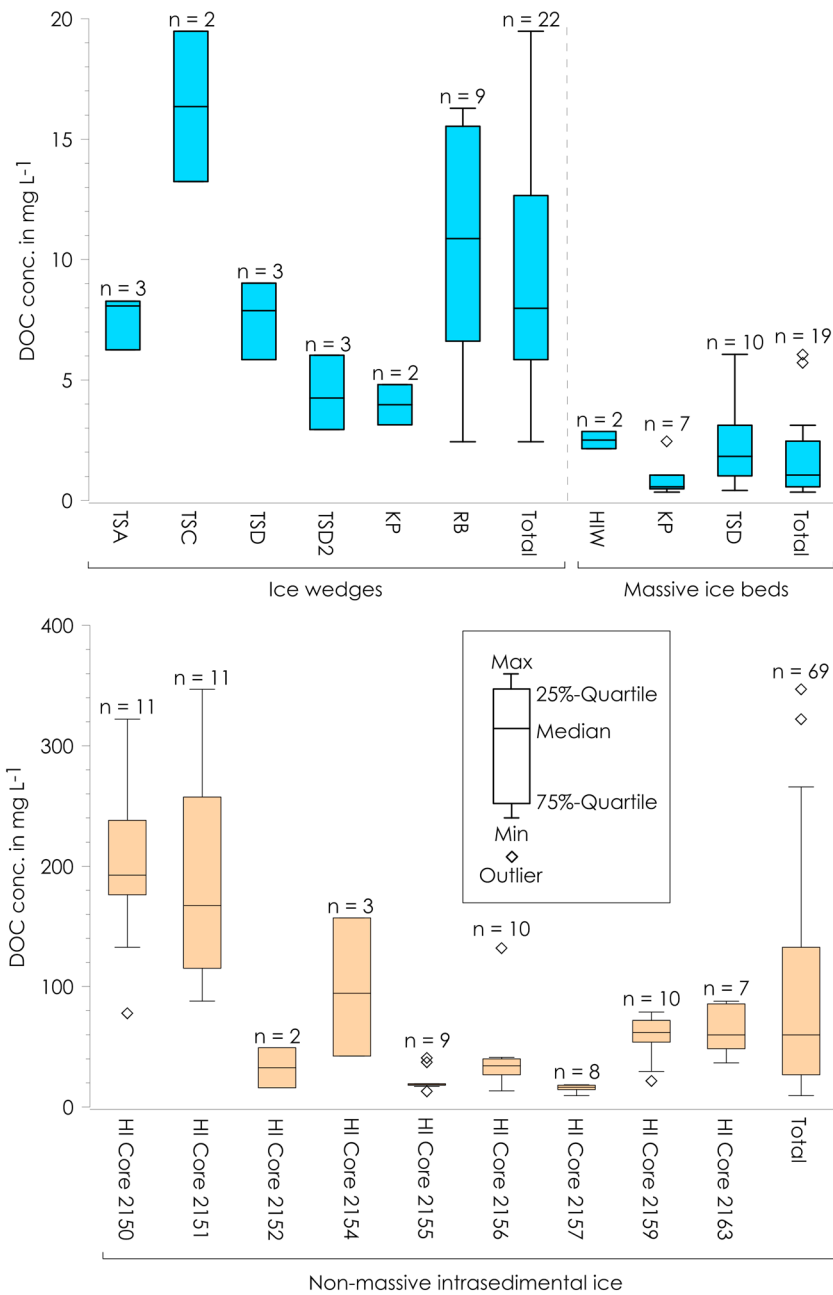
The DOC concentrations vary strongly for the different ice types (Table 2 and Figure 3). Median DOC concentration in ice wedges is 8.0 mg L<sup>-1</sup> and 1.1 mg L<sup>-1</sup> concentration in massive ice beds. The highest DOC concentrations have been found in non-massive intrasedimental ice with a median of 58.7 mg L<sup>-1</sup>.

