Potential for Microbial Degradation of Terrestrial Dissolved Organic Carbon in Coastal Hudson Bay

by

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Abstract

The fate of terrestrial organic carbon (OC) in the global ocean is largely unknown and it is speculated to be rapidly degraded in the coastal waters. Arctic marine waters, especially Hudson Bay, have a disproportionally large terrestrial dissolved organic carbon (tDOC) input compared to the global ocean, which is increasing due to climate change. The findings of these first studies of microbial degradation of terrestrial OC in Hudson Bay have revealed the presence of high Apparent Oxygen Utilization in a subsurface, winter-ventilated water mass that cannot be explained by respiration of settling marine-produced OC as currently understood. I hypothesize that tDOC deposited into coastal waters ultimately gets degraded (consuming oxygen) under the ice cover. The findings from incubation experiments that 20-50% of the tDOC deposited into Hudson Bay by southern rivers in late winter is biodegradable within a few weeks are consistent with this hypothesis.

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Chapter 1. Introduction

1.1 Objectives and importance of this thesis

The Arctic Ocean has the greatest terrestrial dissolved organic carbon (tDOC) input in the global ocean (**McGuire et al. 2009).** The large input of tDOC has led to the Arctic Ocean harbouring the highest concentrations of tDOC (**Benner et al. 2005**). Furthermore, recent trends towards climate-change induced increasing river discharge (**Déry et al. 2011; McClelland et al. 2006; McGuire et al. 2009**) and permafrost thaw (**Vonk et al. 2015**) leads to an increased transport of tDOC into high-latitude coastal areas. At present, the fate of tDOC in coastal waters remains largely unknown and it is a matter of debate how riverine tDOC impacts the biogeochemistry of high-latitude coastal seas (**Bianchi et al. 2012; Benner 2004**).

Hudson Bay is located on the southern margin of the Arctic, where climate change is rapidly modifying watershed processes (**Déry et al. 2011)**. The Bay receives remarkably high tDOC input (**Mundy et al. 2010; Godin et al. 2017**) relative to its limited surface area and seawater volume (**Granskog et al. 2011**). It is speculated that a substantial amount of tDOC supplied by rivers to the Arctic Ocean is rapidly degraded, mostly through microbial remineralization of the organic matter in coastal waters (**Hedges et al. 1997; Opsahl and Benner 1997; Fichot and Benner 2014; Benner 2004; Bianchi et al. 2012; Bélanger et al. 2006; Ward et al. 2016**). To date, no research has been published describing microbial degradation of terrestrial organic carbon in Hudson Bay.

My thesis aims to examine microbial degradation of tDOC in coastal Hudson Bay. The main objectives of this study are:

i. exploring the apparent magnitude, location, and time of year for microbial degradation of tDOC using *in situ* observations from coastal Hudson Bay;

ii. assessing experimentally the microbial degradation potential of tDOC in riverine and coastal waters of southwestern and southeastern Hudson Bay in late winter.

1.2 Thesis outline

The structure of this thesis is as follows. After the general introduction and literature review, each objective is described and expanded upon in its own chapter that includes sections for introduction, methods, results, discussion, and conclusions. The first objective is addressed in Chapter 3, entitled '**Organic carbon degradation in coastal Hudson Bay as inferred from water mass distribution and Apparent Oxygen Utilization dynamics in late summer**'. The second objective is addressed in Chapter 4, entitled **'Microbial degradation of dissolved organic carbon in riverine and coastal Hudson Bay waters under landfast ice as inferred from incubation experiments**'. Chapter 5 synthesizes the previous chapters, reviews the main findings and offers suggestions for future work. The last section provides a list of publications referenced throughout this thesis.

Chapter 2. Literature review

2.1 Terrestrial organic carbon cycling in the coastal ocean

The carbon cycle consists of reservoirs (concentrations or amounts of material) connected by fluxes (time-dependent rates), which may be modified by anthropogenic processes. Prior to the industrial revolution (~1750), sources and sinks within the Earth system were in close balance. Since the beginning of the industrial revolution, the anthropogenic production of CO_2 has become increasingly problematic because it is not balanced by CO_2 consumption, which causes the CO_2 concentration in the atmosphere to increase and our planet to warm up (**Chapter 5, Kirchman 2011**). The carbon cycle has several reservoirs of both inorganic and organic material with the largest reservoirs being dissolved inorganic carbon (DIC), mostly bicarbonate, in the ocean, and calcium carbonate (a major mineral in limestone) on land and in oceanic sediments (**Chapter 5, Kirchman 2011**). These large reservoirs exchange carbon on very long time scales, whereas the exchange of carbon among smaller reservoirs such as the atmosphere, plants, and the surface ocean occurs much more rapidly (years to decades).

Organic carbon is the fraction of carbon that is living or has lived and it can be viewed as the common building block of all living things on Earth. Approximately two-thirds of all actively cycling organic carbon is stored on land and one-third in the ocean (**Hedges et al. 1997**). There are two types of organic carbon defined based on their size: dissolved organic carbon (DOC; defined operationally as organic carbon passing through filters of 0.2-0.7 μm nominal pore size) and particulate organic carbon (POC; defined operationally as organic carbon being collected on the filters). DOC makes up the second largest of the bioreactive pools of carbon in the ocean (680–700 Pg C; **Williams and Druffel 1987**; **Hansell and Carlson 1998**), second to the large pool of DIC (38, 000 Pg C; **Hansell 2002**). Marine DOC is the largest ocean reservoir of reduced carbon, representing more than 200 times the carbon inventory of marine particulate biomass and

containing roughly the same amount of carbon present in the atmosphere as CO_2 (**Hansell and Carlson 2001**; **Hansell et al. 2009**). Most marine DOC results from photosynthesis in the surface ocean, and hence serves as substrate supporting vast heterotrophic prokaryote populations (**Hansell 2013**). The organic matter supporting these microbes is biologically labile and thus has a very short lifetime (hours to days), being quickly respired back to CO_2 (**Hansell 2013**). A small fraction of the DOC produced escapes rapid mineralization, is transformed (biotically or abiotically) to resistant material, and accumulates as residual, biologically recalcitrant DOC, thus creating the enormous ocean inventory of DOC (**Hansell 2013**). The size of the marine DOC reservoir, as well as its position as a sink for autotrophically fixed carbon and as a source of substrate to microbial heterotrophs, indicates that DOC plays a central role in the ocean carbon cycle (**Chapter 15, Hansell 2002**). The cycling of DOC in the oceans not only affects the global carbon budget (through, for example, air-sea CO_2 exchange) but also dissolved oxygen concentrations in ocean basins, global nitrogen and phosphorous cycling, trace metal cycling, and the biological productivity and net ecosystem metabolism of ocean margin areas (**Hedges et al. 1997; Cauwet 2002; Benner 2004; Fichot and Benner 2014**).

The coastal ocean represents the interface between land and ocean and thus carbon cycling in coastal waters is acknowledged to be a major component of global carbon cycles and budgets (Fig. 1; **Bauer et al. 2013**). The coastal ocean receives organic carbon derived from terrestrial materials through inputs of river water and coastal erosion, as well as organic carbon derived from marine materials produced *in situ* (through primary production) or carried in shelf sea water (Fig. 1; **Bauer et al. 2013**). Surface waters near continental margins, especially at the locations of coastal upwelling, tend to be very productive relative to the open ocean (**Capone and Hutchins 2013**). Moreover, the coastal ocean waters can be influenced to a greater degree by riverine inputs than by upwelling and tend to show increases in DOC concentrations due to

rivers introducing water with high DOC concentrations (**Chapter 15; Hansell 2002**). Once organic carbon is received in coastal waters, there are several possible fates for this material, which depend primarily on two factors: the relative size of organic carbon (POC or DOC) and its source and chemical composition. Coastal waters tend to experience significant losses of organic carbon owing mainly to the combined influences of sedimentation and degradation, including photochemical oxidation and microbial degradation (Fig. 1). POC, both marine and terrestrial, that does not get degraded in the water column or exported from coastal waters to the offshore is deposited to the sediments (Fig. 1), where it may also undergo degradation with subsequent release of CO_2 and DOC (not shown). However, degradation of organic carbon within sediments tends to occur slowly because of limited oxygen exposure and/or limited supply of other oxidants and the low supply of labile carbon. Thus, the capture and burial of POC in shelf sediments is the most important sink for organic carbon on Earth, potentially removing the organic carbon from active cycling for thousands of years.

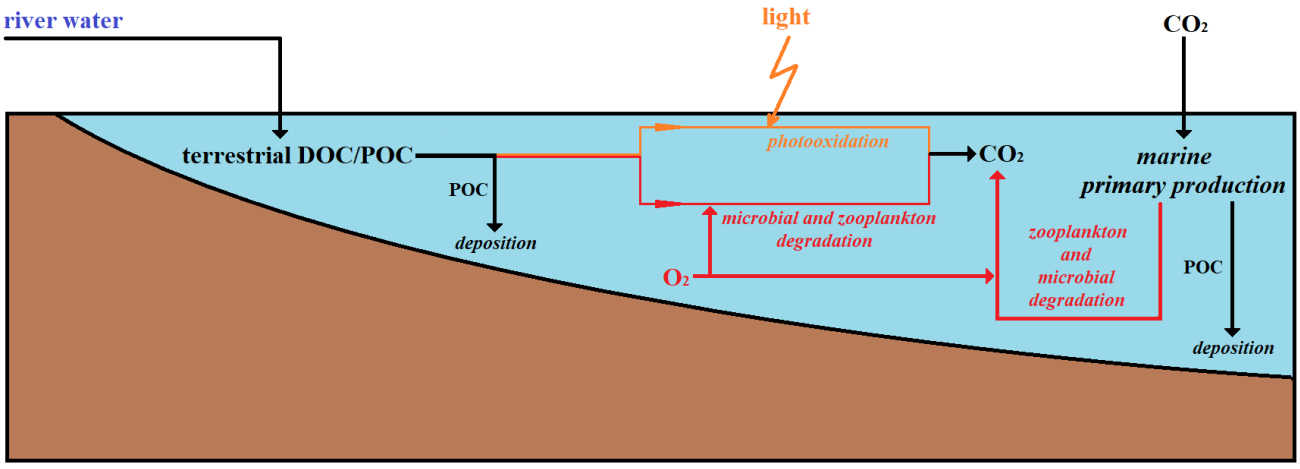


Fig. 1. Major processes affecting organic carbon cycling and fluxes in the river-influenced coastal ocean.

Degradation of organic matter in the coastal waters and sediments is affected by the unique reactivity and residence times of its component parts. Terrigenous DOC is the main source of chromophoric dissolved organic matter (CDOM) to the coastal ocean in nearshore areas. CDOM is the fraction of the DOC pool that absorbs light in the ultraviolet and visible ranges, which makes it susceptible to photobleaching resulting in CO_2 release if fully degraded (**Granskog et al. 2007**; Fig. 1). Both marine and terrestrial DOC may undergo microbial degradation, and their particulate counterpart may be consumed by zooplankton as well as undergo microbial degradation. Microbial and zooplankton degradation of organic carbon results in the release of CO_2 and consumption of O_2. Originally, it was thought that the degradability of marine and terrestrial organic matter substantively differed. Marine POC was found to recycle efficiently throughout the ocean water column and at the water/sediment interface (**Wakeham and Lee 1993**), mostly by zooplankton, and marine DOC was believed to be efficiently recycled by heterotrophic bacteria in the surface ocean (**Williams and Druffel 1987; Benner et al. 1992; Peltzer and Hayward 1996**). In contrast to the highly labile marine organic carbon, terrestrial organic carbon (OC) was assumed to be much more refractory in the ocean because it represents vascular plant material containing high concentrations of recalcitrant, nitrogen-free biomacromolecules such as lignin, tannin, suberin and cutin (**Ertel et al. 1986**; **Ittekkot 1988; Hedges et al. 1997**). However, recently, terrestrial-derived POC was found to support secondary production in estuaries (**Antonio et al. 2010, Cole and Solo mon 2012, Dias et al. 2014**) and, more importantly, the large riverine loads of terrestrial DOC were found to be much more degradable than previously thought (**Bianchi 2012**; **Ward et al. 2016**; **references in Chapter 4, Table 2**).

In the last two decades there has been a major shift in thinking regarding the potential degradability of terrestrial OC leading to the conclusion that it is much more significantly

degraded in the ocean than previously thought, leaving behind a residual that makes up at most a few percent (**Hernes and Benner 2002**) of the total organic carbon in seawater. One piece of evidence supporting this 'new paradigm' (**Bianchi 2012**) was the problem of the so-called "missing" terrestrial DOC and POC, which refers to the fact that only a small fraction of the organic matter dissolved in seawater and preserved in marine sediments appears to be land-derived, despite massive amounts of terrestrial OC entering the world's oceans. This imbalance between sources and identified sinks of organic carbon suggests that both dissolved and particulate organic matter of terrestrial origin suffer rapid and remarkably extensive remineralization at sea. Specifically, isotopic (e.g., $\delta\ ^{13}C$) and biomarker (e.g., abundance of lignin) measurements indicate that terrestrial OC undergoes losses of more than 50% in the marine environment (**Opsahl and Benner 1997**; **Hedges et al. 1997; Bianchi 2012**). Photooxidation (**Skoog et al. 1996**; **Osburn et al. 2009**; **Guéguen et al. 2016**) and microbial degradation (**Ward et al. 2016**; **references in Chapter 4, Table 2**) incubation experiments confirm this "new paradigm" showing substantial terrestrial DOC degradation in river and coastal ocean waters. Nevertheless, many unanswered questions remain, such as where terrestrial OC degradation occurs, in estuaries, transitional coastal waters, or the offshore; when it occurs and whether it depends on certain light conditions, water temperature, nutrients or other properties; and the relative importance of different mechanisms in contributing to the degradation.

2.2 Terrestrial organic carbon in the Arctic Ocean

The drainage basin of the Arctic (~24×10^6 km^2) processes about 11% of the global runoff (**Lammers et al. 2001**), and the corresponding riverine flux of carbon from the pan-arctic watershed to the Arctic Ocean is one key connection between the terrestrial and marine components of the carbon budget in the Arctic (**Guo et al. 2007**). The terrestrial ecosystems of the Arctic, which generally include flora and fauna of the tundra and boreal biomes, cover approximately 25% of the earth's vegetated land surface and contain about one third of the global terrestrial ecosystem's carbon total. These large carbon stores are estimated to include approximately 40% of the world's near-surface degradable soil carbon inventory (**McGuire et al. 1995**). Similar to the global oceans, the majority of the organic carbon transported to the Arctic Ocean from the watershed is in dissolved form, with total annual fluxes of about 33 Tg C yr^{-1} of DOC and 6 Tg C yr^{-1} of POC not including coastal erosion (**McGuire et al. 2009**). Consequently, while the Arctic Ocean is only 1.3% of the World Ocean, out of 250 Tg C y^{-1} of the estimated global annual riverine DOC flux to the World Ocean (**Hedges et al. 1997**), 33 Tg C y^{-1} (or 13%) is received by the Arctic Ocean (**Wheeler et al. 1997**). The influence of riverine DOC on Arctic Ocean waters is felt even far from shore. The river run-off from the Arctic basin constitutes an estimated 25% of the total DOC supply to the central Arctic Ocean with *in situ* production supplying 56% and Pacific water supplying 19% (**Wheeler et al. 1997**). The large supply of DOC by arctic rivers has led to the Arctic Ocean having the highest concentrations of terrestrial DOC (tDOC) of all ocean basins, particularly in the surface waters (**Benner et al. 2005**). Indeed, concentrations of dissolved lignin phenols in polar surface waters are 7-fold and 16-fold higher than those in the Atlantic and Pacific oceans, respectively, and stable carbon isotopic compositions of DOC are depleted in ^{13}C by 1–2‰ relative to those in the Atlantic and Pacific (**Benner et al. 2005**). Moreover, the tDOC inputs into the Arctic Ocean are increasing

due to climate-change driven increased river runoff (**Déry et al. 2011; McClelland et al. 2006; McGuire et al. 2009**), accelerated coastal erosion (**Mars and Houseknech 2007**), and permafrost thaws (**Vonk et al. 2015**). Thus, it has been recommended that integrated regional studies be conducted to link observations of carbon dynamics to the processes that are likely to influence those dynamics, such as riverine input of tDOC, which should contribute to developing a comprehensive carbon-climate model to improve the capability to assess the sensitivity of the carbon cycle of the Arctic to projected climate change (**McGuire et al. 2009**).

While the fate of terrigenous POC in the Arctic Ocean is still not clear (**McGuire et al. 2009**), **Hansell et al. (2004)** estimate a half-life of 7.1 years for tDOC in the Arctic Ocean, with microbial activity and photoreactions being the most probable causes of degradation. Photooxidation of tDOC in the Arctic Ocean is believed to be significant because, if exposed to solar radiation, tDOC undergoes significant photomineralization (**Miller and Zepp 1995; Gao and Zepp 1998; Bélanger et al. 2006; White et al. 2010**), while exposure of plankton-derived DOC to intense solar radiation leads to negligible photomineralization (**Ziegler and Benner 2000; Obernosterer and Benner 2004**). However, microbial degradation must be the dominant mineralization process for tDOC in the Arctic Ocean when considered in its entirety, because photodegradation occurs only near the ocean surface where (and when) sufficient light is available (**Granskog et al. 2007; Timko et al. 2015**). Thus, it is estimated that photooxidation rates in the Arctic Ocean may constitute only ~10% of microbial respiration rates on an annual basis due to the extended sea-ice and snow coverage and relatively low solar irradiation of polar surface waters (**Benner et al. 2005; Bélanger et al. 2006; Ward et al. 2016**). Indeed, according to the mass balance for carbon in the Western Arctic, microbial degradation predominates as the tDOC removal mechanism and constitutes 87% of the total tDOC degradation (**Hansell et al. 2004**). Microbial degradation of tDOC in the Arctic Ocean serves an ecological role, providing a

potentially important source of energy and bioactive elements for microbial communities, with cascading impacts for primary producers and higher tropic levels (**Benner et al. 2005; Holmes et al. 2008**). In addition to young (less than a year old) tDOC, old tDOC, mobilized by deforestation, agriculture, urbanization, and global climate change (e.g., thawing of permafrost soils, melting of glaciers and ice-sheets), has been shown to be consumed by aquatic organisms, sometimes even preferentially as compared to the young DOC (**Guillemette et al. 2017 and references therein**). The microbial degradation of old tDOC is particularly important in winter when other sources of tDOC are limited and, consequently, it plays an important role in stabilizing and increasing the capacity of the local aquatic (e.g., estuarine) food webs.

The outdated view that Arctic river DOC is refractory was developed mainly from the work focusing on the Eurasian side of the basin and the analysis of samples collected during mid to late summer months (**Cooper et al. 2005; Holmes et al. 2008**). This view was upheld by studies of photochemical degradation processes in Arctic coastal waters using CDOM, which revealed that only ~6-10% of DOM can be photomineralized in Arctic estuaries (**Bélanger et al. 2006; Osburn et al. 2009**). However, recently, several workers examining microbial degradation of tDOC in Arctic riverine and coastal ocean waters using incubation experiments have demonstrated a substantial tDOC degradation (~15-35%) over periods ranging from a few weeks to a few months (**Balcarczyk et al. 2009; Herlemann et al. 2014; Holmes et al. 2008; Kawahigashi et al. 2004; Mann et al. 2012; Shirokova et al. 2017; Wickland et al. 2012**). Since the extent and significance of microbial degradation of tDOC in seasonally ice-covered waters characteristic of the Arctic Ocean have only recently gained attention, the topic is still quite poorly understood (**Benner et al. 2005; Herlemann et al. 2014**) and clearly demands further research with a view to broadening the seasonal coverage of the observations (outside the mid to late summer months) and diversifying the studied rivers and coastal areas.

2.3 Microbial degradation of terrestrial organic carbon in coastal waters

The ocean margin, including estuarine, coastal and shelf environments, is the primary interface where most terrestrial OC enters the marine environment, and it is a region where rapid and major transformations of terrestrial OC are very likely to occur (**Benner 2004**). Indeed, the coastal ocean is probably a preferable environment for microbial degradation of terrestrial OC in comparison to rivers for several reasons. First, the presence of highly reactive substrates such as low molecular weight molecules and/or algal polymers abundant in the coastal ocean may stimulate bacterial and enzymatic production, which in turn increases the likelihood of terrestrial OC degradation. This case of enhancement in the degradation of a recalcitrant substance by microorganisms as a result of the presence of a readily degradable substrate is referred to as the priming effect (or co-metabolism) (**Bianchi 2012; Ward et al. 2016**). Second, it is expected that low nutrient levels in rivers may limit terrestrial OC consumption, resulting in a pulse of activity once the riverine terrestrial OC enters a relatively nutrient-rich environment such as the coastal ocean (**Holmes et al. 2008**). Variables that provide insight into the degradation rates of organic carbon include DOC/POC, dissolved CO_2 and other contituents of dissolved inorganic carbon (DIC), and dissolved oxygen (DO) concentrations or Apparent Oxygen Utilization (AOU). Other approaches used to gain insight into the dynamics of the microbial processes that contribute to the transformation of organic carbon in the coastal ocean, include 'omics' approaches (i.e. metagenomics, metatranscriptomics, metaproteomics and metabolomics) and the analysis of the connections between microbial metabolism and the chemical structure of organic carbon compounds, and long-term incubation experiments (**Zhang et al. 2018**).

2.4 Terrestrial organic carbon in Hudson Bay

Hudson Bay (including James Bay) (~0.84×10^6 km^2) represents one of the most southerly extensions of Arctic marine waters (**Granskog et al. 2011**) (Fig. 2). It experiences a complete annual sea ice cover, and, like the Arctic Ocean, receives very high river discharge, more than 760 km^3 or about 30% of the total Canadian river runoff (**Déry et al. 2011**). As a result, the annual runoff yield for Hudson Bay is approximately 0.9 m, which is almost three times higher than that of the Arctic Ocean (**Serreze et al. 2006**). The receiving volume of the bay is considerably smaller than the Arctic Ocean, further enhancing the significance of the large inputs of runoff water (**Granskog et al. 2011**). River runoff is introduced to the strong anti-clockwise surface coastal current system. Thus, in summer, its presence is largely confined to a coastal corridor ~ 100-150 km wide, while surface freshening in the offshore is largely controlled by sea-ice melt (**Granskog et al. 2011**).