### 4.3. DOC Stocks and Fluxes

The DOC stock in ground ice varies for the different ice types and is in total 13.6 ± 3.0 g m<sup>-3</sup> (Table 3). Almost the entire DOC is stored in non-massive intrasedimental ice. Despite high ground ice contents,

**Table 2.** Summary of DOC Concentrations in Ice Wedges (IW), Massive Ice Beds (MIB), and Non-massive Intrasedimental Ice (NMI)

Ground Ice Type	Number of Samples	DOC Concentration Range (mg L <sup>-1</sup> )	DOC 25% Quartile (mg L <sup>-1</sup> )	DOC Median (mg L <sup>-1</sup> )	DOC 75% Quartile (mg L <sup>-1</sup> )
IW	22	2.4–19.5	5.6	8.0	12.8
MIB	19	0.3–6.1	0.6	1.1	2.5
NMI	69	9.5–347.0	25.3	58.7	165.2
Total	110	0.3–347.0	6.3	19.4	81.0



**Figure 3.** Box plot for DOC concentrations in ice wedges, massive ice beds, and non-massive intrasedimental ice for each sampling site individually and in total. TSA: Thaw slump A; TSC: Thaw slump C; TSD: Thaw slump D; KP: Kay Point; RB: Roland Bay; HIW: Herschel Island West; and HI: Herschel Island. Note the different scales in the two charts.

ice wedges and massive ice beds contain only small DOC stocks. Besides the differences between the ice types, DOC stocks vary across geologic units (Table 4 and Figure 4). The amount of DOC stored in ground ice is highest in lacustrine plains, outwash plains or valley trains, ice-thrust moraine ridges, and rolling moraines. Low amounts of DOC are stored in outwash fans, floodplains or deltas, and stream terraces. No DOC or very low DOC stocks were calculated for marine beaches, bars, or spits, and alluvial fans. In the formerly glaciated parts of the coast, the DOC stock is more than twice as high as in non-glaciated parts. For the entire YC, a DOC flux of  $54.9 \pm 0.9 \text{ Mg yr}^{-1}$  was estimated. Almost the entire DOC is released from non-massive intrasedimental ice. Only a small portion is released from ice wedges and massive ice beds. DOC fluxes differ between the geologic units. By far most of the DOC is released from ice-thrust

**Table 3.** Summary of DOC Stocks and Fluxes in and From Ice Wedges (IW), Massive Ice Beds (MIB), and Non-massive Intrasedimental Ice (NMI)<sup>a</sup>

Ground Ice Type	DOC Stock (g m <sup>-3</sup> )	DOC Flux (Mg yr <sup>-1</sup> )	DOC Flux (Mg yr <sup>-1</sup> km <sup>-1</sup> )
IW	0.3	0.7	-
MIB	0.04	0.2	-
NMI	13.2	54.0	-
Total	13.6 ± 3.0	54.9 ± 0.9	0.18

<sup>a</sup>Weighted averages were used for the DOC stock to account for the different lengths of the coastal segments.

moraine ridges. Lower amounts are released from lacustrine plains, rolling moraines, and stream terraces. Virtually, no DOC is released from alluvial fans or floodplains and deltas. The formerly glaciated regions dominate the DOC flux, with fluxes being 16 times higher than from non-glaciated regions.

## 5. Discussion

### 5.1. DOC Concentrations in Ground Ice

This study showed that DOC in substantial quantities is stored in ground ice along the YC. Only a few studies have reported on DOC concentrations in ground ice or in permafrost directly. Those reports are mainly from other Arctic regions and are only available for specific ground ice types or for outflows related to thermokarst and erosion (Table 5).

The median DOC ice wedge concentrations from this study (median of 8.0 mg L<sup>-1</sup>) are in good agreement with a recent study by *Fritz et al.* [2015] (average of 9.6 mg L<sup>-1</sup>), which examined ice wedges from the Canadian, Alaskan, and Siberian Arctic. Our results are also consistent with studies by *Vonk et al.* [2013b], who reported an average DOC concentration of 11.0 mg L<sup>-1</sup> in East Siberian ice wedges, and by *Douglas et al.* [2011], who gave a mean value of 28.8 mg L<sup>-1</sup> for Alaskan subarctic ice wedges.

For massive ice beds, our study showed a median DOC concentration of 1.1 mg L<sup>-1</sup>, which is in good agreement with the study by *Fritz et al.* [2015], which showed an average DOC concentration of 1.8 mg L<sup>-1</sup> for basal glacier ice from the Canadian Arctic. In contrast, *Douglas et al.* [2011] reported exceptionally high values of up to 613.6 mg L<sup>-1</sup> for cave ice from Alaska, most likely caused by the exclusion of solutes and organic-rich sections within the massive ice during ice formation. Closer to the range of this study is the work by *Skidmore et al.* [2000], which shows low concentrations of 0.3 to 1.2 mg L<sup>-1</sup> DOC in glacier ice of the High Arctic.

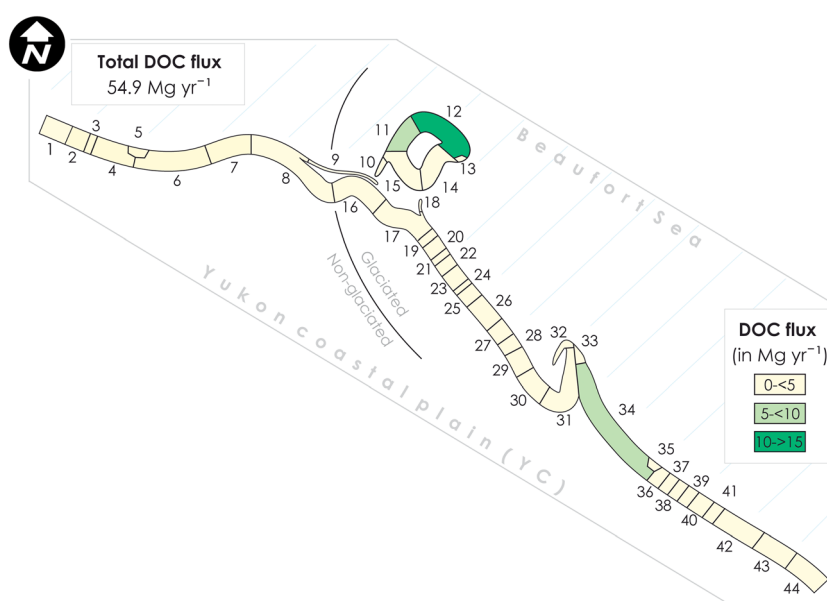
For non-massive intrasedimental ice, we show a median DOC concentration of 58.7 mg L<sup>-1</sup>. This value is hard to compare with other studies, because DOC is commonly included within the TOC pool and not differentiated. However, DOC measurements do exist for thermokarst outflows providing an indication of possible DOC concentrations in intrasedimental ground ice. Indeed, several types of ground ice contribute to the outflows indicated by the large range of values. Nonetheless, the DOC in these outflows should mainly come from massive ice. The wide range of DOC concentrations, from 2.6 to 95.4 mg L<sup>-1</sup>,

**Table 4.** Summary of DOC Stocks and Fluxes along the Yukon Coast<sup>a</sup>

	%YC	DOC Stock (g m <sup>-3</sup> )	DOC Flux (Mg yr <sup>-1</sup> )
Non-glaciated	33.2	7.0	3.1
Glaciated	66.8	16.8	51.8
Lacustrine plain	18.0	22.3	8.4
Marine beach, bar, or spit	20.2	1.6	0.1
Stream terrace	4.2	18.9	3.9
Alluvial fan	13.8	0	0
Ice-thrust moraine ridge	22.1	20.2	36.6
Rolling moraine	12.9	19.3	5.2
Outwash plain/Valley train	4.5	18.0	0.2
Floodplain or delta	3.5	14.8	0
Outwash fan	0.9	15.8	0.8
Total	100	13.6 ± 3.0	54.9 ± 0.9

<sup>a</sup>Weighted averages were used for the DOC stock to account for the different lengths of the coastal segments.