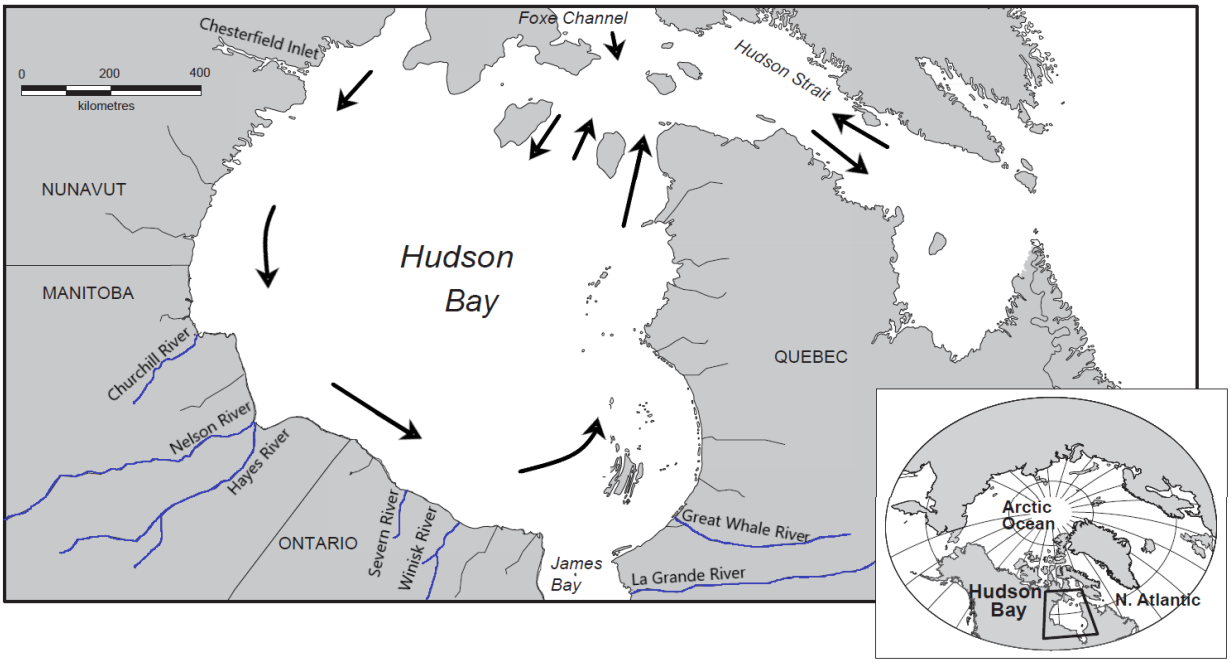


Fig. 2. A map of Hudson Bay showing general circulation patterns (solid arrows, **Mundy et al. 2010**) and main river input (highlighted in blue) into the bay.

Hudson Bay river input varies in response to shifts in climate and flow regulation associated with hydroelectric development. **Déry et al. (2016)** shows that the total annual river discharge in northern Canada has increased by 18.1% relative to mean annual discharge over the study period (1964-2013). This increase in river discharge is the result of warming air temperatures and reductions in Arctic sea ice extent causing increase in precipitation across northern Canada. While water control, including dams have a small net affect on total annual river discharge in Hudson Bay, they do seasonally impact river discharge. The past century has seen significant hydroelectric development on large rivers flowing into Hudson Bay including the Nelson River, which is located in southwestern Hudson Bay, and the La Grande River in eastern James Bay (Fig. 2). Hydroelectric development of these large rivers has led to a notable shift towards higher winter discharge and lower freshet discharge into Hudson Bay (**Déry et al. 2011**).

DOC concentrations measured in Hudson Bay were found to be within the upper range of those found in the Arctic Ocean with the median of 1.3 mg/l (1 to 2.4 mg/l) for the salinity range of 25.5 to 33.2 PSU (**Mundy et al. 2010**). In western Hudson Bay, a deep-water cold layer is associated with high DOC, possibly released by ice algae during spring blooms and transported to depth as a result of brine rejection making dense water (**Mundy et al. 2010**). The highest DIC concentrations (over 2250 µmol/kg) in Hudson Bay were found to be in the depths of central Hudson Bay, which is mostly due to the respiration of organic matter (90% of the DIC increase compared to the source waters) (**Azetsu-Scott et al. 2014**).

The Hudson Bay riverine DOC and POC inputs are estimated at 5.5 Tg C yr^{-1} (**Mundy et al. 2010**) and 0.46 ± 0.33 Tg C yr^{-1} (**Kuzyk et al. 2009**) respectively. Thus, tDOC substantially dominates over its particulate counterpart in Hudson Bay to a greater degree than in the Arctic Ocean. The southern rivers (Churchill, Nelson, Hayes, Severn, and Winisk rivers) have a distinct

composition of the organic matter and significantly higher values of both POC and DOC than other rivers (**Godin et al. 2017**). This pattern is mainly due to the difference in vegetation type, with coniferous forest stands in the south and tundra vegetation in the north (**Godin et al. 2017**). Moreover, southern Hudson Bay has extensive peat deposits, wetlands, and permafrost, which are mostly responsible for the elevated supply of riverine DOC into southern Hudson Bay and the substantial dominance of riverine DOC over riverine POC in the bay (**Godin et al. 2017**). Finally, hydroelectric development, for example in Churchill and Nelson rivers, may contribute to the elevated DOC in the southern Hudson Bay rivers and to a surprisingly 'old' ^{14}C-age of the DOC in the Churchill River (Fig. 2, **Godin et al. 2017**).

DOC concentrations in Hudson Bay rivers are generally lower than in the major rivers draining directly into the Arctic Ocean, which is a function of the vegetation and soil cover of the drainage basin (**Mundy et al. 2010**). However, as was mentioned, the rivers draining into the bay have a high range of DOC concentrations, with Churchill, Nelson, and Hayes rivers having DOC concentrations 2–6 times greater than other Hudson Bay rivers (**Mundy et al. 2010**). Indeed, the total riverine DOC input to Hudson Bay represents about 17% of the riverine DOC inputs to the Arctic Ocean, resulting in a much greater riverine input of tDOC on a per volume basis to Hudson Bay than to the Arctic Ocean (**Mundy et al. 2010; McGuire et al. 2009**).

The counter-clockwise circulation at the surface in Hudson Bay carries boundary water from Foxe Basin into southwestern Hudson Bay with a concomitant increase in DOC concentrations due to river input from Chesterfield Inlet and other large rivers in southwestern Hudson Bay including the Churchill, Nelson, Hayes, Severn and Winisk Rivers (Fig. 2, **Mundy et al. 2010**). As the water circulates to southeastern Hudson Bay, its DOC concentration is also strongly influenced by numerous rivers draining into James Bay (**Mundy et al. 2010**). Furthermore, **Mundy et al. 2010** demonstrates conservative behavior and stability of DOC

concentrations as the water exits out of the Hudson Bay system along the southern coast of Hudson Strait. In coastal Hudson Bay, DIC concentrations were found to be low in the southwestern part, higher in the eastern part of the bay and lower in the water mass flowing toward Hudson Strait (**Azetsu-Scott et al. 2014**). Assuming that waters are transported along lines of constant density, **Burt et al. (2016)** calculated that there is an apparent addition of approximately 90-110 μmol/kg DIC at δ_t = 25 kg/m^3 (25-50 m) and approximately 70 μmol/kg at δ_t = 26 kg/m^3 (40-100 m) between western and eastern coastal waters of Hudson Bay by the month of July, consistent with degradation of DOC. The results of a study by **Else et al. (2008)** showed that the marine-influenced waters on the western shelf of Hudson Bay act as a sink of CO_2 and the coastal, riverine-influenced waters of southern Hudson Bay and James Bay act as a source. This difference suggests that a combination of thermodynamic effects of warmer water on pCO_2 and the oxidation of riverine carbon are driving outgassing of CO_2 along the coast, while the CO_2 absorption in the offshore regions is most likely due to different source water, cooler temperatures and sea ice melt which is typically depleted in CO_2.

Recent studies have examined the photodegradation of tDOC in Hudson Bay (**Guéguen et al. 2011, 2016; Granskog et al. 2007, 2012**). Certainly, photodegradation plays an important role in degradation of the riverine DOC in the Hudson Bay system during the open-water period. The half-lives of Nelson/Hayes tDOC undergoing photobleaching were found to be about 4.9 to 9.9 days (**Guéguen et al. 2016**). Whether or not photodegradation plays as minor a role in the degradation of tDOC on an annual basis as it does in the Arctic Ocean (~10% of microbial respiration (**Ward et al. 2016**)) is unknown but snow and ice cover are primary limiting factors for photoprocesses and they cover the surface of Hudson Bay for more than half the year (December-June) (**Hochheim and Barber 2014**). The photobleaching of tDOC in the estuaries of the Nelson and Hayes rivers was found to decrease with increasing salinity (**Guéguen et al.**

2016), and therefore the coastal ocean could be a preferable environment for microbial degradation of tDOC due to the priming effect/co-metabolism (**Bianchi 2012; Ward et al. 2016**) and higher concentrations of available nutrients (**Holmes et al. 2008**). If one takes into account that the residence time of tDOC in rapidly flowing rivers is very small compared to that in the coastal corridor in Hudson Bay, the biologically active coastal ocean environment is where one expects much of the tDOC would be biodegraded before export from the Bay. Furthermore, **Burt et al. (2016)** found that rivers draining into Hudson Bay have a highly enriched $\delta\ ^{13}$C-DIC signature compared to other marine regions, which suggests that degradation of tDOC, which is low in $\delta\ ^{13}$C, does not have a significant effect on the $\delta\ ^{13}$C-DIC signature in the rivers. In spite of the expectation that microbial degradation of tDOC may be of significance for the carbon cycle in Hudson Bay, to date no research has been published on this topic. Thus, it is important to assess microbial degradation of tDOC in Hudson Bay in order to understand the role of tDOC in the carbon budget of Hudson Bay and the rest of the Arctic Ocean.

Chapter 3. Organic carbon degradation in coastal Hudson Bay as inferred from water mass distribution and Apparent Oxygen Utilization dynamics in late summer

3.1 Introduction and study area

Terrestrial organic carbon (terrestrial OC), mostly in the form of terrigenous dissolved organic carbon (tDOC), is delivered to oceans mainly by rivers and can reach the open ocean within months of the time of discharge (**Benner 2004**). The majority of the organic carbon transported to the Arctic Ocean from the watershed is also in dissolved form, with total annual fluxes of about 33 Tg C yr^{-1} of dissolved organic carbon (DOC) and 6 Tg C yr^{-1} of particulate organic carbon (POC) not including coastal erosion (**McGuire et al. 2009**). As a result, the Arctic Ocean has the highest concentrations of tDOC of all ocean basins, particularly in the surface waters (**Benner et al. 2005**). Hydrological changes in northern watersheds, such as climate-change driven increasing river discharge (**Déry et al. 2011; McClelland et al. 2006; McGuire et al. 2009**) and permafrost thawing (**Vonk et al. 2015**), are altering the transport of organic carbon into high-latitude coastal areas, and further change is expected with regional warming. It remains a matter of debate how these increased transports of terrigenous organic carbon will impact the biogeochemistry of high-latitude coastal seas because the fate of terrigenous organic carbon in coastal waters remains largely unknown (**Bianchi et al. 2012; Benner 2004**).

Hudson Bay represents one of the most southerly extensions of Arctic marine waters and is similarly characterized by substantial riverine DOC and POC inputs estimated to be 5.5 Tg C yr^{-1} (**Mundy et al. 2010**) and 0.46 ± 0.33 Tg C yr^{-1} (**Kuzyk et al. 2009**), respectively. The fate of the significant amount of riverine terrestrial OC received by Hudson Bay remains mostly unknown. However, there is strong evidence suggesting that ocean margins act as major "filters" of terrestrial OC between the land and ocean, where terrestrial OC undergoes extensive and rapid

destruction in the coastal waters leading to little terrestrial OC residing in the open ocean (**Hedges et al. 1997; Opsahl and Benner 1997; Fichot and Benner 2014; Benner 2004; Bianchi et al. 2012**). In the Arctic Ocean, riverine organic carbon must be degraded primarily through microbial degradation as photo-oxidation rates are only ~10% of microbial respiration rates on an annual basis, with snow and ice cover being one of the primary limiting factors for photo-processes (**Ward et al. 2016**). Hudson Bay is further south than the Arctic Ocean but still experiences a complete snow and sea-ice cover between December and June (**Hochheim and Barber 2014**), which implies that microbial degradation determines the extent of degradation of riverine organic carbon delivered during at least half the year. Moreover, Hudson Bay has experienced increased winter river discharge during recent decades due, in part, to climate change but primarily regulation of its largest rivers (Nelson River and La Grande; **Dery et al. 2011**). This implies that delivery of riverine organic carbon to Hudson Bay during the ice-covered period presumably has increased. This work seeks to address the question of this material's fate.

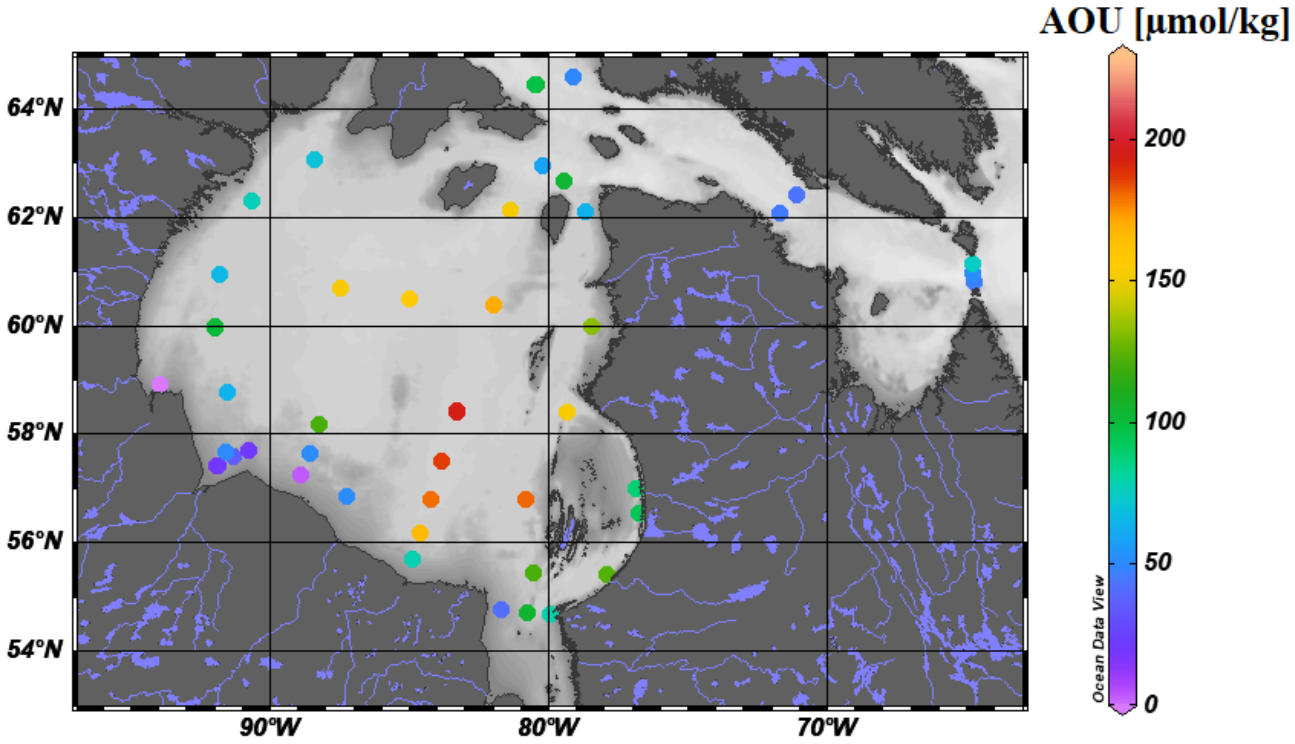
The extent of degradation of organic matter in the ocean can be directly traced by change in DOC/POC, dissolved CO_2 and other constituents of dissolved inorganic carbon (DIC), and dissolved oxygen (DO) concentrations or Apparent Oxygen Utilization (AOU). Specifically, given the right conditions, AOU has proven to be a reliable tracer of respiration in ocean waters (**Doval and Hansell 2000; Carlson et al. 2010; Pan et al. 2004**). Indeed, if primary production (PP) and oxygen exchange with the atmosphere do not affect AOU readings, change in AOU is primarily the result of organic carbon respiration by microbes, with the POC respiration by zooplankton often being negligible (**Pan et al. 2004; Del Giorgio and Duarte 2002**). Another advantage of AOU over geochemical tracers is that readings may be obtained reliably from ship's CTD-rosette systems, which yield continuous vertical profiles that may capture features in

the water column that could be missed by discrete water samples collected at limited depths. The robustness (e.g., degree of seasonal and inter-annual variability) of features can be assessed by comparing AOU observations from multiple cruises.

The greatest AOU maximums in Hudson Bay occur in the central part of the bay where water depths reach ~250 m (Fig. 3A-B). The highest AOU occurs specifically in the deep waters that underlie and are distinct from the seasonally-mixed winter surface mixed layer (WSML) (Fig. 3C). The maximum AOU distribution presented in Fig. 3 agrees well with the observations by **Azetsu-Scott et al. (2014)** for the period of August-October where the highest DIC concentrations (over 2250 µmol/kg) in Hudson Bay were observed deep in central Hudson Bay. If approximately 6–18% of the annual river input is exported into the deep offshore layer by winter densification in polynyas as suggested by **Granskog et al. (2011**), then degradation of riverine organic carbon may in part contribute to this AOU maximum. Unfortunately, in central Hudson Bay, it is very hard to derive the amount of annually degraded Hudson Bay-produced organic carbon from DIC or AOU readings, because it is speculative how and where deep waters in Hudson Bay are produced (**Granskog et al. 2011**), and, more importantly, the residence time of the deep waters in Hudson Bay is poorly constrained with a wide range of at least 4-14 years (**Pett and Roff 1982**). In contrast, the DIC and AOU is presumably modified annually by wintertime brine rejection within the deepest layer in the coastal domain of Hudson Bay, the WSML, which typically extends to the depth of 60-100 m (**Prinsenberg 1986**; **Saucier et al. 2004**; **Granskog et al. 2009**). Thus, any changes in AOU in the WSML, especially up to 100 m depth, may be assumed to be independent of the atmosphere and thus the result of the *in situ* physical and biological processes in this layer since winter, making it possible to approximate the amount of degraded organic carbon in the coastal corridor.

The central question this study aims to answer is whether or not riverine (mostly terrestrial) organic carbon is oxidized in the coastal margin of Hudson Bay. In order to address the question of microbial degradation of terrestrial OC, I have examined physical and chemical parameters, including AOU, in the coastal Hudson Bay waters during three oceanographic cruises spanning the early-late summer period of July-October. First, I specify the water masses persisting in coastal Hudson Bay during the period. Second, I infer the magnitude and important locations and times of year for the organic carbon oxidation from spatial and temporal patterns in AOU. Finally, I compare potential contributions of the PP and terrestrial OC degradation towards the observed change in AOU in coastal Hudson Bay.

A)



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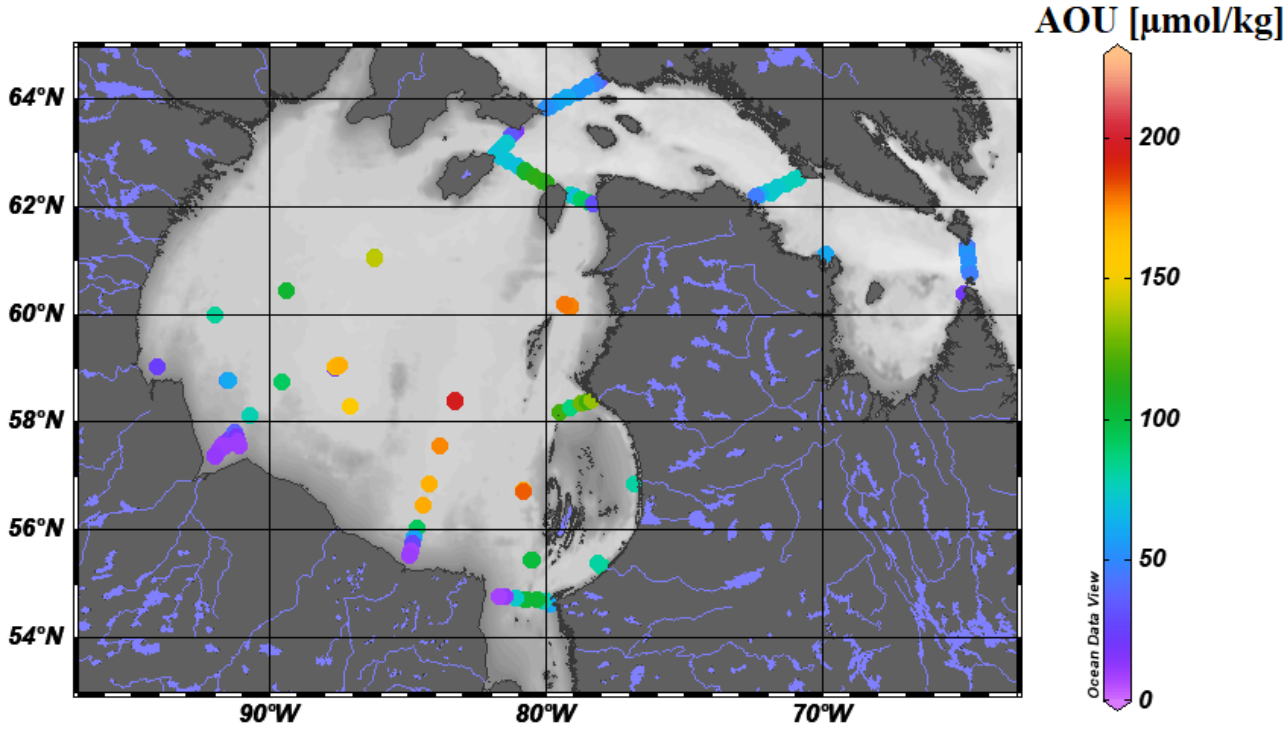


C)

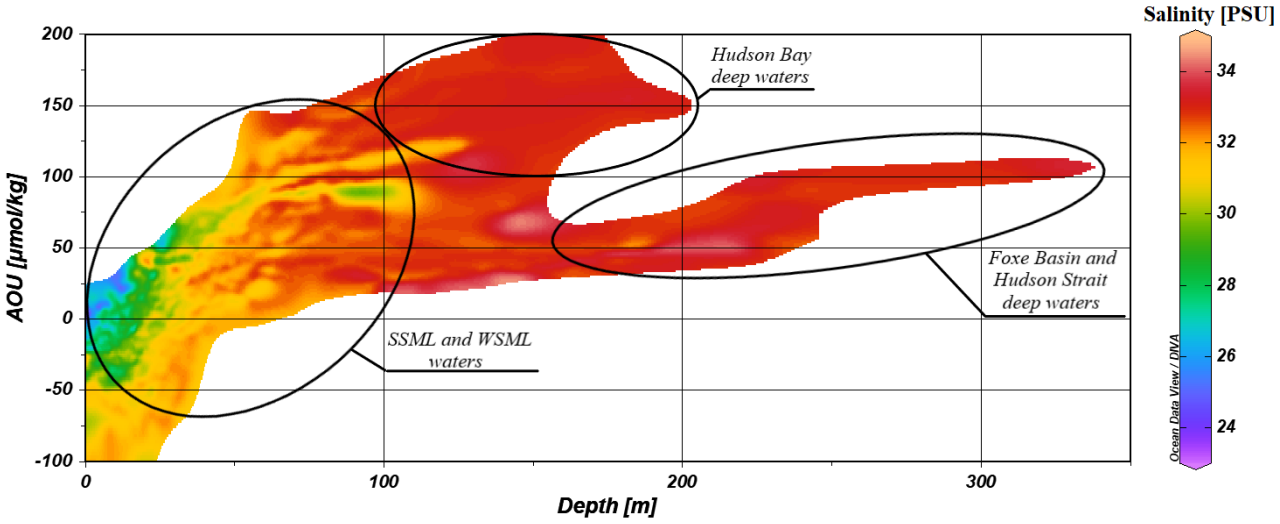


Fig. 3. Distribution of AOU maximums in Hudson Bay in A) July 2010, and B) September-October 2005 (scale at right). C) Relationship between AOU and depth with salinity displayed using colour shading (scale at right) for July 2010. The data was obtained from ArcticNet through Polar Data Catalogue.

The study was conducted along a transect shown in Fig. 4 (from now on referred to as "the coastal Hudson Bay transect"). This transect consists of twelve distinct numbered stations and includes common, composite and stand-alone stations. Common stations were sampled in more than one cruise. Composite stations (e.g., 3, 9, 10 and 11), are the "stations" uniting a few proximal stations from different cruises and given the same station number on the transect (note that I considered stations within 70 km as 'proximal' for identifying composite stations). The variability in properties among stations forming one composite station is no greater than the variability at a common station. Stand-alone stations have distinct colors on the map depending on the cruise. They are either completely separate stations on the transect (e.g., 4 and 5) or included in the composite stations.

Fig. 4 also portrays the following rivers (denoted with red stars) in the order of the increasing section distance counter-clockwise around the coastal corridor: Chesterfield Inlet, Ferguson River, Tha-anne River, Thlewiaza River, Seal River, Churchill River, Nelson River, Hayes River, Severn River, Winisk River, James Bay rivers (Ekwan River, Attawapiskat River, Albany River, Moose River, Harricana River, Nottaway River, Broadback River, Rupert River, Pontax River, Eastmain River, and La Grande River), Great Whale River, Nastapoca River, Innuksuac River, Kogaluq River, and Povungnituk River.

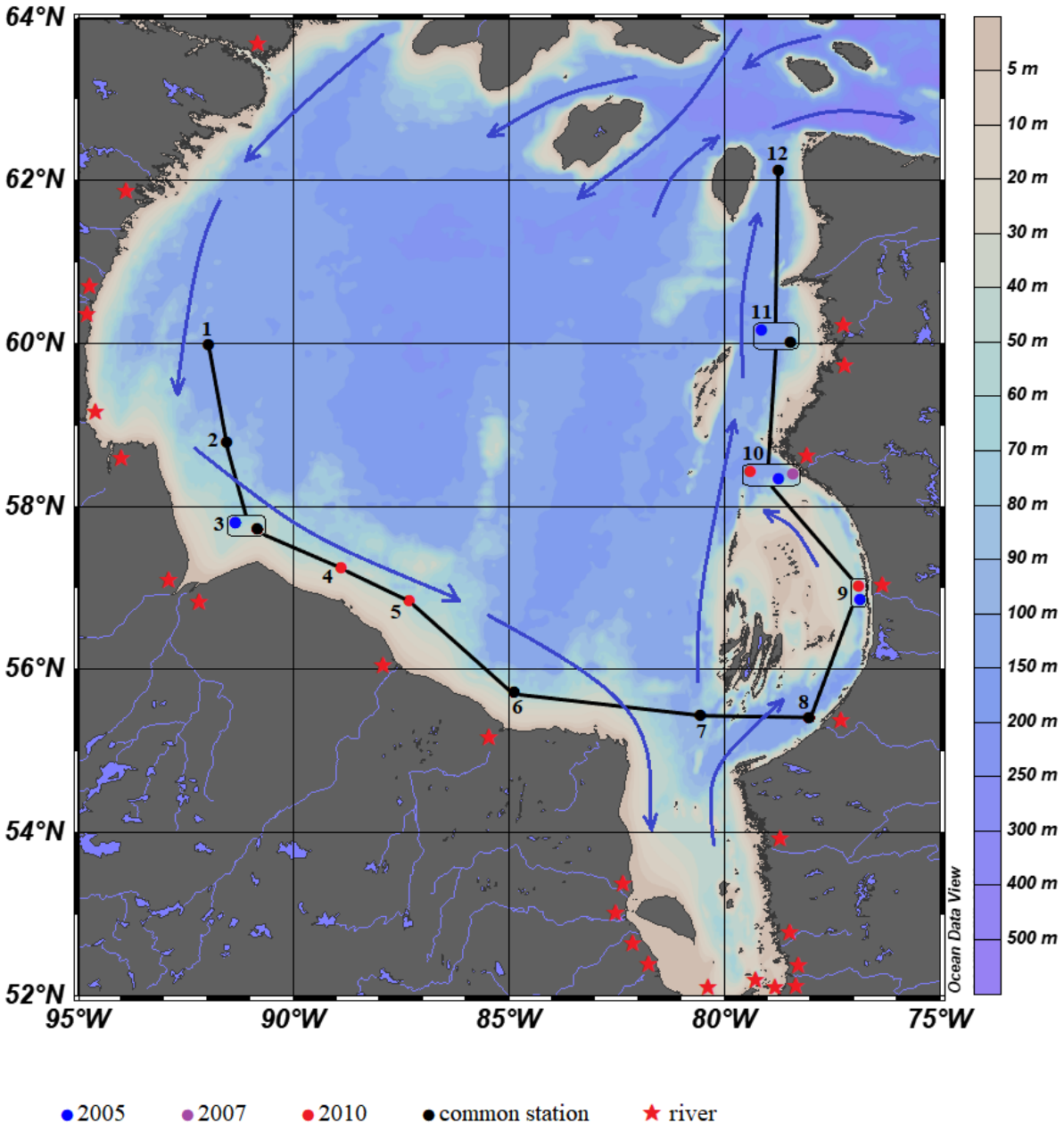


Fig. 4. Bathymetric map of the Hudson Bay system showing the common coastal corridor transect for the stations sampled during 2005, 2007 and 2010 *CCGS Amundsen* expeditions (bathymetry scale at right). Rivers specified were used for DOC budget calculations. Arrows represent water circulation in the bay (**Saucier et al. 2004**; **Mundy et al. 2010**).

3.2 Methods

3.2.1 Sampling and physical measurements

The data presented and analyzed here were obtained from ArcticNet through Polar Data Catalogue (www.polardata.ca). The data were collected in July 2010, August 2007, and September-October 2005 from aboard *CCGS Amundsen*. The parameters analyzed include dissolved oxygen (DO), *in situ* temperature, freezing temperature, salinity and chlorophyll *a* (chl *a*). The measurements were made using sensors ancillary to the ship's CTD-rosette system. The DO sensor was calibrated by comparing Winkler values with CTD-DO values in the same bottle. Also, a delay was added to the DO-CTD data in order for pressure, salinity and temperature data to align with the O_2 data by depth and subsequently be used to correct the raw DO. The temperature data used is the *in situ* temperature as opposed to the potential temperature. The chlorophyll *a* data was measured by Seapoint™ Chlorophyll Fluorometer with the minimum detectable level of 0.02 mg/l.

3.2.2 Calculation of Apparent Oxygen Utilization and Apparent Carbon Degradation

Apparent Oxygen Utilization (AOU, μmol/kg) was computed in Ocean Data View™ using dissolved oxygen, temperature and salinity as the input parameters.

Apparent Carbon Degradation (ACD) was computed using the following formula:

$$ACD = AOU * 0.72, \quad (1)$$

where 0.72 is a molar ratio representing the stoichiometric relationship between oxygen consumption and inorganic carbon production as a result of organic matter remineralization (**Anderson 1995**).

For calculating cumulative ACD (gC/m^2) for 50-100 m, the ACD readings were translated from μmol/kg to gC/m^3 using the *in situ* density.

3.3 Results

3.3.1 Distribution and properties of the water masses in coastal Hudson Bay

Fig. 5, Fig. 6 and Fig. 7 portray the difference between *in situ* and freezing temperature ($T\text{-}T_{freezing}$), chlorophyll *a*, and AOU along the coastal Hudson Bay transect, respectively. In these figures, the isolines represent constant *in situ* density anomalies (δ_t).

Fig. 5 highlights the summer surface mixed layer (SSML) mostly occupying the water column from surface to δ_t = ~23 g/cm^3. Its distinguishing characteristics in these data sets are relatively high temperature and low salinity, reflecting its formation by seasonal freshwater inputs (river runoff and ice melt) and surface warming (**Granskog et al. 2011; Ferland et al. 2011)**. As evident in Fig. 4, this layer extends to a depth of about 20 m in July but deepens to a depth of about 45 m by September-October, likely as a result of wind-induced and tidal mixing (**Prinsenberg 1986**). The SSML is the layer through which summer heating and mixing has penetrated and, hence, DO concentration has reached equilibrium with the atmosphere. The water density in the layer is influenced primarily by temperature. Since the SSML is also being penetrated by light, in Fig. 6, one can see abundant chl *a* hotspots in this layer. The chl *a* hotspots provide an approximate location and intensity of PP. Below the SSML lies the remnant of the WSML, which has relatively low temperature, high salinity, and insignificant PP. Since the depth of the coastal corridor is ~100 meters, the WSML occupies the remaining water column below the SSML. Unlike the SSML, these waters do not have direct contact with the atmosphere during the period of observations, nor have they interacted with the atmosphere since they were formed (made salty and cooled to the freezing point) in the winter. The water density in WSML is influenced primarily by salinity.

Fig. 7A shows that the AOU in the SSML is significantly below zero (0 to -25 μmol/kg) in July, which is likely a result of the water being well-oxygenated, recently warmed, and

harbouring a significant amount of PP at chl *a* hotspots. From August until October (Fig. 7B and 5C), AOU in the SSML is mostly around zero, which is usually expected from a mixed layer in equilibrium with the atmosphere. During the period of August-October, in the SSML, the AOU-lowering effect of the PP is probably being cancelled out by the high-AOU WSML waters being mixed into the layer as it deepens with time. Below the SSML, AOU decreases with depth and, consistently during the period of July-October, reaches more than 125 μmol/kg at stations 10 and 11.

Fig. 8 shows the relationship between temperature and salinity for the full water column along the coastal Hudson Bay transect. The general temperature range is -2 to 8 ºC, and salinity ranges mostly between 28 and 33 PSU. In this figure, AOU is displayed using color shading. During the period of July-October, substantial AOU hotspots (> 75 μmol/kg) are observed only at a temperature below 0 ºC and salinity greater than 30 PSU, suggesting an existence of a specific WSML water mass carrying the signal of a substantial organic matter degradation. The lowest AOU is generally found at relatively high temperatures, which represent SSML waters in immediate contact with the atmosphere. However, some low AOU (≤ 0 μmol/kg) waters are also found at temperatures less than -1 ºC, likely as a result of the local high PP.

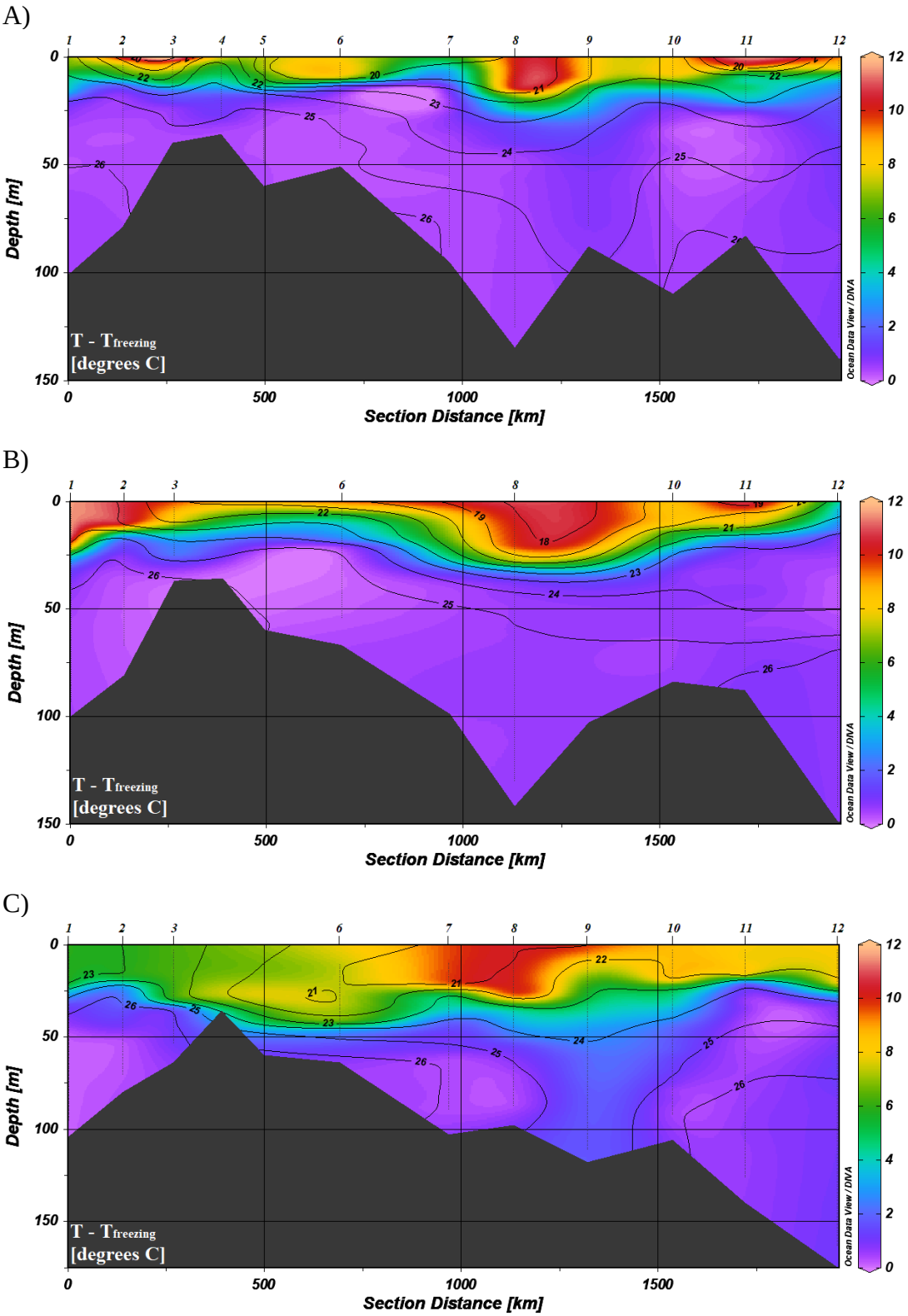


Fig. 5. Variations in the difference between *in situ* and freezing temperatures along the coastal Hudson Bay transect in A) July 2010, B) August 2007, and C) September-October 2005 (numbers on the top of the graphs represent stations). Isolines depict constant *in situ* density anomalies (δ_t, g/cm^3).

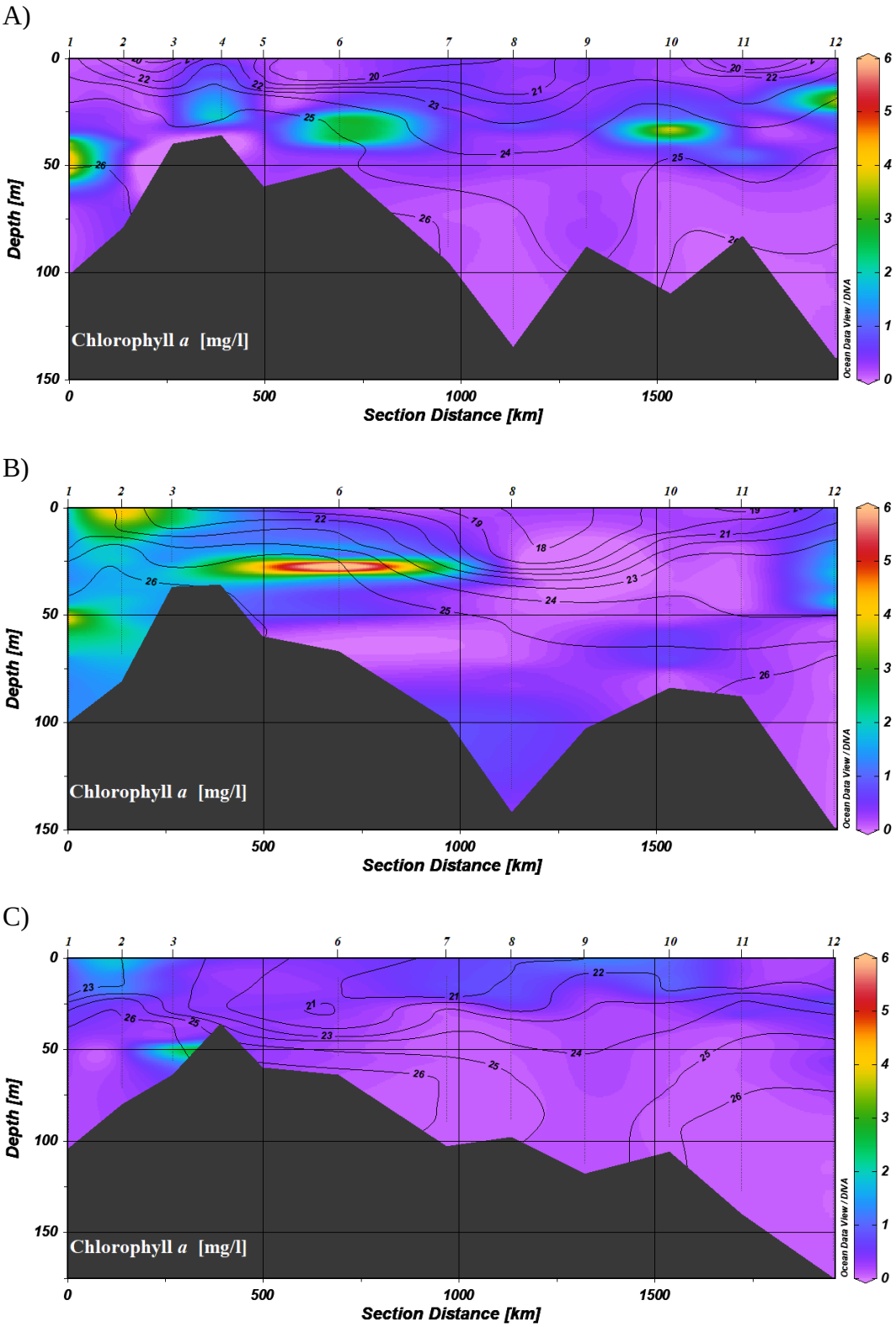


Fig. 6. Variations in chl *a* along the coastal Hudson Bay transect in A) July 2010, B) August 2007, and C) September-October 2005 (numbers on the top of the graphs represent stations). Isolines depict constant *in situ* density anomalies (δ_t, g/cm^3).

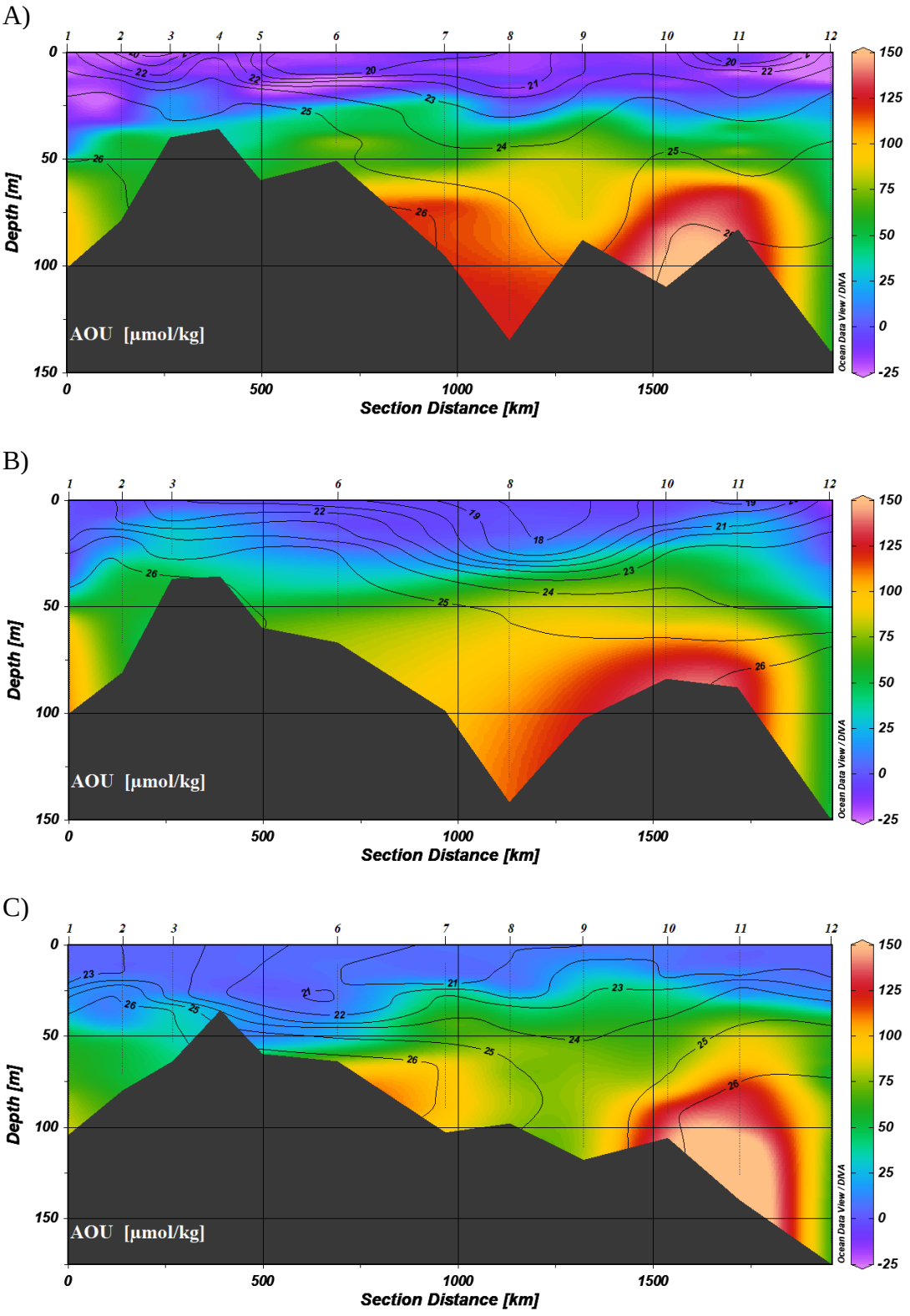
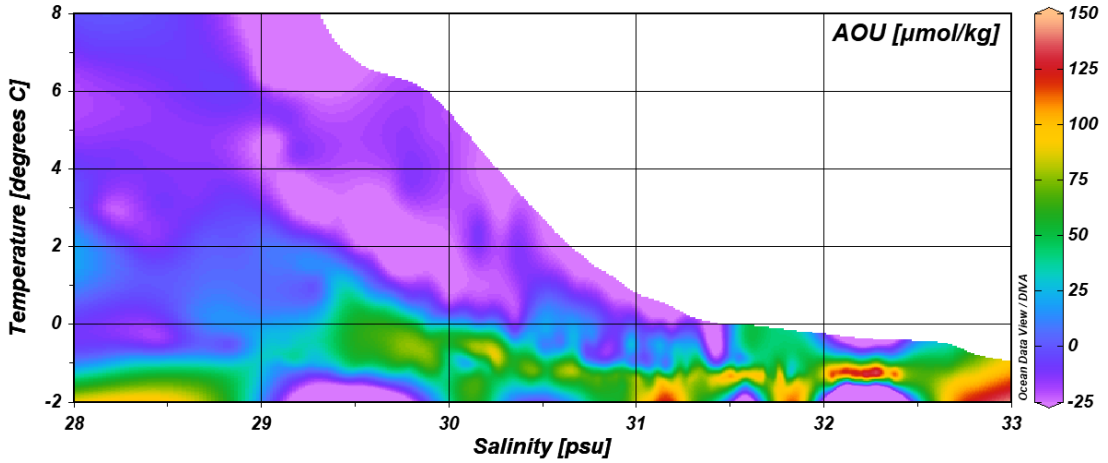


Fig. 7. Variations in AOU along the coastal Hudson Bay transect in A) July 2010, B) August 2007, and C) September-October 2005 (numbers on the top of the graphs represent stations). Isolines depict constant *in situ* density anomalies (δ_t, g/cm^3).