**Figure 4.** Annual DOC fluxes from the Yukon coast segments. Modified and adapted from Couture [2010]; numbers represent the 44 coastal segments (see Data Set S2 in the supporting information).

presented by Abbott *et al.* [2014] for the Alaskan Arctic tundra, most likely shows the contribution of different ice types to the outflow, with the highest values exceeding values presented in this study. Dubinenkov *et al.* [2015] showed low DOC concentrations of  $4.8 \pm 1.4 \text{ mg L}^{-1}$  for the permafrost meltwater creeks in the Lena River Delta. With thawing Yedoma contributing to outflows, DOC concentrations can rise abruptly. Vonk *et al.* [2013a] reported DOC concentrations of  $196 \pm 71 \text{ mg L}^{-1}$  in streams from thawing ice-rich Yedoma in Siberia, likely due to the high OC contents in Yedoma [e.g., Schirmeister *et al.*, 2011; Strauss *et al.*, 2013]. This is in good agreement with Mann *et al.* [2015], who reported a DOC concentration of  $131.4 \pm 15.4 \text{ mg L}^{-1}$  for Yedoma thaw streams.

Our results show a strong variation of DOC concentrations between ice types. These variations are likely related to a combination of factors, as shown by Fritz *et al.* [2015]. Ice wedges have in contrast to massive ice bodies slightly higher DOC contents. They receive DOC mainly from surface water during snowmelt,

**Table 5.** Comparison of DOC Concentrations in Ground Ice and Thermokarst Outflows<sup>a</sup>

Reference	Ice Type	Number of Samples	DOC Mean ( $\text{mg L}^{-1}$ )	DOC Concentration Range ( $\text{mg L}^{-1}$ )
<i>This study</i>	IW	22	8.0	2.4–8.8
Fritz <i>et al.</i> [2015]	IW	66	9.6	1.6–28.6
Vonk <i>et al.</i> [2013b]	IW	3	11.0	8.8–15.0
Douglas <i>et al.</i> [2011]	IW	6	28.8	18.4–68.5
<i>This study</i>	MIB	19	1.1	0.3–6.1
Fritz <i>et al.</i> [2015]	BI	22	1.8	0.7–3.8
Douglas <i>et al.</i> [2011]	CI	2	-	8.7–613.6
Skidmore <i>et al.</i> [2000]	BI, GI	NA	1.2, 0.3	-
Abbott <i>et al.</i> [2015]	EP	24	$14.6 \pm 5.0$	-
<i>This study</i>	NMI	69	58.7	9.5–347.0
Abbott <i>et al.</i> [2014]	TKO	19	-	2.6–95.4
Mann <i>et al.</i> [2015]	YTS	5	$131.4 \pm 15.4$	-
Dubinenkov <i>et al.</i> [2015]	PMC	NA	$4.8 \pm 1.4$	4.8–7.9
Vonk <i>et al.</i> [2013a]	TKO	6	$196 \pm 71$	154.0–336.0

<sup>a</sup>Ice wedge (IW), massive ice bed (MIB), non-massive intrasedimental ice (NMI), basal glacier ice (BI), glacier ice (GI), cave ice (CI), exposed ice in permafrost (EP), permafrost meltwater creeks (PMC), and Yedoma thaw streams (YTS) from different studies; for this study the median was used. From Skidmore *et al.* [2000] 24 and 100  $\mu\text{M}$  have been recalculated to 0.3 and 1.2  $\text{mg L}^{-1}$ ; from Abbott *et al.* [2014] 219–7943  $\mu\text{M}$  have been recalculated to 2.6–95.4  $\text{mg L}^{-1}$ ; from Abbott *et al.* [2015] 1213  $\pm$  413  $\mu\text{M}$  have been recalculated to  $14.6 \pm 5.0 \text{ mg L}^{-1}$ ; from Dubinenkov *et al.* [2015] 399  $\pm$  115  $\mu\text{mol CL}^{-1}$  have been recalculated to  $4.8 \pm 1.4 \text{ mg L}^{-1}$ , and from Mann *et al.* [2015] 10,939  $\pm$  1278  $\mu\text{M}$  into  $131.4 \pm 15.4 \text{ mg L}^{-1}$ .