A)



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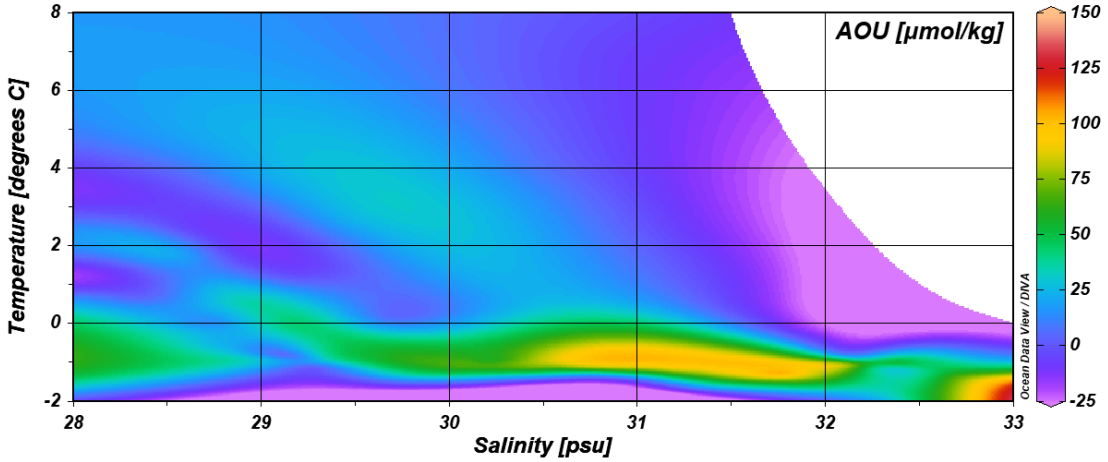


C)

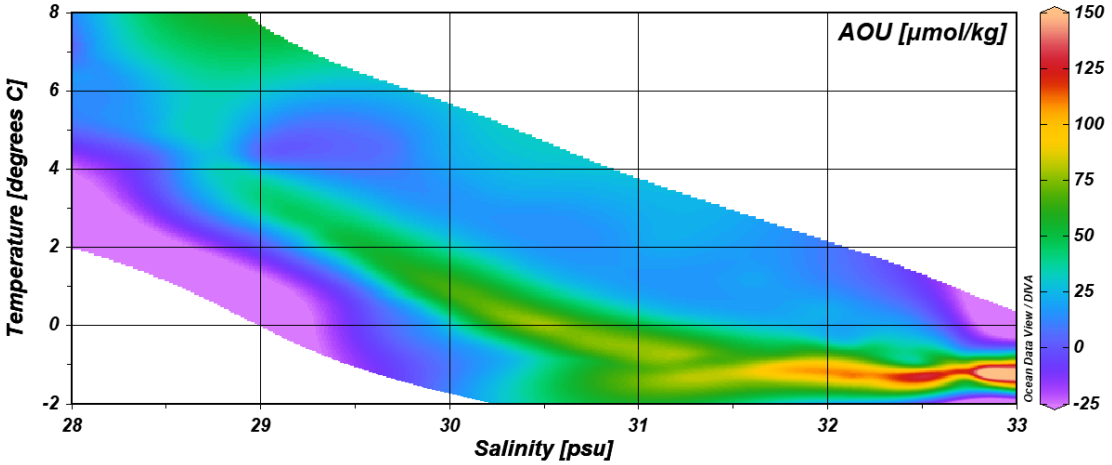


Fig. 8. Relationship between *in situ* temperature and salinity with AOU displayed using colour shading (scale at right) in A) July 2010, B) August 2007, and C) September-October 2005 in coastal Hudson Bay.

3.3.2 Apparent Carbon Degradation in coastal Hudson Bay

In order to reliably calculate ACD, the AOU used for the calculation should not have been affected by oxygen exchange with the atmosphere or PP. In order to avoid SSML and the waters with PP as much as possible, and yet represent ACD change along the constant *in situ* density anomaly most representative of WSML, average ACD during the period of July-October at δ_t = 25 g/cm^3 was chosen to be portrayed along the coastal transect in Fig. 9A. Moreover, in order to have a more reliable understanding of the change in ACD in the WSML along the coastal transect, stations 7 to 12 were chosen to calculate the average cumulative ACD at 50-100 m during the period of July-October. The choice of the stations and the part of the water column (the depth range) depended on the stations' bottom depth, data availability and absence of PP and oxygen exchange with the atmosphere at the chosen part of the water column. Error bars in Fig 9A portray standard errors resulting from averaging up the data from three different cruises.

Annual new production and cumulative riverine DOC input for the period of December-July along the coastal transect are provided for comparative and discussion purposes (Fig. 9B and 9C). The rivers used to graph the cumulative riverine DOC input are denoted with red stars in Fig. 4. In order to estimate the cumulative riverine DOC input during the period of December-July, the annual river discharge data and monthly mean river discharge for the western and eastern Hudson Bay drainage basins were taken from **Dery et al. (2005, 2016)**. The river DOC concentration data were taken from **Godin et al. (2017)**, **Granskog et al. (2007)**, and **Mundy et al. (2010)**. The graphed new production was estimated for the period of March-October using the monthly averaged phytoplankton production integrated over the upper 80 m of the water column and *f*-ratio (i.e. the ratio of new production to total primary production) reported in **Sibert et al. (2011)** for coastal Hudson Bay for the year 2003. It is assumed that the total annual PP is Hudson Bay is very close to the total PP happening during the period of March-October.

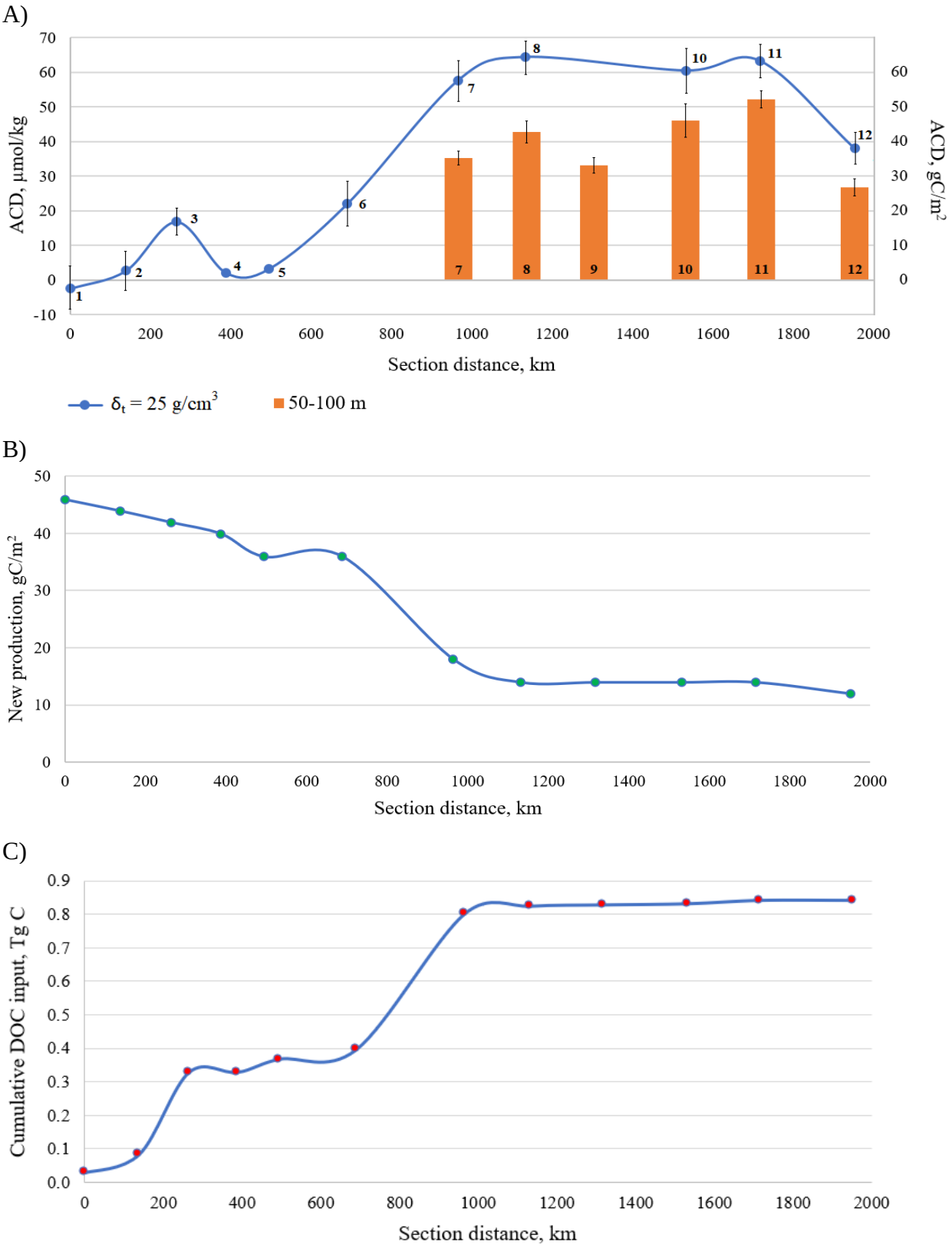


Fig. 9. A) Average ACD at δ_t = 25 g/cm^3 and cumulative ACD at 50-100 m in late summer, B) annual new production, and C) cumulative riverine DOC input along the coastal Hudson Bay transect during December-March (numbers near the dots and on the bars denote stations).

3.4 Discussion

3.4.1 Distribution and properties of the water masses in coastal Hudson Bay

From Fig. 5, it is evident that the water column is stratified during the period of July-October with fresh water occupying the top ~20, ~30 and ~45 meters in July, August, and September-October respectively. Although a WSML with near-freezing temperatures persists throughout the coastal corridor, the SSML is slowly integrating some of the WSML waters with time. The SSML at stations 7-9 is deeper and has higher temperature, which is likely to be a consequence of the substantial riverine input from James Bay (~50% of the total riverine input into Hudson Bay) (**Dery et al. 2011**) exiting mostly along the southeastern coast of Hudson Bay (**Saucier et al. 2004**; **Mundy et al. 2010**). The temperature readings and the behavior of constant *in situ* density anomalies (specifically, δ_t = 25 g/cm^3 and δ_t = 26 g/cm^3) at station 9 in July and, especially, in September-October point at a significant mixing in of the SSML waters into the WSML.

Chlorophyll *a* hotspots can serve as an indicator of the location and intensity of PP. In Fig. 6, one can see that southwestern Hudson Bay (stations 1-6) has substantially more PP throughout summer than eastern Hudson Bay (stations 8-12). Since new production is the product of *f*-ratio and PP, it is not surprising that the same pattern is observed in Fig. 9B, where the production decreases substantially after station 6 along the coastal Hudson Bay transect.

In Fig. 7, it is evident that the SSML has AOU mostly close to zero as a result of the established oxygen equilibrium between the surface layer and the atmosphere, and the occasional negative AOU hotspots correspond to PP. Some of the cold waters in the WSML (along δ_t = 25 g/cm^3) also have negative or close to zero AOU as a result of the local PP. Yet, overall, the WSML is characterized by high AOU, which increases both with depth and along the transect, as it progresses from the relatively shallow southwestern Hudson Bay enriched in PP to the deep

eastern Hudson Bay. The yellow-red hotspot of very high AOU (~100-150 μmol/kg) in the WSML between stations 7 and 12 with the peak in AOU at stations 10 and 11 is persistent throughout the whole period of July-October. The observed decrease in AOU (to ~75-100 μmol/kg) in the "middle" (station 9) of the hotspot in July and September-October is due to the mentioned significant mixing in of the SSML waters into the WSML in southeastern Hudson Bay, which serves as the location of the riverine water outflow from James Bay. Since the high AOU hotspot shows stability in temperature and salinity, as depicted in Fig. 8, and does not seem to be influenced by oxygen exchange with the atmosphere (except for the mentioned mixing in at station 9) or PP, the hotspot can be treated as a separate water mass within the WSML, which, in term of AOU, carries only the signal of substantial organic matter degradation.

3.4.2 Apparent Carbon Degradation in coastal Hudson Bay

The constant *in situ* density anomaly of $\delta_t = 25$ g/cm^3 was chosen to follow the change in ACD in WSML along the coastal Hudson Bay transect. $\delta_t = 25$ g/cm^3 never goes through the SSML, represents well the average *in situ* density anomaly in WSML, and persists throughout most of the transect in spite of it varying substantially in depth. Unfortunately, $\delta_t = 25$ g/cm^3 goes through high PP southwestern Hudson Bay waters in August making it a less reliable indicator of ACD in this area. Nonetheless, ACD starts increasing from values close to zero at station 5 located near the Severn River, to its peak of 64 μmol/kg at station 8 located near the riverine water outflow from James Bay. ACD remains as high as 60-64 μmol/kg in the 'downstream' eastern Hudson Bay stations until station 11, after which it drops to a substantially lower but still relatively high value of 38 μmol/kg. Overall, this pattern indicates a substantially higher degradation of organic matter in the eastern Hudson Bay WSML as compared to the southwestern Hudson Bay WSML. My calculated 60-70 μmol/kg ACD difference at $\delta_t = 25$

g/cm^3 (20-100 m) between western and eastern coastal waters in July-October is very similar to the apparent addition of approximately 90-110 μmol/kg DIC at δ_t = 25 kg/m^3 (25-50 m) and approximately 70 μmol/kg at δ_t = 26 kg/m^3 (40-100 m) between western and eastern coastal waters of Hudson Bay by the month of July, as calculated by **Burt et al. (2016)**.

In order to understand the extent of organic matter degradation in the high AOU water mass persisting in the eastern Hudson Bay WSML, stations 7s to 12 were chosen and cumulative ACD was calculated for the same depth span of 50 to 100 meters for all the stations. It is important to note that the high AOU water mass extends substantially deeper at some of the stations, reaching the depth of 150 meters, and in the deeper water, AOU and, consequently, ACD are even higher. Thus, the reported cumulative ACD underrepresents the extent of the organic matter degradation happening in the high AOU water mass. Overall, cumulative ACD in the high AOU water mass, between 50 and 100 meters, varies mostly between 40 and 50 gC/m^2. The cumulative ACD between 50 and 125 meters reaches 89 gC/m^2 at station 11 in September-October (data not shown).

There are two potential significant sources of the organic matter degraded in the high AOU water mass: new production, the part of the PP deposited to and degraded in WSML, and terrestrial organic matter/carbon deposited into coastal Hudson Bay by the local rivers. The annual new production in eastern Hudson Bay, according to **Sibert et al.** (**2011**), is estimated to be consistently ~15 gC/m^2 (Fig. 9B), which makes it an unlikely primary source of the degraded organic matter in the high AOU water mass, with a maximum contribution of ~35% towards the ACD. However, the southwestern Hudson Bay annual new production is mostly between 35 and 45 gC/m^2 (Fig. 9B, **Sibert et al. 2011**). Thus, in order for the degradation of PP in WSML to be the main cause for the observed ACD values in the high AOU water mass, the southwestern PP occurring after the winter up to the period of July-October has to be quickly transported to

eastern Hudson Bay and deposited into the local WSML, likely through the horizontal transfer of particulate organic matter, to fuel the respiration in eastern Hudson Bay. Although there is counter-clockwise coastal water circulation in Hudson Bay (**Saucier et al. 2004**; **Mundy et al. 2010**), a mechanism making this specific scenario possible has not yet been described. Another scenario of PP contributing a larger fraction of the high ACD is sequestration of the PP occurring during the previous summer SSML into the newly formed WSML in winter and subsequent degradation after a newly formed SSML is established. However, both particulate and dissolved PP is considered to be very labile (**Wakeham and Lee 1993**; **Williams and Druffel 1987; Benner et al. 1992; Peltzer and Hayward 1996**) and would probably be respired quickly during fall concurrent with the formation of the WSML, with the resulting AOU increase being immediately offset by oxygen exchange with the atmosphere as a result of mixing.

One likely source of the organic matter fuelling degradation to produce the observed ACD in the high AOU water mass is the riverine tDOC that is delivered into coastal Hudson Bay during the formation of the previous summer SSML, and subsequently being incorporated into the newly formed WSML. Another likely source would be the terrestrial OC deposited in winter during the WSML formation, which is very likely in the view that river discharge during the ice-covered period has presumably increased in Hudson Bay due to climate change and river regulations. Indeed, due to the enormous riverine input, the amount of the tDOC deposited by the rivers is high enough to control the DOC concentration in coastal Hudson Bay (**Mundy et al. 2010**; **Gueguen et al. 2016**; **Chapter 4;** Fig. 9C). Thus, we speculate that the tDOC deposited by Hudson Bay rivers, especially by Churchill, Nelson, Severn, and Winisk Rivers as well as James Bay rivers, during spring-late summer and during the WSML formation in winter eventually accumulates in the eastern Hudson Bay WSML as a result of winter mixing and sluggish counterclockwise coastal water circulation in WSML (**Saucier et al. 2004**). During this process,

the tDOC undergoes relatively slow degradation, which in turn forms the observed high AOU water mass by summer.

It is important to note that most of the tDOC is deposited into the coastal Hudson Bay in dissolved form (**Mundy et al. 2010**; **Kuzyk et al. 2009**) making a potential in-real-time contribution of horizontal transfer of terrestrial POC insignificant. Whereas zooplankton requires POC as a food source, heterotrophic bacteria are the only important group of organisms (concerning their role in carbon dynamics) which can use POC as well as DOC (**Gocke et al. 2003**). Only the low molecular fraction (mostly monomers) of DOC can be incorporated directly by bacteria, while the high molecular DOC and POC compounds have to be hydrolyzed by exo-enzymatic processes before the resulting products can be taken up (**Gocke et al. 2003**).

In order to assess the legitimacy of my conclusions regarding the importance of tDOC degradation in the eastern Hudson Bay WSML and in particular the sensitivity of the approach to variation in O:C ratios, I revisited formula (1) used to derive ACD from AOU. I chose to use the molar ratio $-\Delta C/O_2 = 0.72$ to calculate ACD from AOU because this fixed ratio allowed the comparison of results shown here against those shown by others (**Doval and Hansell 2000**; **Carlson et al. 2010**; **Pan et al. 2014**), acknowledging that the ratio was derived by **Anderson et al. (1995)** specifically for marine phytoplankton. Hence, the assumption was made that the O_2 consumption would mostly result from degradation of marine PP. Yet, in the coastal waters significantly influenced by riverine input, such as in the coastal corridor of Hudson Bay, terrestrial organic matter represents another potential source of organic matter and typically has a significantly higher C:N (30:1 to 60:1), whereas organic matter produced by marine phytoplankton in coastal systems has C:N near 7:1 (**Bauer et al. 2013**). As a result, if degradation of the tDOC indeed plays an important part in forming the observed AOU values in the eastern Hudson Bay, the molar ratio $-\Delta C/O_2 = 0.72$ should be significantly higher and thus

the ACD values reported here likely underestimate the amount of carbon degraded/released. This would further support my conclusion that, besides PP, there needs to be another more significant source of organic matter (e.g. tDOC) in the WSML, degradation of which could produce the high AOU values in eastern Hudson Bay.

3.5 Conclusions

During the period of July-October the water column in the coastal corridor of Hudson Bay is stratified. The top layer, the SSML, consists of warm fresh waters in which the majority of chl *a* is observed. Oxygen exchange with the atmosphere and PP give rise to negative or close to zero AOU in this layer. The mid-depth to bottom layer, the WSML, is characterized by high AOU during July-October, which increases both with depth and along the coastal Hudson Bay corridor from the relatively shallow southwestern Hudson Bay enriched in PP to the relatively deep eastern Hudson Bay.

ACD in the coastal corridor of Hudson Bay is close to zero in the western part of the bay, starts peaking near the Severn River and reaches its peak in the eastern part of the bay along the constant density anomaly of δ_t = 25 g/cm^3. Similarly, AOU maximums were observed to be much greater in the eastern coastal waters than in the southwestern coastal waters. Moreover, the eastern Hudson Bay WSML harbors a high AOU water mass carrying only the signal of substantial organic matter degradation. Cumulative ACD in the high AOU water mass, between 50 and 100 meters, varies mostly between 40 and 50 gC/m^2. The annual new production in eastern Hudson Bay is consistently ~15 gC/m^2, which makes it an unlikely primary source of the degraded organic matter in the high AOU water mass with maximum contribution of 35% towards the ACD. The most likely primary sources of the organic matter that has been degraded to produce the observed ACD in the high AOU water mass are riverine tDOC deposited into

coastal Hudson Bay during the formation of the previous summer's SSML, and during the formation of the WSML in winter. In view of the significant contribution of tDOC supplied by rivers, it is paramount to explore the extent of microbial degradation of tDOC in river and coastal waters of Hudson Bay a the year. This investigation would serve to support or oppose a newly established hypothesis: tDOC deposited by Hudson Bay rivers, during spring-late summer and during the WSML formation in winter, eventually accumulates in the eastern Hudson Bay WSML, as a result of winter mixing and sluggish counterclockwise coastal water circulation in WSML, and undergoes relatively slow microbial degradation, which in turn forms the observed high AOU water mass by late summer.

Chapter 4. Microbial degradation of dissolved organic carbon in riverine and coastal Hudson Bay waters under landfast ice as inferred from incubation experiments

4.1 Introduction and study area

Terrestrial dissolved organic carbon (tDOC) concentrations in ocean waters depend not only on inputs but also on rates of degradation. When discussing dissolved organic carbon (DOC) degradability, DOC can be divided into three pools: labile DOC (LDOC) that is consumed by heterotrophic bacteria directly in hours to days, semi-labile DOC (SLDOC) that needs bacterial enzymatic activity to be transformed into LDOC and has a turnover time of weeks to years, and refractory DOC (RDOC) that can be transformed into LDOC only after photooxidation and has a turnover rate of millennia (**Carlson et al. 2002**). In contrast to autochthonous (marine) forms of DOC, which are highly labile (**Vonk et al. 2017; Brogi et al. 2018**) and turned over very rapidly in the ocean (within hours to days; **Hansell 2013**), tDOC may be expected to be much more refractory in large part because it represents very highly degraded vascular plant materials (**Ertel et al. 1986**; **Ittekkot 1988**). The turnover of recalcitrant material including tDOC ranges from months to years in the surface ocean to 40,000 years in the deep ocean (**Hansell 2013**). However, all indications are that a portion of tDOC is significantly degraded in the ocean leaving behind a residual that makes up at most a few percent of the total DOC in seawater (**Hedges et al. 1997; Hernes and Benner 2002**). Thus, although DOC in the ocean is, on average, thousands of years old, there is a portion of the DOC (including tDOC) that cycles on much shorter time scales (days to decades) (**Druffel et al. 2017**). The proportion of tDOC that is degradable is significant for biogeochemical cycles, influencing the role of coastal oceanic waters (sources or sinks of carbon) in the global carbon budget. Sources and lability of tDOC delivered to the ocean, particularly in Arctic areas, are thus an important area of research.

Photodegradation and microbial degradation are the main pathways through which tDOC is removed in ocean basins, but the significance of these processes for tDOC degradation in polar surface waters is uncertain (**Benner et al. 2005**). Photodegradation of tDOC occurs near the ocean surface where (and when) sufficient light is available (**Granskog et al. 2007; Timko et al. 2015**). As a result, in the Arctic Ocean and surrounding rivers, photooxidation rates are typically ~10% of microbial respiration rates on an annual basis, with snow and ice cover being one of the primary limiting factors for photoprocesses (**Ward et al. 2016**). This makes microbial degradation the main pathway of tDOC remineralization in the Arctic Ocean.

One view, developed mainly from work focusing on the Eurasian side of the basin and the analysis of samples collected during mid to late summer months, is that arctic river DOC is refractory (**Cooper et al. 2005; Holmes et al. 2008**). However, recent incubation experiments have demonstrated that tDOC in Arctic riverine and coastal ocean waters undergoes significant degradation (~15-35%) over periods ranging from a few weeks to a few months (**Balcarczyk et al. 2009; Herlemann et al. 2014; Holmes et al. 2008; Kawahigashi et al. 2004; Mann et al. 2012; Shirokova et al. 2017; Wickland et al. 2012**). The reported fractions of tDOC undergoing microbial degradation far exceed the 6-10% of DOC that apparently can be photomineralized in Arctic estuaries (**Bélanger et al. 2006; Osburn et al. 2009**). There has been an intensification of studies of photochemical degradation processes in Arctic coastal waters using the coloured or chromophoric portion of dissolved organic matter (CDOM) (cf., **Bélanger et al. 2006; Osburn et al. 2009; Guéguen et al. 2014**). However, the extent and significance of microbial degradation of tDOC in seasonally ice-covered waters characteristic of the Arctic Ocean is still quite poorly understood (**Benner et al. 2005; Herlemann et al. 2014**). In view of the evidence that riverine DOC inputs to the coastal Arctic Ocean are more labile than previously realized, clearly there is a need for further research of microbial degradation potential of tDOC

with a view to broadening the seasonal coverage of the observations (outside the mid to late summer months) and diversifying the studied rivers and coastal areas.

Hudson Bay, a large seasonally ice covered shelf sea in northern Canada (Fig. 10), is an exceptionally good place for studying microbial degradation of tDOC in coastal Arctic waters. Since the bay is located on the southern margin of the Arctic, it is more vulnerable to rapid climate-driven change while at the same time more accessible for research expeditions. DOC substantially dominates over POC in Hudson Bay, which corresponds to the situation along the Arctic Ocean shelves. Hudson Bay receives a large volume of river discharge, which carries a high tDOC load. In particular, high DOC concentrations are typical of the rivers that drain southern Hudson Bay, where peat and permafrost are present (**Godin et al. 2017**). In spite of microbial degradation being the most significant mechanism of tDOC degradation in the Arctic Ocean, to date no research has been published describing microbial degradation of tDOC in Hudson Bay. This data gap needs to be addressed in order to arrive at a meaningful conclusion about the overall lability of tDOC in Hudson Bay and build a reliable model describing the fate of tDOC in Hudson Bay and the Arctic Ocean.

This study examines microbial degradation of DOC in riverine and coastal Hudson Bay waters (Fig. 10) using an incubation experiment approach. The study focuses on late winter, when river waters discharge under snow-covered land-fast sea ice, which is a dark environment in which photooxidation is not expected to be optimal (**Granskog et al. 2007**; **Ward et al. 2016**). Late winter, before the beginning of the spring bloom, is an important time period during which Arctic estuaries may be expected to be energy-limited, which increases the ecological importance of energy potentially made available by degradation of tDOC. The study compares two contrasting riverine-coastal areas, which may be expected to differ in the amount and composition of riverine tDOC and in marine-derived characteristics. Incubation experiments

conducted with river water and coastal sea water for a total of 45 days provide some of the first information about the degradability and lability of tDOC introduced into the coastal waters of Hudson Bay in late winter and the impact on microbial degradation potential of contrasting source waters and coastal settings.

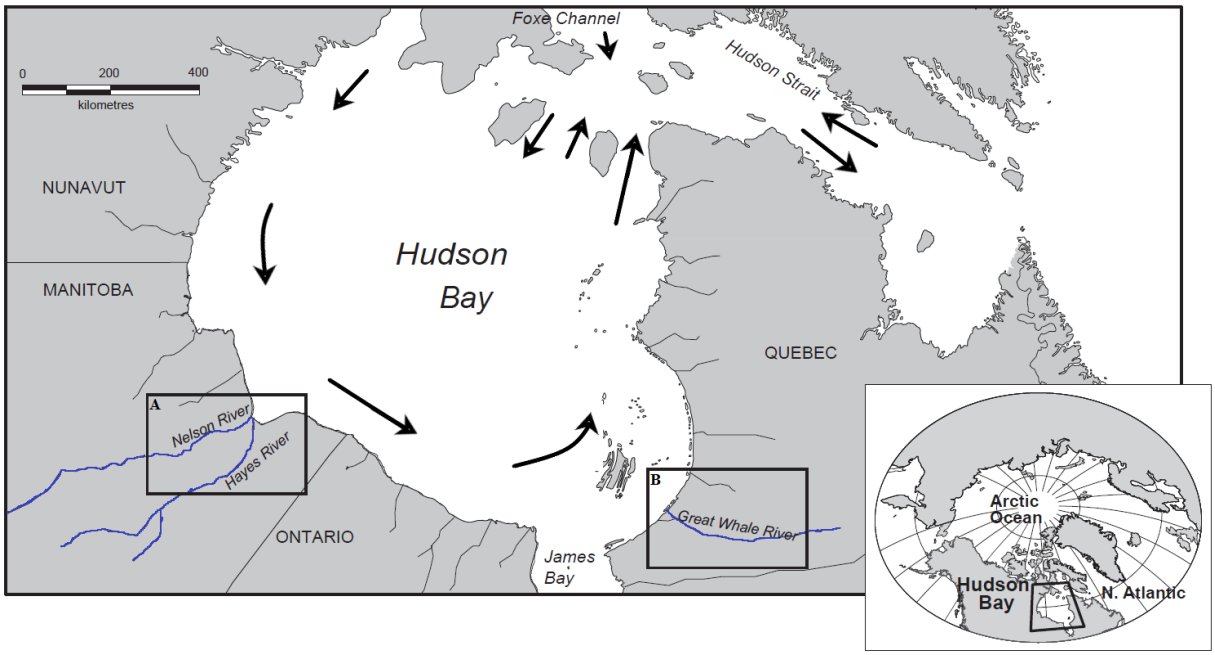


Fig. 10. A map of Hudson Bay showing general circulation patterns (solid arrows, **Mundy et al. 2010**) and the two study sites focusing on the Nelson and Hayes Rivers and the southwestern coastal waters (A) and the Great Whale River and southeastern coastal waters (B). The rivers are highlighted in blue.

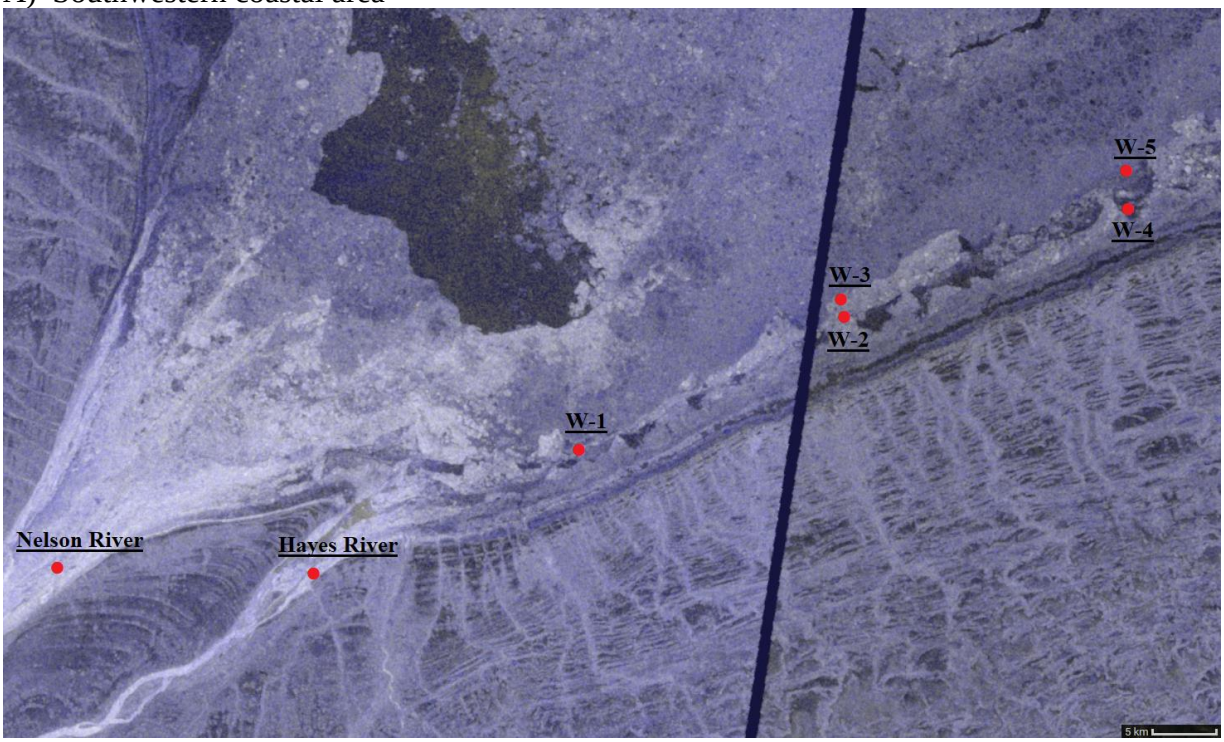
Within Hudson Bay, the study focuses on two riverine-coastal areas: one in southwestern and the second in southeastern Hudson Bay (Fig. 10). The coastal waters of the southwestern study area receive discharge from the Nelson and Hayes River systems. The Nelson River system is the largest river discharging to Hudson Bay with a mean annual discharge of 130.77 km^3/yr for the period of 2004-2013. The drainage basin of the Nelson River is very large (970,000 km^2) and includes Lake Winnipeg. Downstream of Lake Winnipeg, the Lower Nelson River drains an area of about 90,580 km^2 of boreal forest within the Canadian Shield region of Canada. The Churchill River Diversion (CRD) operated by Manitoba Hydro since 1977 also

flows into the Lower Nelson River (**Smith et al. 2015**). Because of river regulation, the Lower Nelson River has a relatively flat hydrograph (Fig. 12) with high winter time flows compared to unregulated rivers. The Hayes River is a smaller (21.31 km^3/yr for the period of 2004-2013; **Dery et al. 2016**), unregulated river with a nival discharge regime (Fig. 12) that drains the massive peatlands of the Hudson Bay Lowlands (among the largest peatlands in the world). The coastal waters of the southeastern study area receive discharge directly from the Great Whale River system, which is a natural river system similar in size to the Hayes (18.98 km^3/yr in 2004-2013; **Dery et al. 2016**). The southeastern Hudson Bay coastal area is also indirectly influenced by river-water rich outflow from James Bay, which is immediately 'upstream' (Fig. 10).

The Nelson and Hayes Rivers discharge together into a large, mostly shallow (~6 m), funnel-shaped estuary (Fig. 11A). The tide in the estuary is semidiurnal and dominated by the M2 tide. At Port Nelson, near the river mouth, the tidal range varies from 2 m to 5 m for neap and spring tides, respectively (**Wang et al. 2012**).

The southeastern coastal area near the Great Whale River is quite different in that the seabed slopes more steeply giving rise to relatively deep nearshore basins (50 m or more in places). The area also has lower tidal amplitudes (<2 m) than the southwestern coast. The Great Whale River, while only moderate in size, plays an important role in modifying the local surface waters, particularly in winter under the landfast sea-ice cover, when the extent of the river plume is felt over a much wider area (typically 500-2000 km^2) compared to the open water periods of summer to fall (typically 50 km^2) (**Ingram et al. 1996**). Snow melt in the river basin usually starts in late April-early May, while the sea ice is still present in the estuary and generates a river freshet with a discharge of 2 to 3 times the annual mean.

A) Southwestern coastal area



B) Southeastern coastal area

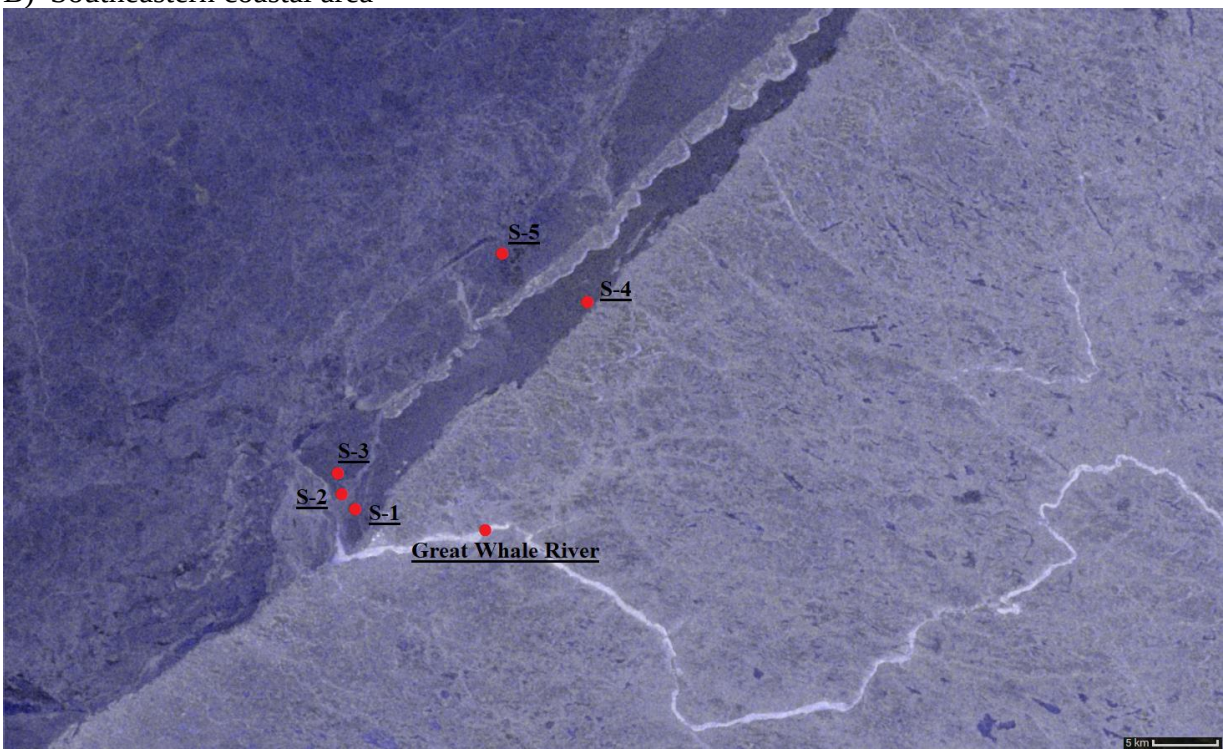
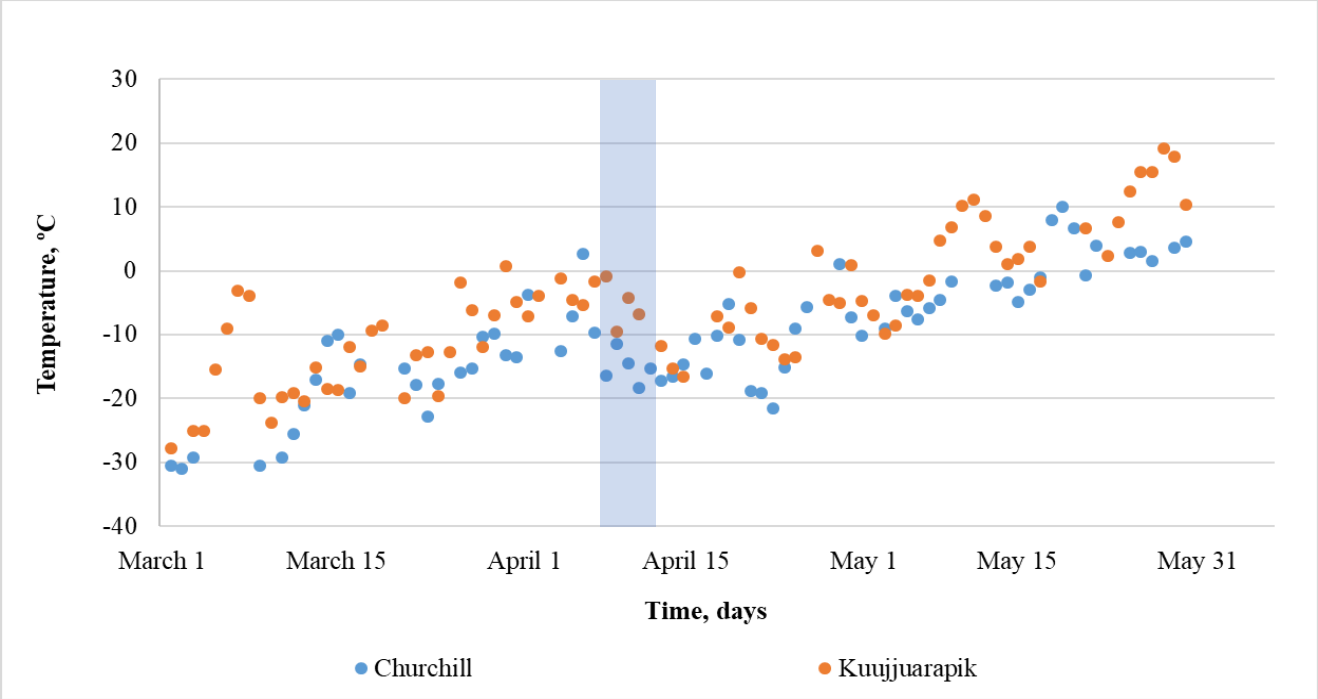


Fig. 11. Southwestern (A) and southeastern (B) riverine-coastal study areas showing location of sampling stations, in addition to ice coverage. The images represent conditions for April 11, 2017 (Sentinel-1, Arctic Eider Society's Interactive Knowledge Mapping Platform for Community-Driven Research).

A)



B)

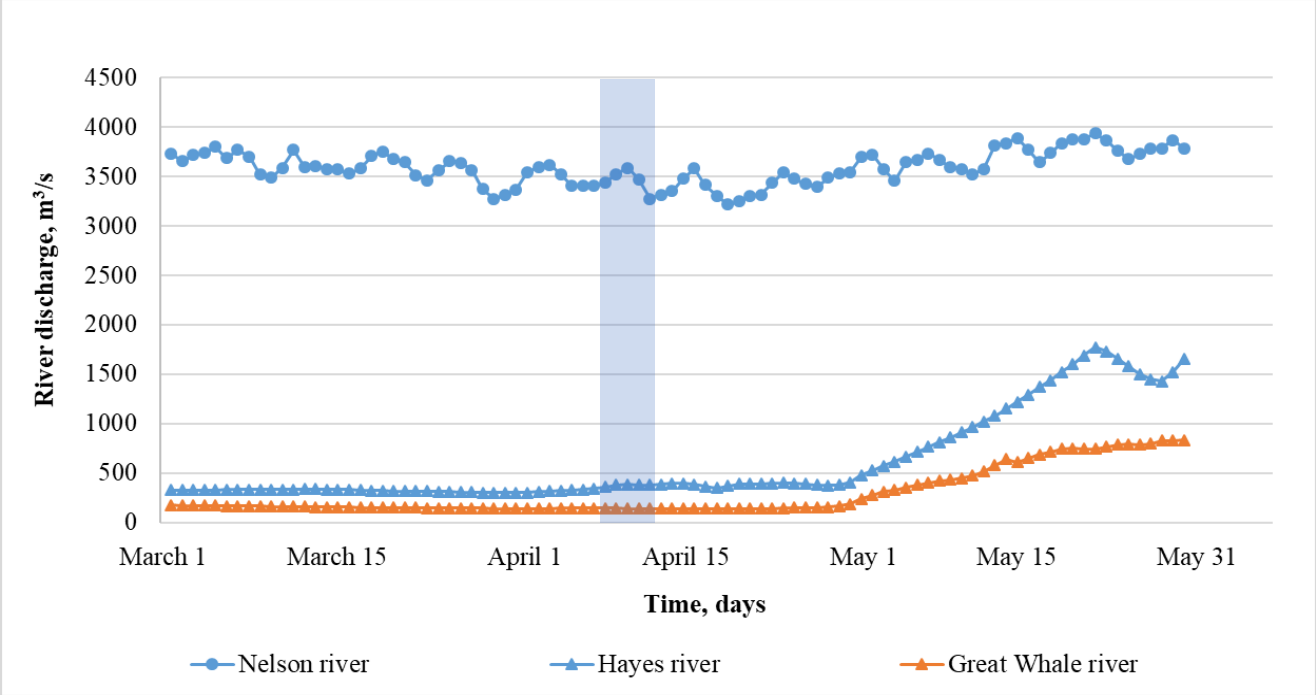


Fig. 12. Daily average air temperatures in southwestern Hudson Bay (Town of Churchill, ~200 km NNW of Nelson River outlet) and southeastern Hudson Bay (Town of Kuujjuarapik, at the Great Whale River outlet) leading up to the sampling period (April 9-13, 2017) (A) and daily river discharges of the Lower Nelson River (average of 2000-2016; 56° 23' 51"N, 94° 22' 10"W), Hayes River (2017; 56° 25' 00"N, 92° 48' 33"W), and Great Whale River (average of 2000-2013; 55° 14' 15"N, 76° 59' 02"W) (B). Data from Environment and Natural Resources, Government of Canada.

4.2 Methods

4.2.1 Sampling and physical measurements

Water sample collection and measurement of temperature and salinity were conducted from the river ice and landfast ice platforms during April 9 to April 13, 2017. The sampling sites in the southwestern Hudson Bay (SWHB) study area were evenly distributed over a distance of about 90 km paralleling the shoreline in an ENE direction and no more than 5 km offshore (Fig. 11A). The sampling sites in the southeastern Hudson Bay (SEHB) study area were distributed over a distance of about 25 km. Some of the SEHB sampling sites were close to the river mouth while the rest were ~25 km away in a NE direction but within 5 km of shore (Fig. 11B).