which leaches soluble components from the organic-rich surface layer that is quickly transported into the cracks [Opel *et al.*, 2011; Fritz *et al.*, 2015]. Leaching of soil layers from undisturbed surfaces [Guo and Macdonald, 2006] and leaching of fresh and young plant litter during snowmelt [Guo *et al.*, 2007] facilitate the DOC incorporation into ice wedges, with the most labile DOC components being incorporated as well due to the quick transport into the cracks [Vonk *et al.*, 2013b]. DOC concentrations in massive ice bodies are very low. The ice originates either from glacier ice that has been buried after deglaciation or from segregated ice fed by glacier meltwater [Fritz *et al.*, 2011, and references therein]. The detected DOC originates most likely from the interactions with the surrounding sediment that could be introduced during water migration through sediments or by interactions of basal ice with subglacial sediments or was even contained in glacier ice before contact with sediments. Knight [1997] and Skidmore *et al.* [2000] showed that interaction of basal glacier ice with subglacial sediments and organic material, mainly composed of cyanobacterial mats, plant material, and roots, affect the hydrochemistry of glacier ice and could probably be the main source of organic carbon. This is supported by a strong relationship (coefficient of determination) between sediment content and the DOC concentration ( $R^2 = 0.93$ ) in our samples. Non-massive intrasedimental ice (including pore ice) has the highest DOC concentrations by far and is assumed to have the strongest interaction with its host sediments and surrounding organic material. DOC sequestered within this ice type is probably derived from a mixture of leached organic matter from the surface and active layer, and organic compounds dissolved from surrounding sediments [Guo and Macdonald, 2006; Guo *et al.*, 2007].

A reliable interpretation of the differences between DOC concentrations in the geologic units is not possible as direct measurements have been only conducted for two out of nine units and have been extrapolated to the other units. However, Couture [2010] reports differences between the same geologic units for soil organic carbon (SOC) contents, which include DOC. Highest contents were found in fluvial and lacustrine deposits and lowest contents in morainal and marine deposits, indicating that probably DOC concentrations in ground ice also differ.

DOC plays an important role for the movement and stabilization of OC and the activity of microorganisms within the soil [Neff and Asner, 2001; Cleveland *et al.*, 2004; Dubinenkov *et al.*, 2015]. Dunton *et al.* [2006] highlighted the ecological relevance of permafrost carbon release through coastal erosion, showing that it can be taken up by fish and thereby directly impact the nearshore food web. The thawing of ice wedges triggers erosion in form of block failures, causing peat blocks to collapse directly into nearshore zone. This is characteristic for the western non-glaciated part of the YC [Hoque and Pollard, 2009]. DOC released from ice wedges is in general highly bioavailable upon thaw [Vonk *et al.*, 2013b; Fritz *et al.*, 2015]. Before entering the ocean, ice wedge meltwater can, however, leach surrounding soil that it becomes in contact with, due to its low ion concentrations, and probably transport "additional" OC that have not been incorporated in the stock before into the ocean [Fritz *et al.*, 2015]. In contrast to ice wedges, thawing massive ice bodies initiate thermokarst outflows that release high DOC concentrations on a point source into the nearshore. This is typical for the former glaciated environment of the YC containing relic glacier ice. Depending on the duration, the most labile DOC portions can be lost by photochemical processes or microbial metabolism [Cory *et al.*, 2013; Vonk *et al.*, 2013b] or additional DOC can be taken up while flowing over the thermokarst feature into the ocean [Abbott *et al.*, 2015].

## 5.2. DOC Fluxes from the YC

DOC fluxes from the YC are mainly derived from non-massive intrasedimental ice that is ubiquitous within the coastal cliffs. Ice wedges and massive ice beds seem to play only a minor role in determining the magnitude of DOC fluxes, because they occupy less volume and are characterized by low DOC concentrations. They do, however, play an important role in triggering mass movements that help to mobilize DOC contained in non-massive intrasedimental ice [Aré, 1988; Wolfe *et al.*, 2001; Lantuit and Pollard, 2008]. Almost the entire amount of released DOC comes from the formerly glaciated parts of the YC, mainly due to higher cliffs and ground ice contents within the glacial limit, which we associate with extensive water supply and stagnant ice that became available with deglaciation [Fritz *et al.*, 2011].

With regard to the geologic units, the highest DOC fluxes have been observed for ice-thrust moraine ridges, lacustrine plains, and rolling moraines. These zones exhibit high cliffs, high ice contents, or high erosion rates. For ice-thrust moraine ridges the high coastline is most important, whereas the high ice content and erosion rate are most important for lacustrine parts. For rolling moraines the high ice content and cliff height are of

primary importance. For stream terraces, marine beaches, bars, or spits, the low or absent ground ice content restricts the DOC yield. In more ice-rich geologic units, like outwash plains and valley trains, low cliffs, and erosion rates restrict the DOC flux. Along floodplains and deltas no erosion occurs to provide DOC fluxes.

### 5.3. DOC Fluxes and the Arctic Carbon Budget

A total DOC flux of  $54.9 \pm 0.9 \text{ Mg yr}^{-1}$  was calculated for the YC (306 km), varying between 0 and  $16.1 \text{ Mg yr}^{-1}$  for different coastal segments, with a flux of  $0.18 \text{ Mg yr}^{-1}$  per kilometer of coastline. For the same section of coast, Couture [2010] showed a SOC release of  $0.4 * 10^5 \text{ Mg yr}^{-1}$  or  $157 \text{ Mg yr}^{-1} \text{ km}^{-1}$ , including DOC within SOC. By examining DOC that is stored in ground ice separately, this study shows that considerable amounts of DOC are stored within the YC and that they contribute organic carbon to the nearshore zone, with an approximate DOC:POC ratio of 1:900 by comparing fluxes per kilometer of coastline. However, this ratio do not take any DOC leaching or degradation processes after thawing and during transport to the ocean into account and should be used only as a representative number.

Besides eroding coasts, rivers are the main pathway for OC into the Arctic Ocean. Rachold *et al.* [2004] showed that rivers transfer  $4.4 \text{ Tg yr}^{-1}$  TOC to the Beaufort Sea. For coastal erosion Wegner *et al.* [2015] reported values of  $4.9$  to  $14 \text{ Tg yr}^{-1}$  TOC. In the vicinity of the YC, the Mackenzie River dominates the terrestrial DOC input into the Beaufort Sea with DOC fluxes between  $1.3$  and  $1.4 \text{ Tg yr}^{-1}$  [Macdonald *et al.*, 1998; Raymond *et al.*, 2007]. DOC fluxes from the small rivers along the YC, like the Blow, Babbage, Malcolm, and Firth River, have not been studied. Thus, DOC fluxes are known from small Alaskan rivers like the Kuparuk, which discharges  $0.014 \text{ Tg yr}^{-1}$  [McGuire *et al.*, 2009, and references therein]. In this context the DOC fluxes presented in this study are low and play only a minor role. However, most of the terrestrially derived DOC is exported during the months of peak discharge from May to July [Benner *et al.*, 2004; Drenzek *et al.*, 2007; Raymond *et al.*, 2007], whereas coastal erosion-induced transfer takes place during the open water season from June to October [Lantuit *et al.*, 2012]. In addition, DOC exported from rivers is dominated by contemporary sources and has already been subject to degradation within the river system during transportation [Wiegner and Seitzinger, 2001; Raymond *et al.*, 2007; Holmes *et al.*, 2008; Mann *et al.*, 2012]. Therefore, it might be more refractory in the nearshore zone, whereas DOC from coastal erosion is fresh and readily available.

Our study shows that the ratio of "DOC:POC" released by coastal erosion in the Arctic is approximately 1:900. This ratio shows that coastal erosion releases OC mostly in form of terrestrial POC that will be buried in the nearshore, from where it can be incorporated in marine ecosystem processes or transported offshore to the shelf edge [Macdonald *et al.*, 1998; Naidu *et al.*, 2000; Macdonald *et al.*, 2015; Wegner *et al.*, 2015]. Nevertheless, even though the amount of DOC is much smaller than the amount of POC, the DOC flux is important because of the labile character of the organic compounds, and it could be significant in terms of biogeochemical degradation [Thurman, 1985; Cory *et al.*, 2013; Vonk *et al.*, 2013a, 2015]. In comparison to POC, DOC can pass through cell membranes and be metabolized directly by microbes [Battin *et al.*, 2008]. Mann *et al.* [2014] showed that ancient dissolved organic matter originating from permafrost is more susceptible to degradation than modern OC. Experiments conducted by Hood *et al.* [2009] revealed that on average, 45% of terrigenous DOC is bioavailable, similar to values from incubation experiments conducted by Vonk *et al.* [2013a] and Mann *et al.* [2015], showing a DOC loss of up to 34% over 2 weeks and  $47.2 \pm 7.6\%$  over 28 days, respectively. This process is catalyzed by ultraviolet light. Freshly exposed organic material from permafrost is ~40% more susceptible to microbial conversion to  $\text{CO}_2$  when exposed to ultraviolet light [Cory *et al.*, 2013]. Since DOC fluxes from coastal erosion occur later than the peak river discharge in spring, DOC fluxes from coastal erosion might be important for the nearshore ecosystems in summer. It is also likely to be more important along coastal sections without major river discharge such as the Arctic coastal plains of Alaska and Canada.