Spring thaw in the Nelson and Hayes River basins had only just begun at the time of sampling. At the nearest climatological station (Churchill, ~200 km NNE of the Nelson River mouth), there had been only one day with an average air temperature above zero (Fig. 12A). There was a small increase in discharge in the Hayes River that occurred during the sampling period but the onset of spring freshet was still weeks away (Fig. 12B). SWHB had a thin snow cover and a partial ice cover at the time of sampling (Fig 12A). Land fast ice extended out from the shore ~5 km or more but there was an area of open water over the deepest central part of the estuary, as is typical of this estuary throughout the winter (**Wang et al. 2012**). In SEHB, there also had been only a single day with average temperatures above zero. Based on visual observations, there had not yet been any significant thaw in the Great Whale River basin, and, in the estuary, there was a continuous cover of landfast sea ice, which was itself covered with snow.

The water samples were collected from depths of 1-6 m in SWHB and 1-50 m in SEHB (Table 1) using a Kemmerer sampler lowered through a hole cut in the landfast ice. The water was placed into glass bottles rinsed three times before filling. The temperature and salinity measurements were performed using a CTD sensor (IDRONAUT), lowered through the hole.

Salinity was also subsequently measured on bottle samples using a Guildline Autosal 8400 salinometer with a precision better than 0.002. Samples were standardized against IAPSO Standard Sea Water.

4.2.2 Incubation experiment

The incubation protocol was loosely based on the standardized DOC incubation protocol described by **Vonk et al. (2015)**. Within 24 hours of sampling, water samples were filtered through 0.7 μm glass fiber filters into sixteen 20 ml glass vials in order to have eight time points in duplicate. Filtration through 0.7 μm glass fiber filters allows not only inanimate DOC but also a sufficient number of bacteria to pass through the filter. The glass vials were tightly sealed and incubated at 4°C in order to have the incubation temperature as close to the *in situ* temperature as practically possible. The vials were incubated in the dark in order to avoid autotrophic respiration and photodegradation. A little headspace was left in each vial in order to avoid oxygen depletion and allow CO_2 outgassing during degradation and acidification.

For each sample, a separate duplicate of the incubation vials was treated with 200 μl of 2 M hydrochloric acid at the following time points: T = 0, T = 0.3, T = 1, T = 3, T = 8, T = 15, T = 25 and T = 45 days. The acidification serves two purposes: terminating all microbial activity and lowering pH of the water to remove inorganic carbon. The time points have a progressively increasing time lapse in order to be able to capture both rapid degradation of labile DOC in the first few days of the experiment and much slower degradation of semi-labile DOC happening over a span of weeks to months. Once poisoned, the samples were stored in the dark at 4 °C until analysis.

All the plastic equipment used in the experiment, such as syringes, forceps, filter holders and vial caps, was rinsed with 10% HCl, while the glass equipment, such as vials, was both

washed with 10% HCl and pre-combusted at 550 °C for 6-12 hours. The glass fiber filters were pre-combusted at 550 °C for 6-12 hours. Special care was taken to avoid organic carbon contamination at all times.

4.2.3 DOC analysis

DOC analysis was conducted using a Thermalox™ TOC-TN analyzer employing the thermal catalytic oxidation technique. Each incubation set, defined as all the incubation time points for the specific water sample, was analyzed in full during a DOC analysis session, so that the same calibration curve would be used for the whole incubation set. A new calibration curve specific for the expected DOC range of the samples analyzed was created for each DOC analysis session. Since the samples collected from coastal Hudson Bay near the Great Whale River often had low DOC values (1-2 mg/l) for the final time points, 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 was used as an additional calibration point when creating calibration curves for these incubation sets.

Five to eight injections were used for each time point depending on the expected DOC range and the resulting coefficient of variation, which had to be equal to or below 2% for the reading to be considered valid. The lower the expected DOC range, the greater the number of injections we used. If the resulting coefficient of variation exceeded 2% after the standard number of injections (4 to 6 depending on the expected DOC range), additional injections (1 to 2 depending on the standard number of injections) were made, after which the outliers (1 to 2 depending on the standard number of injections) were deleted before calculating the average result.

In total, 27 incubation sets were analyzed: 11 for samples collected in SWHB and 16 for

samples collected in SEHB. While all incubation sets were performed in duplicate, 6 sets were chosen to be analyzed in duplicate. The decision regarding which incubation sets to analyze in duplicate was made once all the incubation sets were analyzed and the data produced was plotted. The incubation sets to be analyzed in duplicate were chosen to both confirm DOC degradation dynamics of specific (i.e., noisier) incubation sets as well as achieve the goal of analyzing at least 20% of incubation sets equally representing both study areas, and the full range of water depths, water temperatures and salinities, and DOC concentrations. Coefficients of variation among duplicates were typically less than 5%.

The results of the incubation experiment are reported in % loss of DOC at time point *x* according to the following formula:

$$DOC\ (\%\ loss) = ((DOC_{(T=0)} - DOC_{(T=x)}) / DOC_{(T=0)}) * 100\%,$$

where $DOC_{(T=0)}$ – initial DOC concentration and $DOC_{(T=x)}$ – DOC concentration at time *x*. (2)

The fraction of DOC degraded by day 3 was defined as LDOC and the fraction degraded from day 3 to day 45 was defined as SLDOC.

For each incubation set, biodegradation rate constants, *k'* and *k''*, were computed from the equations of the exponential trendline (3.1 and 3.2 respectively) built to estimate the microbial degradation rate of LDOC and SLDOC respectively:

$$DOC_{(T=x)} = DOC_{(T=0)} * e^{-k' * x} \text{ for } 0 \leq x \leq 3 \quad (3.1)$$

$$DOC_{(T=x)} = DOC_{(T=3)} * e^{-k'' * x} \text{ for } 3 \leq x \leq 45 \quad (3.2)$$

4.3 Results

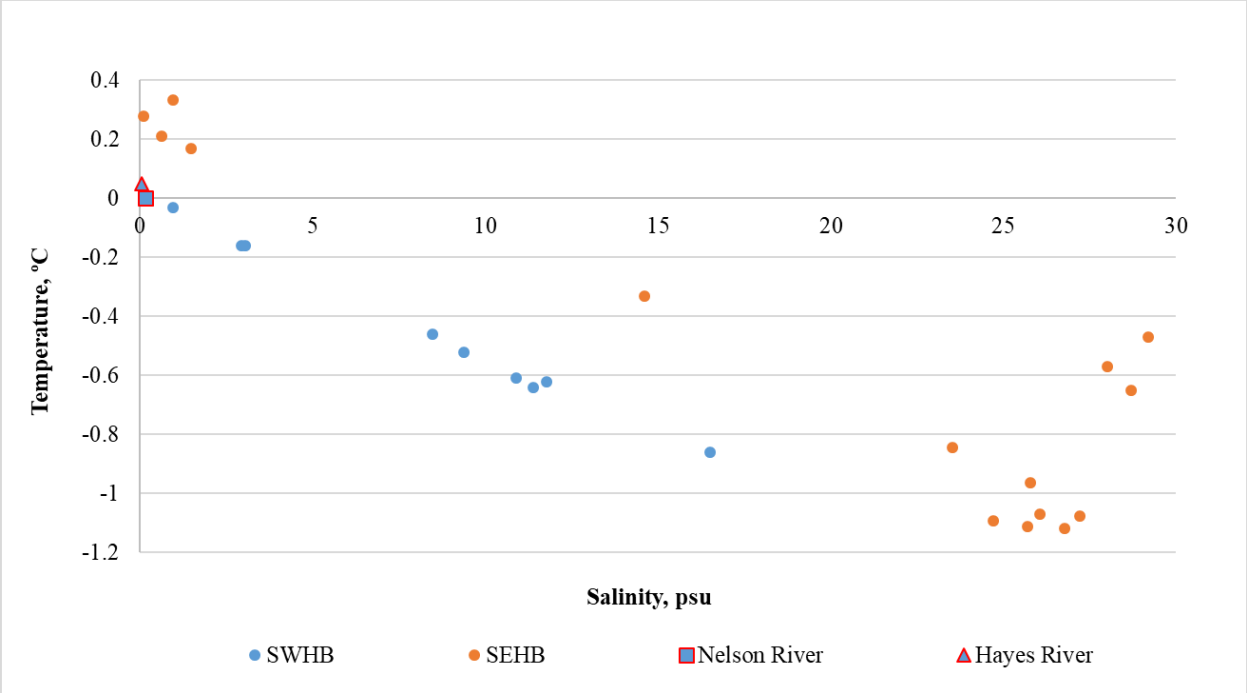
4.3.1 Temperature and salinity of river and coastal waters

The temperature-salinity relationship for all water samples is linear and statistically significant ($p << 0.001$, $R^2 = 0.75$) (Fig. 13A) indicating the primary influence of mixing between warm, low salinity river waters and colder salty marine waters. The range of salinity in the set of SWHB samples (0.06 – 16.51 PSU) is much narrower than that in the set of SEHB samples (0.11 – 29.2 PSU) and in the latter group most samples had either very low or very high salinities (Fig. 13A). The temperature range for all samples was from -1.2 to 0.4 ºC and, similar to salinity, the SEHB samples were not normally distributed within this range but rather had either very low or very high temperatures. The saltiest samples in this study, which were collected from the depths of 35 m or greater in SEHB, lie above the general mixing line in Fig 13A. The temperature and salinity profiles for SEHB coastal waters (Fig. 13C) reveals that these warm saline samples have come from below the WSML (below ~30 m depth) and probably contain heat left over from the previous summer (see **Granskog et al. 2011**; **Eastwood et al. in review**). The elevated *in situ* temperatures (relative to the freezing temperatures) within the WSML in SEHB may be attributed to the enhanced mixing between the warm saline deep waters and the colder fresher surface waters.

At the time of sampling, the study area in the Nelson/Hayes Estuary was weakly stratified with the first significant changes in temperature and salinity being observed close to the bottom, at 4-5 m depth (Fig. 13B). The *in situ* temperatures in SWHB were very close to the freezing temperatures. A maximum salinity for the SWHB samples, 16.51 PSU, was recorded at 6 m depth (Table 1, Fig. 13A). Surface salinity increased from 1-3 PSU at W-2/W-3, located about 10 km east of the Hayes River mouth, to 8-12 PSU at W-4/W-5, located about 20 km east of the river mouth.

In SEHB, the water column in April 2017 was well stratified with a low salinity (<2 PSU) warm surface layer, 3-5 m thick, overlying very saline cold water (25-29 PSU) (Table 1, Fig 13C). The only exception was S-5, which, due to its location, was not influenced by the river input and had a weakly stratified profile. The sampled river waters had near-zero salinities of 0.06-0.15 PSU (Table 1). Note that the temperature and salinity of the Great Whale River was not measured during the study period but a near-zero salinity (~0.05) may be assumed based on previous analyses of the river water (**Granskog et al. 2011**).

A)


0.4
0.2
0
-0.2
-0.4
-0.6
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-1
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5
10
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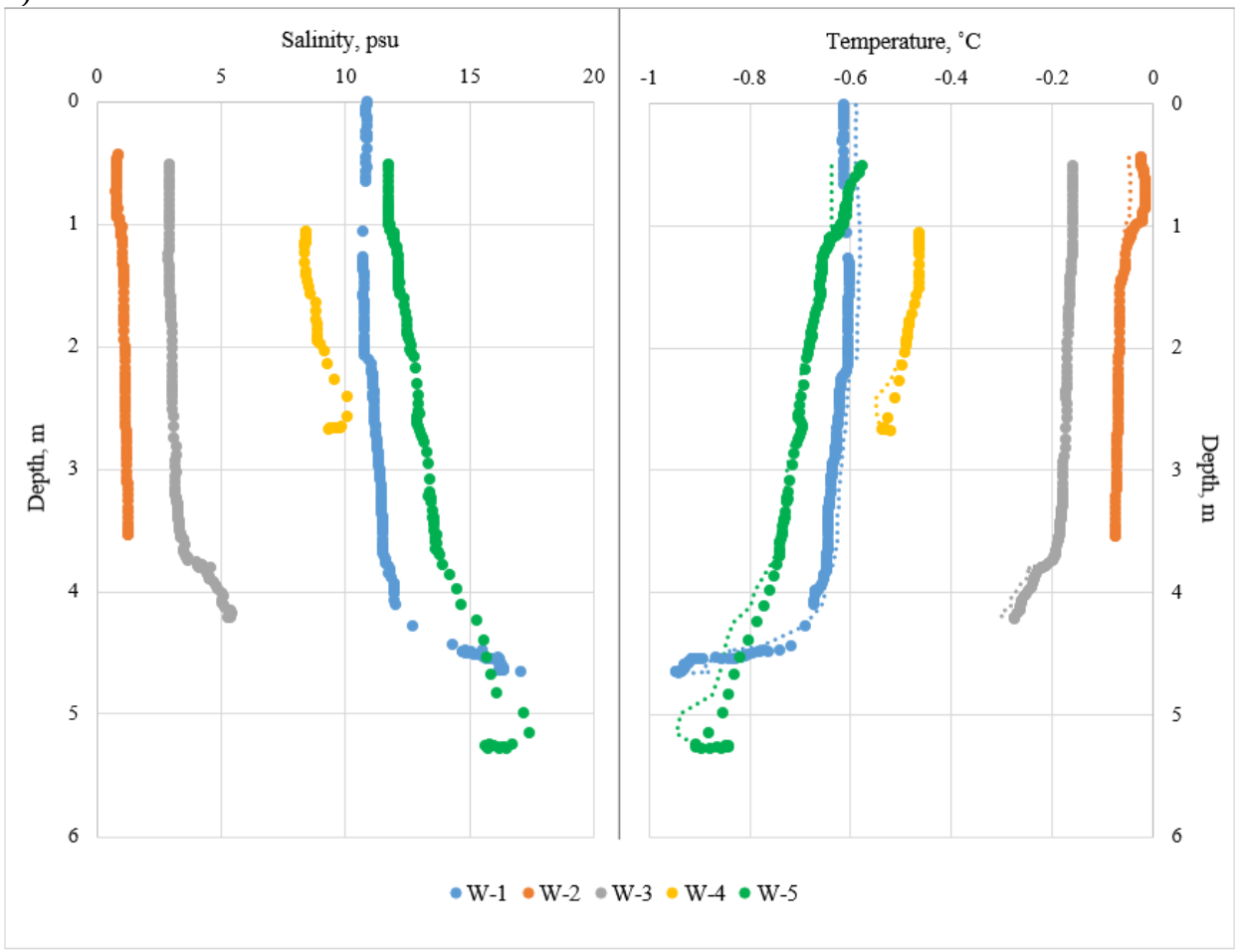
Temperature, °C
Salinity, psu
SWHB
SEHB
Nelson River
Hayes River

B)


Salinity, psu
0
5
10
15
20
Temperature, °C
-1
-0.8
-0.6
-0.4
-0.2
0
Depth, m
0
1
2
3
4
5
6
W-1
W-2
W-3
W-4
W-5

C)

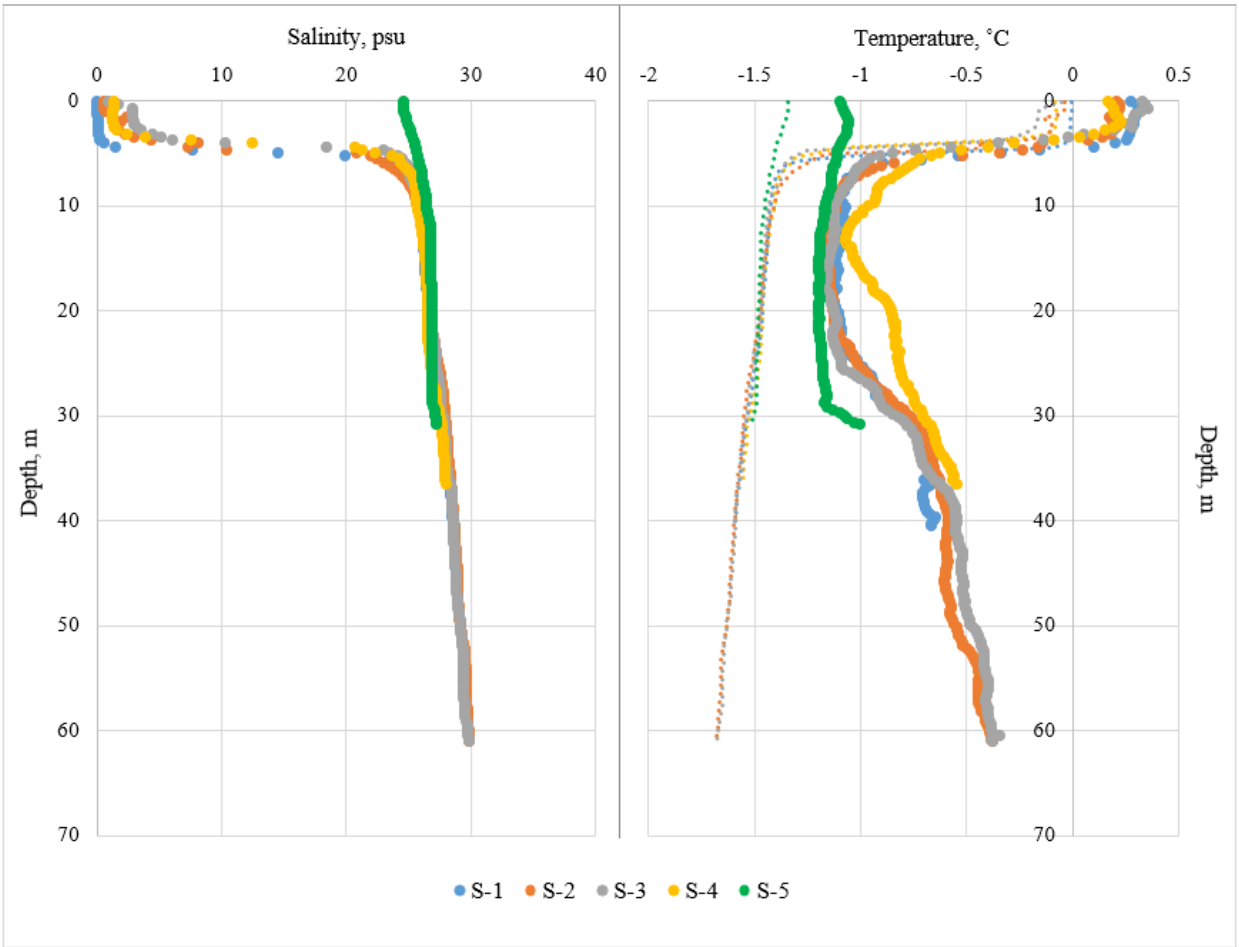


Fig. 13. Temperature and salinity dynamics in the study areas as revealed by the temperature-salinity plot (A) and temperature and salinity depth profiles for SWHB coastal waters (B) and SEHB coastal waters (C). The dotted lines on the temperature profiles represent corresponding freezing temperatures.

Table 1. Initial [DOC], salinity, and DOC degradation parameters (% loss of DOC and biodegradation rate constants) for samples at stations in A) SWHB and B) SEHB.

A) SWHB

Station	Depth, m	Initial [DOC], mg/l	S, PSU	LDOC fraction, %	SLDOC fraction, %	k', d^{-1}	k'', d^{-1}
Nelson River	1	21.4	0.15	47.7	4.7	0.199	0.002
Hayes River	1	14.2	0.06	9.9	10.6	0.039	0.002
W-1	1	16.6	10.9	15.1	2.4	0.038	NSS
W-1	3	14.2	11.4	5.6	18.3	0.005	0.004
W-2	1	12.3	0.97	1.6	5.7	NSS	NSS
W-3	1	17.3	2.94	27.7	12.2	0.057	0.002
W-3	2	10.1	3.05	-	-	-	-
W-4	1	12.2	8.46	10.7	6.1	0.046	NSS
W-4	3	12.0	9.37	-	18.3	-	0.004
W-5	1	13.4	11.76	-	21.6	-	0.006
W-5	6	10.3	16.51	-	32.5	-	0.008

B) SEHB

Station	Depth, m	Initial [DOC], mg/l	S, PSU	LDOC fraction, %	SLDOC fraction, %	k', h^{-1}	k'', h^{-1}
Great Whale River	1	7.6	~0.05	-*	23.5	-	0.007
S-1	1	5.1	0.11	-	3.2	-	NSS**
S-1	5	2.4	14.6	-	-	-	-
S-1	10	5.0	26.06	37.5	13.9	0.025	0.005
S-1	40	1.8	28.7	-	-	-	-
S-2	1	4.6	0.63	-	-	-	NSS
S-3	1	6.9	0.96	11.2	10	0.008	0.008
S-3	5	3.4	23.52	-	3.3	-	0.003
S-3	20	2.4	26.78	7.9	3.7	0.014	NSS
S-3	50	1.8	29.2	-	-	-	-
S-4	1	5.0	1.47	-	-	-	-
S-4	10	2.9	25.78	-	15.3	-	NSS
S-4	35	2.5	28	-	-	-	-
S-5	1	2.5	24.71	-	13	-	0.002
S-5	5	2.1	25.7	-	-	-	-
S-5	30	4.2	27.22	49.8	7.5	0.100	0.002

* absence of degradation is denoted with "-"
** NSS is "not statistically significant" ($R^2 < 0.40$)

4.3.2 Initial DOC concentrations

Table 1 provides initial DOC concentrations for all samples and Fig. 14 presents the relationship between initial DOC concentrations and salinity. As evident from inspection of the figure, there is a clear separation between the initial DOC concentrations in SWHB and SEHB, with the former having significantly higher DOC concentrations. The samples from the Nelson, Hayes and Great Whale Rivers had initial DOC concentrations of 21.4 mg/l, 14.2 mg/l and 7.6 mg/l respectively. In both SWHB and SEHB, DOC concentrations decrease with increasing salinity according to the following trends:

$$DOC_{SWHB} = -0.23 * S + 15.6 \qquad R^2 = 0.15,\ p = 0.23 \qquad (4)$$

$$DOC_{SEHB} = -0.11 * S + 5.8 \qquad R^2 = 0.60,\ p < 0.001 \qquad (5)$$

The DOC-salinity relationship for SEHB is statistically significant and portrayed with a trendline in Fig. 14. The DOC-salinity relationship for SWHB is not statistically significant but we note that it could be due to the SWHB salinity range being much narrower than the SEHB salinity range. Variability in DOC at zero salinity is due to differences between the Nelson and Hayes.

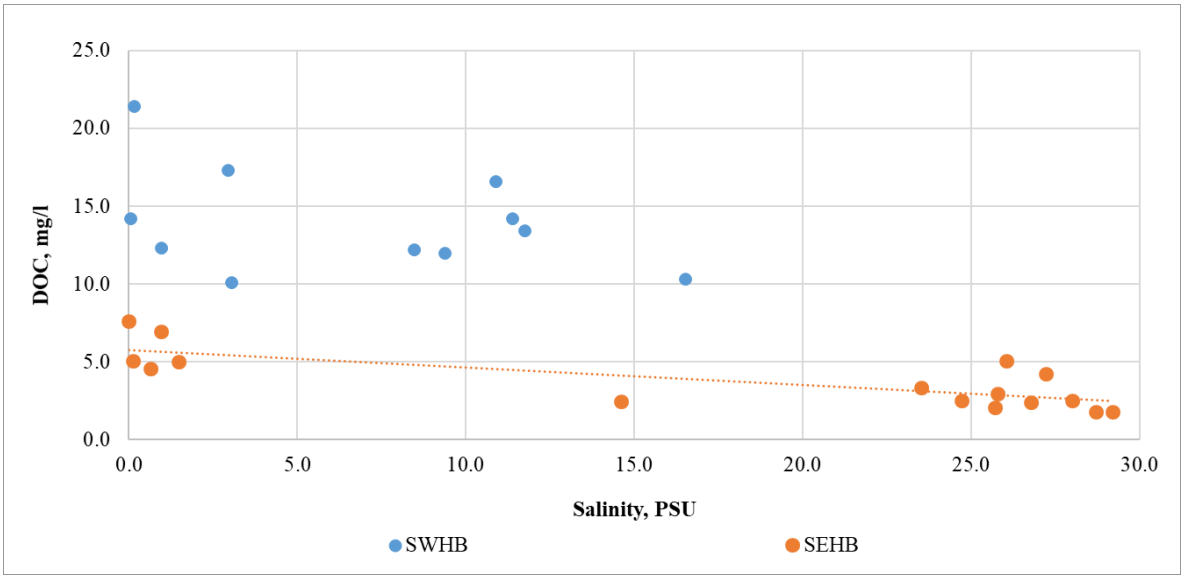


Fig. 14. Relationship between initial DOC concentration and salinity. The dotted line represents a statistically significant trendline.

4.3.3 DOC microbial degradation

Fig. 15 presents % loss of DOC after 45 days in relation to the initial DOC concentration with salinity being color-coded. For easier visualization, only the samples showing significant DOC degradation are portrayed (see Table 1 for the full list). There is a clear separation in DOC concentration between SWHB and SEHB with SWHB having significantly higher DOC concentrations. Overall, DOC degradation seems to increase with DOC concentration. The two low-salinity samples with the highest DOC concentration and very high DOC degradation are the Nelson and Hayes Rivers. Very high DOC degradation is also observed in two high-salinity samples with low DOC concentration in SEHB. The Great Whale River had the highest DOC concentration among SEHB samples and showed a substantial loss of DOC. According to Table 1 and Fig. 15, more than half of the coastal water samples, regardless of salinity, showed 5-35% losses of DOC.

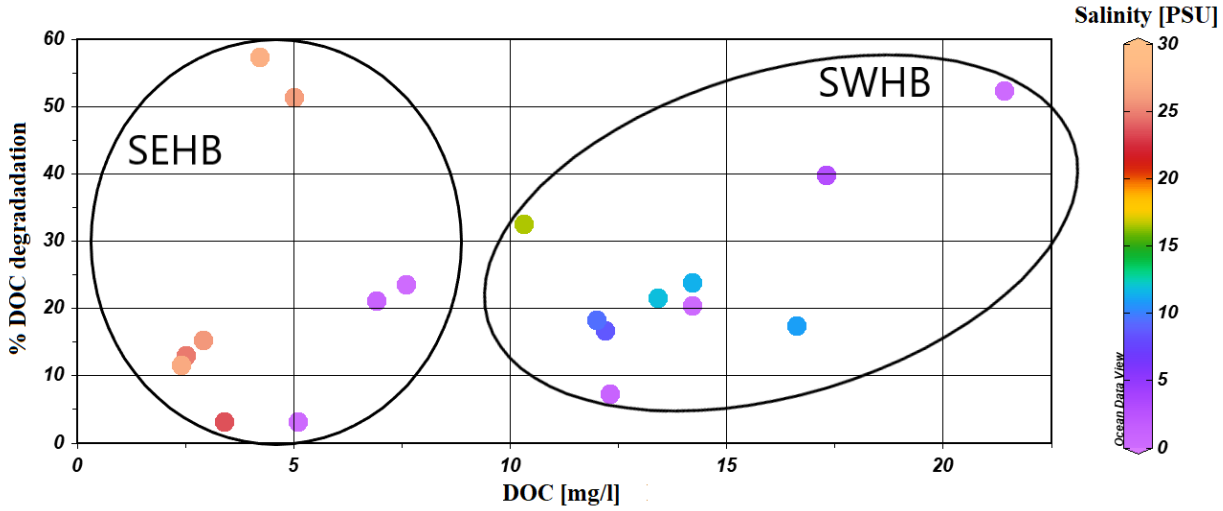
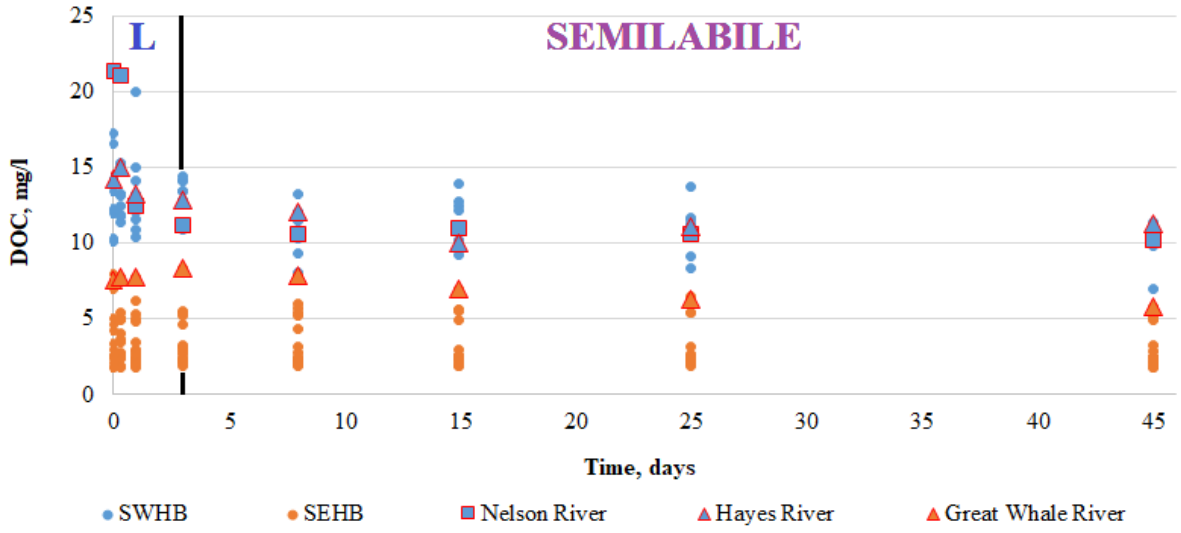


Fig. 15. Relationship between the percentage of degraded DOC and initial DOC concentration with salinity displayed using colour shading (scale at right).

A) DOC concentration (mg/l)



B) % Loss of DOC

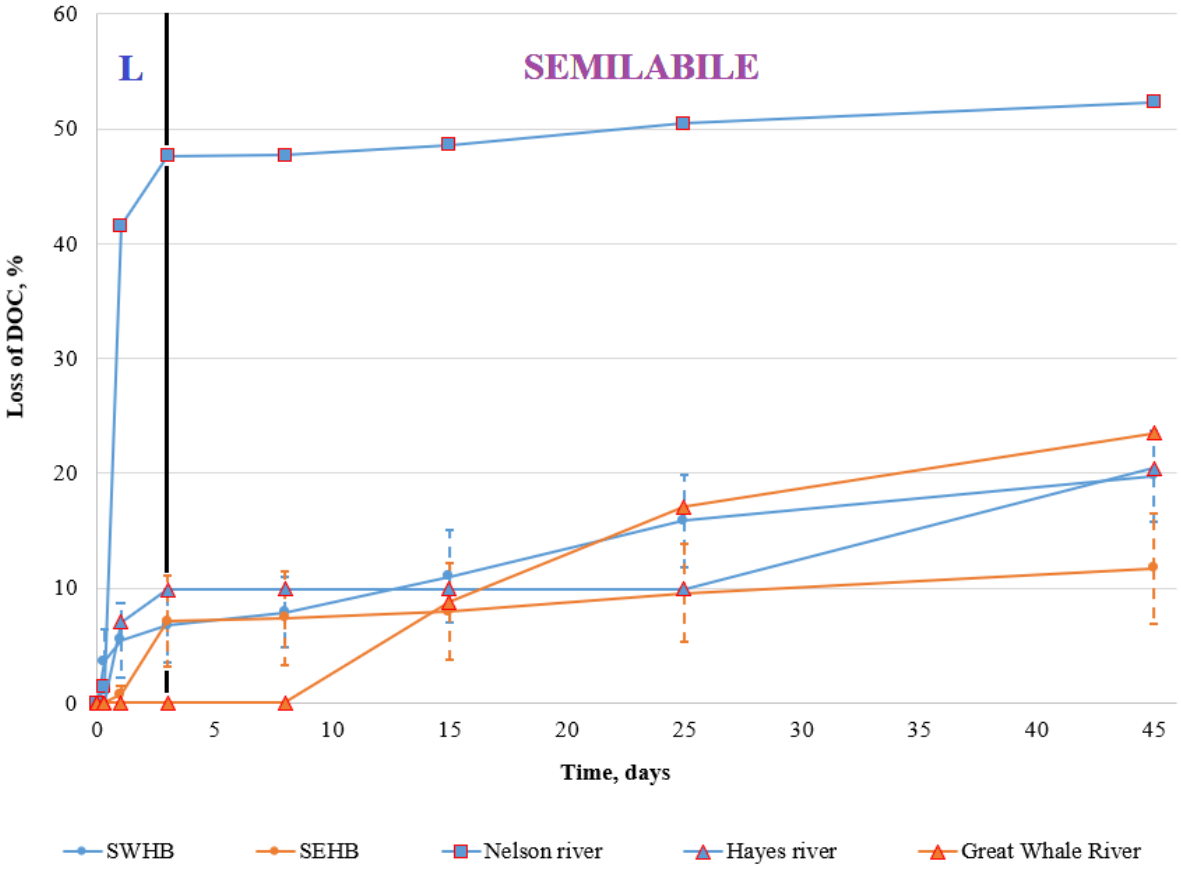


Fig. 16. Microbial degradation of DOC in Nelson, Hayes and Great Whale River and in the adjacent coastal waters of southwestern (SWHB) and southeastern (SEHB) Hudson Bay over 45-day incubation period presented as A) DOC concentration (mg/l) and B) average % loss of DOC. The vertical bold line at 3 days separates labile (L) and semi-labile fractions of DOC.

For roughly half of the coastal water samples, most of the loss in DOC occurred during the first three days of the incubation, which suggests that there is a significant amount of labile DOC (LDOC) in the coastal Hudson Bay waters (Table 1). Moreover, the average % loss of DOC in SWHB coastal samples was already exceeding 5% at the 1.5 day time point, while in SEHB, a pronounced change in DOC concentrations was noticed between the 1.5 day and 3 day time points. LDOC biodegradation rate constants (*k'*) for SWHB and SEHB coastal samples were 0.005 – 0.057 d^{-1} and 0.008 – 0.100 d^{-1}, respectively, where a saline, subsurface sample (S-5, 30 m depth), had the highest *k'* value (Table 1). Despite the difference in degradation rate constants for the labile fraction, there is no significant difference in the average resulting % loss of DOC by day 3 between SWHB and SEHB coastal samples (Fig. 16B). There was also no difference in degradation rate constants for the semi-labile fraction (i.e., *k''*) between SWHB and SEHB coastal samples, with the samples in the two regions having positive rates in the range of 0.002 – 0.008 d^{-1} (Table 1).

Fig. 17 provides information on degradability of the DOC in the various samples. The height of the bar in Fig. 17 reflects the total proportion of the DOC in the sample that was degradable (as indicated by the 45-day incubation), and the coloured shading indicates how much of that degradable DOC was labile (in blue) vs. semi-labile (in orange). Again, like in Fig. 16, the rivers and the coastal waters are plotted separately. The high bar for the Nelson River reflects the fact that a relatively high proportion (>50%) of the DOC in that sample was degradable. The Hayes River, Great Whale River and coastal waters of SWHB show a similar proportion of degradable DOC (~20%) and significantly more than in the SEHB coastal samples. The large amount of blue shading for the Nelson and Hayes Rivers in Fig. 17 shows that, in these river waters, a high proportion of the biodegradable DOC is labile, while the lack of blue shading in the bar for the Great Whale River indicates that LDOC was not present in the Great Whale

River sample. It is striking that the proportions of LDOC in coastal waters in SWHB and SEHB are similar, despite LDOC being absent in the Great Whale River water.

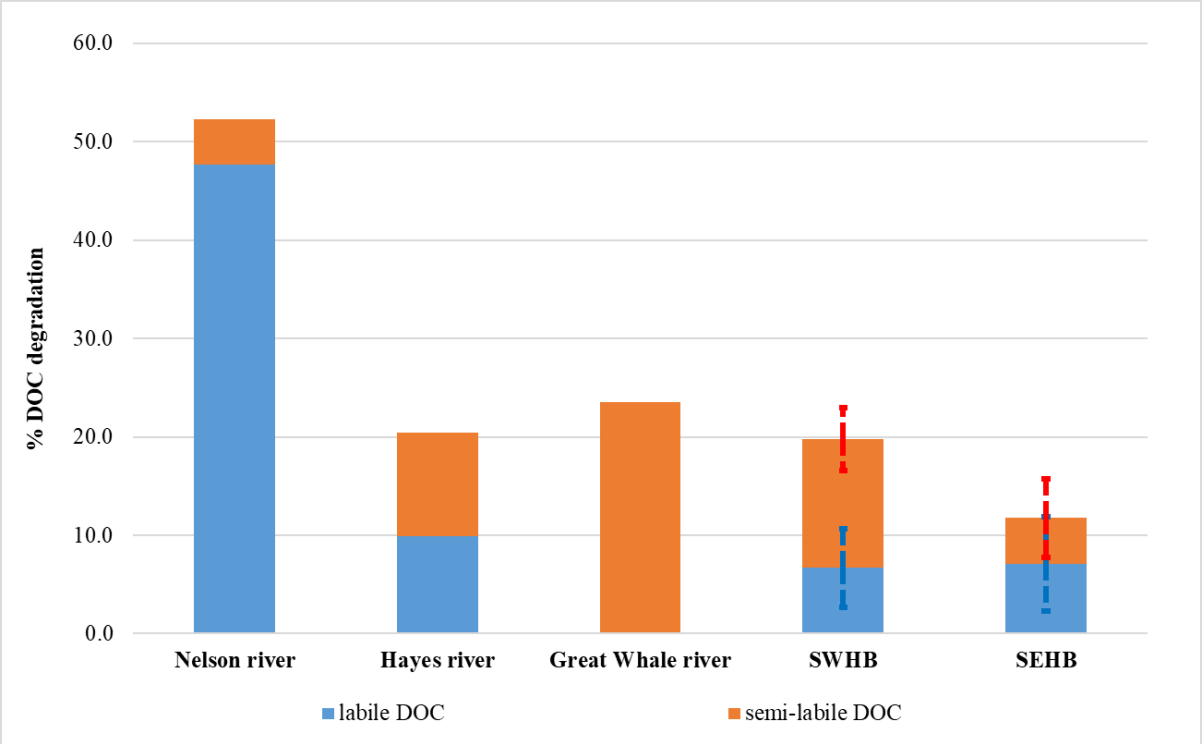


Fig. 17. Relative proportion of labile and semi-labile DOC in Nelson, Hayes and Great Whale River and in the adjacent coastal waters of southwestern (SWHB) and southeastern (SEHB) Hudson Bay.

4.4 Discussion

Although the photooxidation process of the DOC-rich coastal waters of Hudson Bay, including those near the Nelson and Hayes Rivers (**Gueguen et al. 2016**), has been studied, the potential rates of microbial degradation of river-derived tDOC in this system remain poorly known. We chose to do this study in the winter and under an ice cover because, during this season, the photooxidation rates are likely very small (**Granskog et al. 2007**). Any tDOC released into coastal waters will thus persist and add to the pool of circulating DOC in the world's oceans unless it is degraded by microbial means. With the season of sea-ice cover in Hudson Bay projected to decrease in the coming decades, it may be expected that the balance of microbial degradation versus photooxidation may be altered, which will require sufficient baseline data to detect. Because many of the rivers discharging to Hudson Bay drain large watersheds with headwater lakes, the wintertime flux of tDOC into the coastal waters may not be insignificant at the present time and it may become increasingly significant in the future in view of the trends toward increasing wintertime river runoff due to climate change. Furthermore, hydroelectric development has, in places, enhanced winter river discharge. The nature (i.e., intrinsic lability) of the DOC released into coastal waters in the winter is also an interesting question. One may expect significant differences in the lability of DOC released in winter and early spring compared to that released during the better-studied open water period due to the nature of discharge and temperature difference. One may also expect that the amount and properties of DOC will differ among rivers based on properties of the watershed. Below, we first consider DOC concentrations and biodegradability for the Nelson, Hayes and Great Whale River waters. Secondly, we consider the findings on DOC concentrations and biodegradability for coastal waters of southwestern and southeastern Hudson Bay. Thirdly, we discuss the limitations

associated with the approach of performing incubation experiments designed to examine microbial degradation of tDOC.

4.4.1 DOC concentration and lability in rivers

Our results show significant spatial (regional) variability in both the concentrations of DOC in river water and the degradability of that DOC in April. The Nelson and Hayes Rivers had significantly higher DOC concentrations than the Great Whale River. Indeed, previous work has shown that the Churchill, Nelson and Hayes rivers, which drain river basins southwestern of Hudson Bay, have DOC concentrations 2-6 times greater than other Hudson Bay rivers (**Mundy et al. 2010**). The primary reasons for this difference in DOC concentration are probably the local vegetation types, hydroelectric development and permafrost cover. First, the Nelson River and Hayes River are located in the boreal forest and peatlands, while the Great Whale River is located in the taiga shield, a transitioning mixed forest-tundra zone (**Godin et al. 2017**). Tundra is generally considered an ecosystem rather decoupled from the river system, while the boreal forest, mostly conifers, and peatlands constitute an important source of tDOC (**Rontani et al. 2014**). Second, hydroelectric development impact on the Nelson River, including flooding during reservoir development, probably contributes to the elevated DOC concentration (**Godin et al. 2017**). Finally, melting of permafrost would also result in increased organic carbon concentrations in affected rivers in the Arctic (**Benner et al. 2003; Godin et al. 2017**). The Nelson River and Hayes River mouths are located in a continuous permafrost zone, while the Great Whale River is located in a sporadic discontinuous (10-50%) permafrost zone (**Godin et al. 2017**). Consequently, DOC release due to permafrost thaw would be more likely to enhance DOC concentrations in the Nelson and Hayes Rivers.

It should be noted that the DOC concentrations measured in the Nelson, Hayes and Great Whale Rivers in April 2017 are about 1.2-2.4 times higher than those reported recently by **Godin et al. (2017)** for samples collected from these rivers in July-August 2010. The DOC concentrations in **Godin et al. (2017)** (9.0 mg/l, 11.9 mg/l, and 4.4 mg/l, respectively) are in agreement with those reported for these rivers for September – October 2005 by **Granskog et al. (2007)** (9.8 mg/l, 11.2 mg/l, and 3.0 mg/l, respectively). Moreover, the DOC concentration in the Nelson River in April 2017 (21 mg/l) is higher than most of the concentrations reported for other Arctic rivers in Table 2, although the Yenisei River contained even higher DOC concentrations (up to 30 mg/L) in August (**Kawahigashi et al. 2004**). Yet, our high DOC concentration for the Nelson River in April is still within the annual range reported by **Kirk and St. Louis (2009)**: 15.1 ± 19.7 mg/l. Thus, we assume that the higher DOC concentrations measured in this study arise from a difference in the timing of sampling. Our sampling was done in late winter-early spring rather than in summer-fall like the previous works. Indeed, during the period of our sampling, the ground would be mostly frozen, so water generated by snow melt would flow across the surface or along shallow flow paths on its way to the river channel picking up DOC along the way, while cold temperatures would limit microbial processing of DOC allowing most of the labile DOC to reach the river channel unaltered (**Holmes et al. 2008**). Moreover, in both SWHB and SEHB, there had been only one day with above-zero local air temperature prior to our sampling period in April 2017 (Fig. 12A). Consequently, it is unlikely that snowmelt contributed to observed concentrations. Snowmelt could result in the dilution of DOC concentrations. Another possibility is that during the late winter, the low base flow in the rivers is maintained by release of DOC-rich water from wetlands, which constitute a substantial portion of the Nelson and Hayes River basins (> 20% coverage by fens and bogs) (cf., **Smith et al.**

2015). The Nelson River also has large headwater lakes such as Lake Winnipeg that presumably maintain its flow (and DOC concentrations) in late winter.

The observed 21% and 24% losses of tDOC after 45 days of incubation for the Great Whale River and Hayes River respectively generally agree with the range of DOC degradability reported for other Arctic rivers in late winter - early spring before the freshet (Table 2). For example, **Mann et al. (2012)** reported up to 10% DOC degradation for the Kolyma River during the pre-flush period in May, while **Wickland et al. (2012)** reported 27-35% degradation for the Yukon River during winter (Table 2). However, the Nelson River 52% loss of tDOC after 45 days is significantly higher than the tDOC degradation in the Arctic rivers reported in previous studies summarized in Table 2 and encompassing the period of late winter - early summer. Indeed, the upper limit of degradability reported in previous winter studies is in the order of 35%. It is not known whether the high % loss of DOC in the Nelson River are related to the influence of hydroelectric development, which ensures a relatively even river discharge throughout the year, or natural aspects of the Nelson River basin (such as the presence of large lakes or specific vegetation cover), or effects of climate change (such as permafrost thaw). Yet, during the time of the sampling, the Nelson River would have open water areas near the dams, where some photooxidation could be happening. While photooxidation in these areas at this time of the year would not result in a measurable degradation of DOC, it could still facilitate photo-enhanced biomineralization of DOC (**Fichot and Benner 2014**).

Another striking result is that while biodegradable DOC in the Nelson and Hayes rivers is mostly labile, the Great Whale River completely lacks LDOC. It is possible that extremely labile DOC was degraded during sample handling prior to beginning the incubation experiments but this would potentially affect all samples as there was no difference in handling time between the study areas. The high proportion of labile DOC in the Nelson River and Hayes River, compared

to the Great Whale River, may be attributed to differences in vegetation cover between these two regions or, more likely, from the differences in permafrost cover, which can provide a source of ancient but highly labile DOC (**Godin et al. 2017; Guillemette et al. 2017 and references therein**).

It was established that riverine-influenced waters of southern Hudson Bay and James Bay act as a source of CO_2 (**Else et al. 2008**). Moreover, higher concentrations of riverine tDOC deposited into the coastal ocean, due to high river discharge or intrinsic properties of the river's watershed causing high riverine DOC concentrations, and its subsequent degradation would lead to higher CO_2 emissions (**Lapierre et al. 2013**). Thus, as a result of the exceptionally high DOC concentrations and high DOC biodegradability in the Nelson and Hayes rivers, it is expected that Nelson/Hayes estuary would support substantially higher CO_2 emission than the Great Whale River estuary in late winter.

Table 2. Summary of recent incubation experiments examining microbial degradation of tDOC in the Arctic.