We postulate that although DOC fluxes from ground ice released by coastal erosion are only a small part of the terrestrial OC flux into the Arctic Ocean, they could nevertheless affect selected locations in the nearshore zone due to the labile character of the DOC and its massive release over very small areas from large thermokarst landforms such as retrogressive thaw slumps, which are ubiquitous along the coastlands of the Beaufort Sea [Lantuit and Pollard, 2008; Pelletier and Mediolli, 2014]. These landforms have been shown to have a strong local impact on the biogeochemistry and the food web of aquatic systems because they deliver large quantities of OC and nutrients from a point source [Dunton *et al.*, 2006; Woods *et al.*, 2011;

Kokelj et al., 2013; Moquin et al., 2014]. The labile terrestrial DOC can, however, be rapidly removed from Arctic shelf waters in 2 to 5 years [Alling et al., 2010; Letscher et al., 2011]. This shows that the fate and residence time of DOC in the ocean are not well understood and should be the subject of further studies.

## 6. Conclusion and Outlook

The aim of this study was to determine the stocks of DOC contained in ground ice along the YC and to estimate DOC fluxes from coastal erosion into the Arctic Ocean. Based on DOC concentrations measured in different ground ice types, DOC fluxes were computed and brought into the context of Arctic OC fluxes from coastal erosion and rivers on a regional scale for the western Canadian Arctic. The following specific conclusions can be drawn from this study:

1. In total,  $13.6 \pm 3.0 \text{ g m}^{-3}$  of DOC is stored in ground ice along the YC. Nearly all permafrost DOC ( $13.2 \pm 2.9 \text{ g m}^{-3}$ ) is stored within non-massive intrasedimental ice.
2. The annual DOC flux from the YC is  $54.9 \pm 0.9 \text{ Mg yr}^{-1}$ ; ice-thrust moraines, lacustrine deposits, and rolling moraines are the main geologic units yielding DOC.
3. DOC fluxes from coastal erosion are minor in comparison to POC and DOC release from rivers and POC release from coastal erosion.
4. The ratio of DOC to POC in OC fluxes from coastal erosion along the YC is approximately 1:900.
5. DOC released from ground ice could play an important role for nearshore marine ecosystems and the biogeochemistry in late summer, when discharge from rivers has decreased compared to the spring peak discharge.

Coastal erosion-induced DOC fluxes into the nearshore zone of the Beaufort Sea are low in the context of the regional carbon budget. However, since ground ice contents along the YC are among the highest on a pan-Arctic scale, the western Canadian Arctic could be a key region for dissolved OC transport from ground ice to the Arctic Ocean.

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## Erratum

In the originally published version of this article, several instances of text were incorrectly typeset. The following have since been corrected and this version may be considered the authoritative version of record. Please see the corrected instances below.

In the Key Points: “DOC fluxes from ground ice possibly play a secondary role in late summer, when dominating river discharge is low” should have been printed as “DOC fluxes from ground ice possibly play a greater role in late summer, when dominating river discharge is low”.

In the 3rd line of the Abstract, the sentence should have read “Numbers on flux exist for particulate organic carbon (POC) and total or soil organic carbon (TOC, SOC).”

In Table 5, the Number of Samples from Mann et al. [2015] should have been printed as 5.

In the caption of Table 5, on page 9, “1278” should have been printed as “10,939 ± 1278”.

On page 14, the following citation should be removed: Schirrmeister, L., and S. Wetterich (2011), Palaeoclimatic information from stable water isotopes of Holocene ice wedges on the Dmitrii Laptev Strait, northeast Siberia, Russia, *Permafrost Periglacial Processes*, 22, 84–100, doi:10.1016/j.geomorph.2016.02.014.