Study referenced	Study site	Sampling time	Initial [DOC], mg/l	Incubation time, days	Incubation temperature, ºC	Parameter analysed	% DOC degraded
Kawahigashi et al. (2004)	Yenisei River (65º49' to 67º30')	August	4-30	97	20	CO_2	4-28
Holmes et al. (2008)	Alaskan rivers (Kuparuk, Sagavanirktok, and Colville 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	pre-flush (May)	2-3	28	20	DOC	up to 10
		freshet (May-June)	8-14	28	20	DOC	1-20
Wickland et al. (2012)	Yukon River	winter	2-3	28	5	CO_2	27-35
		spring freshet	5-17	28	5	CO_2	2-29
		summer	3-7	28	5	CO_2	4-19
Herlemann et al. (2014)	Kalix River	June	5	28	10	DOC	7 ± 1
	mix of surface coastal Baltic Sea and Kalix River waters	June	4	28	10	DOC	16 ± 6
Shirokova et al. (2017)	Severnaya Dvina River	June (spring flood)	10-15	~25	20	DOC	negligible
		August	12-15	~25	20	DOC	15-20
This study	SWHB	April	10-21	45	4	DOC	up to 52 ($\bar{x}$ = 23)
	SEHB	April	2-8	45	4	DOC	up to 57 ($\bar{x}$ = 13)

4.4.2 DOC concentration and lability in coastal waters

The river discharge rates greatly influence local coastal ocean salinity and DOC concentration in both study areas during the winter period, providing estuarine conditions within which DOC degradation could occur. However, the two coastal environments were very different in part because of the much higher discharge of the Nelson River compared to the Great Whale River. Furthermore, the Nelson River had a much higher DOC concentration, which results in a low-salinity, high-DOC coastal environment in SWHB, compared to widely varying salinity and low to moderate DOC concentrations in SEHB.

According to formulas (4) and (5), there is a cumulative loss of 0.23 mg/l and 0.11 mg/l of tDOC per unit salinity decrease in SWHB and SEHB respectively. This is comparable to a cumulative loss of 0.15 mg/l of tDOC per unit salinity decrease in the Western Arctic (**Hansell et al. 2004**). It is somewhat surprising that initial DOC concentrations and salinity were not more strongly correlated in SWHB (Fig. 14 and formula (4)). A strong correlation has been previously reported for the Nelson/Hayes estuary during summer (**Gueguen et al. 2016**). With the strong tidal influence in this coastal environment, we speculate that there is a high degree of mixing and recirculation of river water and associated DOC, which would effectively pre-age some of the DOC in the estuary and thus contribute to variability in its DOC concentrations and lability. The SEHB coastal environment is less energetic and surface salinity likely reflects more directly the influence of recent river discharge.

Despite differences in DOC dynamics in the coastal environment, the significantly higher proportion of biodegradable DOC in the Nelson and Hayes rivers compared to the Great Whale River is reflected in the difference in the proportion of biodegradable DOC in SWHB and SEHB (20% and 12% respectively). While positive correlation between initial DOC concentration and DOC degradation was universal but not statistically significant, it is still important to note that,

in natural aquatic environments, bacterial growth efficiency and, consequently, DOC biodegradation rate, increases with increased DOC concentration because the fraction of the total acquired energy allocated to support nongrowth processes, such as synthesis of extracellular enzymes, decreases with increasing total substrate concentration (**Eiler et al. 2003**).

The high proportion of biodegradable DOC that is labile in the Nelson and Hayes rivers (Fig. 17) is not reflected in the low proportions of biodegradable DOC that are labile in the associated coastal waters (Fig. 17). This finding is consistent with our hypothesis that the Nelson/Hayes River estuary is well-mixed due to strong tidal exchange (Fig. 13B) and, as a result, could contain older, semi-labile, tDOC. Indeed, previous workers have suggested that the average residence time of river water in the Nelson/Hayes estuary could be months (**Granskog et al. 2009**).

More puzzling is that although the Great Whale River lacked labile DOC, more than half of the biodegradable DOC in SEHB was labile. Since the proportions of LDOC in SWHB and SEHB are very similar despite the absence of LDOC in the Great Whale River waters, it is tempting to conclude that the LDOC in SEHB coastal waters is not tDOC supplied by the Great Whale River. If this is true, then we may have observed a rapid degradation of mostly marine DOC during the incubation, which is unlikely because in April, one expects that riverine DOC is practically the only significant source of DOC for coastal Hudson Bay waters. Ice algae are a possible source of marine-derived DOC but significant algal inputs to surface waters seem unlikely because the DOC concentrations were not higher in those samples (at a given salinity) than in samples collected from greater depths. Two SEHB samples had remarkably high LDOC fractions (38% and 50%): S1 (10 m) and S5 (30 m) (Table 1). Both are subsurface samples with high salinity and relatively high DOC concentrations. Based on salinity and temperature depth profiles (Fig. 13C), station S1 is influenced by the under-ice plume of the Great Whale River,

while station S5 is not (Fig. 13C). The high DOC concentration in the sample S5, 30 m could be due to the influence of river-water rich outflow from James Bay, which is immediately 'upstream' of SEHB. For the James Bay outflow to be the source of the labile tDOC, requires that labile tDOC supplied by James Bay rivers survives transport to station S5. Finally, it is peculiar that the SEHB samples from 35 m depth and deeper have not shown any degradation signs. This is probably due to the waters below 30 meters being the remnants of the previous summer SSML, where all the tDOC have already been degraded and no fresh tDOC is being deposited to during winter.

Regardless of the source of the labile tDOC, the question remains why such rigorous tDOC degradation happens in the saline marine waters rather than in the Great Whale River or the fresher riverine-influenced surface layer in SEHB. We propose that the trend may have a complicated, biological, explanation, such as difference in microbial community and the environment it occupies. Stability of water properties, water residence times, and nutrient regimes may all be contributing factors. Indeed, the definition of "labile" and "semi-labile" is complicated because it is informed not only by the organic composition of the DOC but also by the ability of the local microbial community to degrade the given DOC, which depends on conditions other than the DOC itself. Thus, previously "semi-labile" riverine DOC becomes "labile" once it enters the SEHB marine environment. Indeed, in both SWHB and SEHB, in the coastal surface layer, neighboring samples show significantly more degradation in the more oceanic (aka saline) environment (Table 1: W2-W3, W4-W5, S1-S2-S3, S4-S5). This phenomenon may be a result of the priming effect / co-metabolism and change in nutrient levels: the marine environment could be characterized by a more diverse and abundant microbial community as well as contain a substantially higher proportion of labile marine organic matter and nutrients as compared to the riverine environment, all of which could result in a more

rigorous degradation of tDOC (**Bianchi 2012; Holmes et al. 2008; Ward et al. 2016**). This effect is more pronounced in SEHB, which is to be expected due to a much greater change in salinity (i.e., a much sharper transition from riverine to marine environment). Thus, most of the Nelson River and Hayes River tDOC is preferably degraded in the rivers and most of the Great Whale River tDOC is preferably degraded in the coastal ocean environment. Although overall higher rates of degradation of tDOC in the river waters, compared to coastal waters, does not support the priming effect, an enhancement in labile DOC in SEHB coastal waters, compared to the associated river waters, may be a more subtle manifestation of this effect.

It is interesting to note that microbial community is also strongly dependent on physical environmental parameters such as temperature. Temperature increase promotes heterotrophic metabolic activity and, therefore, increases in the *in situ* temperature can increase the remineralisation rate of DOC (**Table 2: Balcarczyk et al. 2009; Bendtsen et al. 2015; Rivkin and Legendre 2001**). SWHB samples were ~0.3 ºC closer to the freezing point than SEHB samples. Since bacterial communities are known to be very sensitive to increase in *in situ* temperature, all else being equal, this seemingly small change could help to promote a more rigorous degradation of tDOC in SEHB as compared to SWHB.

4.4.3 Biodegradation rate constants

Our reported *k'* (0.005 – 0.057 d^{-1} and 0.008 – 0.100 d^{-1} for SWHB and SEHB coastal waters respectively) and *k''* (0.002 – 0.008 d^{-1} for both SWHB and SEHB coastal waters) values were lower than the reported average labile (0.32 ± 0.1 d^{-1}) and semi-labile (0.019 ± 0.004 d^{-1}) total organic carbon remineralization constants in the upper ocean pan-oceanic study of **Bendtsen et al. (2014)**. This difference in rates is likely due to a difference in temperature as well as intrinsic lability of DOC (terrestrial organic matter vs marine primary production).

Indeed, our biodegradation rate constants for the coastal waters were similar to the exponential decay constants for the microbial mineralization of lignin reported for the mixed layer of the South Carolina coast after a ~90 day incubation: 0.002 to 0.007 d^{-1} (**Fichot and Benner 2014**). Our *k'* values for Nelson and Hayes rivers were 0.199 d^{-1} and 0.039 d^{-1} respectively. The Great Whale River *k''* was 0.007 d^{-1} reflecting a substantial degradation of SLDOC in the river, while the Nelson and Hayes River *k''* were both only 0.002 d^{-1} stressing the relatively small significance of the degradation of the semi-labile tDOC in these rivers. Our reported biodegradation rates were more than 10-fold lower than DOM photobleaching rates (0.005 to 0.030 h^{-1}) in Nelson/Hayes River estuary (**Gueguen et al. 2016**). However, taking into account that only a limited DOC fraction is chromophoric, that Hudson Bay is seasonally ice-covered, and that light is attenuated with depth, microbial degradation of DOC may be considered to be of greater quantitative and qualitative significance.

4.4.4 Recalcitrant DOC

According to formulas (4) and (5), typical DOC concentrations at salinity 30 PSU in SWHB and SEHB may be predicted to be 8.7 mg/l and 2.5 mg/l, respectively. In spite of the salinity-DOC relationship not being statistically significant for SWHB (possibly due to distribution of data), both results are close to the RDOC (estimated as the DOC that did not degrade during the 45-day period) concentrations for the respective inflowing rivers. This similarity means that by the time tDOC gets incorporated into the 30 PSU marine environment, only the RDOC portion of the tDOC remains. The calculated DOC at salinity 30 PSU at SWHB and SEHB is significantly higher than the DOC concentration in Hudson Bay at 30 PSU reported in **Mundy et al. (2010)** (1.4-1.7 mg/l). However, this difference may be due to the fact that, in **Mundy et al. (2010)**, the stations corresponding to 30 PSU were not located in the coastal ocean

and, thus, not highly influenced by river input. Freshwater introduced by sea ice melt may be expected to contain less DOC than the equivalent amount of river water.

4.4.5 Implications of tDOC degradation for DIC concentrations and river water residence time in the Nelson/Hayes estuary

Based on the results of our incubation experiment and the measured DOC concentrations and river discharge data, we estimate that the supply of DOC by the Nelson and Hayes rivers collectively during the winter time and its subsequent degradation, could produce the following excess DIC concentration in waters flowing out from the Nelson/Hayes estuary:

$[([DOC] * \text{loss of DOC} * \text{discharge})_{Nelson} + ([DOC] * \text{loss of DOC} * \text{discharge})_{Hayes}]$ / collective discharge = [(21.4 mg/l * 0.52 *3700 m^3/s) + (14.2 mg/l * 0.21*350 m^3/s)] / 4050 m^3/s = 10.4 mg/l or 869 µmol/l of DIC released.

Approximating the Nelson/Hayes estuary area to be 4500 km^2 and its average depth to be 25 m, the calculated volume of water is 1.13 x 10^{11} m^3. Thus, it will take an equivalent of 10.7 winter months for the Nelson and Hayes rivers to fill the estuary. According to **Burt et al. (2016)**, in July, the Nelson/Hayes river estuary has an elevated DIC concentration as compared to the coastal Hudson Bay corridor, which could result from degradation of the highly labile DOC deposited by the rivers. The excess DIC concentration is ~100 µmol/kg (≈ 100 µmol/l) and we assume it to be of the same order in winter and early spring. Taking into the account the DIC released by the degradation of DOC supplied by the rivers, the estimated time needed for the rivers to fill the estuary and the DIC excess observed by **Burt et al. (2016)**, we calculated the residence time of the river water in the estuary to be 1.2 months:

(100 µmol/l / 869 µmol/l) * 10.7 months = 1.2 months.

Please note that in spite of our total incubation time being 1.5 months, which is slightly greater than the calculated residence time, the results imply that it takes only a month to degrade > 95% of the labile and semi-labile riverine DOC deposited into estuary. The results of this calculation somewhat agree with the assumption of **Granskog et al. (2009)** that the average residence time of river water in the Nelson/Hayes estuary could be months.

4.4.6 Limitations of incubation experiments examining microbial degradation of tDOC

There are some limitations associated with the approach of performing incubation experiments in order to examine microbial degradation of tDOC. First, in general this approach is time-consuming and labour-intensive. A good possible alternative to the incubation experiments would be a reliable proxy measurement tightly coupled to DOC lability, such as compositional changes in DOC. Second, incubation experiments, especially using the time series approach, are very hard to interpret because the confinement of marine or freshwater samples may result in shifts in prokaryotic community structure and stimulate bacterial activity and the development of bacterivorous protists, even without substrate amendment (**Herlemann et al. 2014**). Although changes in community structure do not always imply changes in general microbial activity, it is hardly possible to judge whether the processes observed during the incubations mimic those that occur *in situ*. Consequently, it may be better to use a subsampling approach, where all the incubation is happening in one closed system which gets subsampled in the least invasive manner, rather than the time series approach, where each time point is represented by a separate vial. Increasing replication may also help address this issue. Third, some natural conditions, such as solar radiation resulting in photooxidation, which could potentially help with biodegradation, cannot be accounted for during this type of incubation experiment and thus may have led to an underestimation of natural tDOC microbial degradation.

As a final remark, it is suggested that future similar incubation experiments are paired with an analysis of DOC composition and bacterial community structure.

4.5 Conclusions

The results of my incubation experiments showed that, first, in late winter, more than 50% of the DOC delivered by the Nelson River is biodegradable, while 20-25% of the DOC delivered by the Hayes River and Great Whale River is biodegradable. While the Great Whale River and Hayes River biodegradation results were similar to the biodegradation observed in other Arctic rivers, the Nelson River had a relatively high loss of DOC. Second, in the Nelson and Hayes rivers, a high proportion of the biodegradable DOC is labile meaning it degraded within about three days, while in the Great Whale River, the degradable DOC was only semi-labile (degrading during 3-45 days). Third, the difference in lability of DOC between the Nelson/Hayes and Great Whale Rivers was not reflected in the biodegradation of DOC in the coastal waters influenced by these respective rivers (SWHB and SEHB coastal waters). The experiments showed that SWHB DOC is mostly semi-labile, despite there being a high proportion of labile DOC in the Nelson/Hayes River water flowing into this coastal setting. The anomalously low lability of the DOC in the SWHB coastal waters could be due to the long residence time of tDOC in the estuary of the Nelson/Hayes Rivers. The calculated residence time of the river water in the Nelson/Hayes estuary is 1.2 months. On the other hand, the DOC in the SEHB coastal waters influenced by the Great Whale River is mostly labile, despite low lability in river water itself. I speculate that the rapid degradation of DOC in SEHB coastal waters may be explained by priming effect / co-metabolism and higher nutrient concentrations in the coastal ocean as compared to the river.

The results of the incubation experiments imply that most of the Nelson River and Hayes River tDOC is probably degraded in the rivers and inner estuaries near the river mouths while most of the Great Whale River tDOC is probably degraded in the coastal ocean environment. The apparent labile DOC biodegradation rate constants were 0.005 – 0.057 d^{-1} and 0.008 – 0.100 d^{-1} for SWHB and SEHB coastal waters respectively, and semi-labile DOC biodegradation rate constants were 0.002 – 0.008 d^{-1} for both SWHB and SEHB coastal waters. As expected, these constants were similar to the exponential decay constants for the microbial mineralization of lignin in a coastal ocean and lower than the total organic carbon remineralization constants for the upper layer of the global ocean due to the difference in the nature of the organic matter degraded (terrestrial organic matter vs marine primary production). The Nelson and Hayes rivers labile DOC biodegradation rate constants were 0.199 d^{-1} and 0.039 d^{-1} respectively, while the semi-labile DOC biodegradation rate constants were only 0.002 d^{-1}. The Great Whale River semi-labile DOC remineralization constant was 0.007 d-1. These constants are more than 10-fold lower than the photobleaching rates in the Nelson/Hayes estuary, highlighting the potentially higher rates of overall tDOC degradation during the summer (open-water) period, compared to the winter. Nevertheless, the DOC concentrations measured in the Nelson, Hayes and Great Whale Rivers in April 2017 are about 1.2-2.4 times higher than those reported in September-October 2005 and July-August 2010. The Nelson and Hayes rivers, in particular, appear to have high DOC concentrations in winter. As a result of the high DOC concentrations together with high DOC biodegradability in the Nelson and Hayes rivers, it is expected that the Nelson/Hayes estuary would have a substantially higher CO_2 emission than the Great Whale River estuary when the ice comes off in spring. Overall, I conclude that there is potential for significant microbial degradation of tDOC in Hudson Bay riverine-coastal waters in late winter fueled by a combination of moderate to high river discharge, high DOC concentrations in river water, and

high degradability of the DOC being delivered at this time. Moreover, by the time riverine tDOC gets incorporated into the 30 PSU marine environment, only relatively recalcitrant (degraded during > 45 days) portion of the tDOC remains.

In spite of its effectiveness, the incubation approach has several significant limitations and needs to be constantly improved or, if possible, replaced with a more efficient and reliable alternative. Moreover, to date, the majority of incubation experiments examining degradation of tDOC have utilized inconsistent methodologies making a cross comparison difficult. For future studies, it would be beneficial to follow a general standard protocol such as described in **Vonk et al. (2015)**.

We expect our results would contribute to quantitative estimation of the degree of tDOC microbial degradation in rivers and coastal ocean zone and will be useful in modeling ocean biochemistry dynamics as well as predicting its response to the on-going climate change in the Arctic Ocean.

Chapter 5. Summary and perspectives

The coastal ocean represents the interface between land and ocean and thus carbon cycling in coastal waters is acknowledged to be a major component of global carbon cycles and budgets. The coastal ocean receives organic carbon derived from terrestrial materials through inputs of river water and coastal erosion, as well as organic carbon derived from marine materials produced *in situ* (through primary production) or carried in shelf sea water. Coastal waters tend to experience significant losses of organic carbon owing mainly to the combined influences of photochemical oxidation, microbial degradation, and deposition.

In contrast to the highly labile marine organic carbon, until recently, terrestrial organic carbon (OC) was expected to be much more refractory in the ocean, leading to the belief that it gets mainly deposited to the sediments before having a chance to degrade in the water column. However, in the last two decades, there has been a major shift in thinking regarding the potential degradability of tDOC (cf., **Bianchi et al. 2012**). From these more recent investigations and analyses, which span multiple fields and perspectives, all indications are that tDOC is significantly degraded in the ocean leaving behind a residual that makes up at most a few percent of the total organic carbon in seawater. Since the major source of tDOC to the world's oceans is river inflow and the majority of tDOC delivered by rivers is in dissolved form, the last two decades has seen intensive study of the sources and fate of terrestrial dissolved organic carbon (tDOC). Although there is substantial evidence suggesting ocean margins act as major "filters" of tDOC between the land and ocean, leading to little tDOC residing in the open ocean, the actual extent of tDOC removal in these environments, the active processes (photooxidation vs. microbial degradation), and the environmental controls remain mainly unknown.

The Arctic Ocean has the highest concentrations of tDOC of all ocean basins, particularly in the surface waters, and tDOC inputs into the Arctic Ocean are currently increasing due to

climate-change driven increased river runoff (**Déry et al. 2011; McClelland et al. 2006; McGuire et al. 2009**), accelerated coastal erosion (**Mars and Houseknech 2007**), and permafrost thaws (**Vonk et al. 2015**). Despite the evidence suggesting that tDOC in the Arctic Ocean undergoes extensive and rapid destruction in the ocean margin, the fate of tDOC during its transport in arctic rivers and within the Arctic Ocean remains uncertain and largely unknown. In the Arctic Ocean, microbial degradation of tDOC significantly predominates over photooxidation due to the extended sea-ice and snow coverage and relatively low solar irradiation of polar surface waters (**Benner et al. 2005; Bélanger et al. 2006; Ward et al. 2016**). Specifically, a number of recent publications examining microbial degradation of tDOC in Arctic riverine and coastal ocean waters using incubation experiments have reported substantial tDOC degradation (~15-35%) over periods ranging from a few weeks to a few months (**Bianchi 2012; Ward et al. 2016; references in Chapter 4, Table 2**). Since the extent and significance of microbial degradation of tDOC in seasonally ice-covered waters characteristic of the Arctic Ocean have only recently gained attention, the topic is still quite poorly understood and demands further research with a view to broadening the seasonal coverage of the observations (outside the mid to late summer months) and diversifying the studied rivers and coastal areas.

Hudson Bay (including James Bay) represents one of the most southerly extensions of Arctic marine waters and, like the Arctic Ocean, experiences a complete annual sea ice cover and receives very high river discharge. The annual runoff yield for Hudson Bay is almost three times higher than that of the Arctic Ocean (**Serreze et al. 2006**). In Hudson Bay, tDOC substantially dominates over its particulate (terrestrial POC) counterpart (**Mundy et al. 2010; Kuzyk et al. 2009**), and this dominance is much more pronounced than in the Arctic Ocean. As of now, similar to the Arctic Ocean, the fate of the significant amount of tDOC received by Hudson Bay remains mostly unknown. However, the pCO_2 (**Else et al. 2008**) and DIC measurements (**Burt et**

al. 2016) in coastal Hudson Bay waters point at a significant organic carbon degradation and suggest that the coastal waters of southern Hudson Bay, strongly influenced by the river input, act as a source of CO_2. While photodegradation of DOC in Hudson Bay has been assessed (**Gueguen et al. 2011, 2016**), to date no research has been published describing microbial degradation of tDOC in Hudson Bay. In view of the fact that microbial degradation is a much more important remineralization pathway in the Arctic Ocean waters, it has become imperative to assess microbial degradation of tDOC in Hudson Bay in order to arrive to a meaningful conclusion about lability of the tDOC and build a reliable model describing the fate of the tDOC in the bay. An advance in understanding the fate of tDOC in Hudson Bay, in turn, would significantly improve our understanding of the extent and significance of microbial degradation of tDOC in the Arctic and World Oceans in general.

My thesis addresses the question of how important microbial degradation of tDOC is in coastal Hudson Bay. The main aim of Chapter 3 was to establish potential magnitude and important locations and times of year of microbial degradation of tDOC in coastal Hudson Bay. It was found that by late summer, WSML in eastern coastal Hudson Bay harbours a high AOU water mass. It was concluded that, instead of annual new production, the most likely primary sources of the organic matter degraded within the high AOU water mass are the riverine DOC inputs deposited into the coastal Hudson Bay during the formation of the previous summer SSML and during the formation of the WSML in winter. As a result, in the view of the significant contribution of the tDOC supplied by the rivers to SSML in spring-summer and to WSML in winter, it was decided that it is paramount to explore the extent of the microbial degradation of the dominating tDOC supplied by the rivers into the coastal Hudson Bay around the year. This investigation would serve to support or oppose a newly established hypothesis: tDOC deposited by Hudson Bay rivers, during spring-late summer and during the WSML

formation in winter, eventually accumulates in the eastern Hudson Bay WSML, as a result of winter mixing and sluggish counter-clockwise coastal water circulation in WSML, and undergoes relatively slow microbial degradation, which in turn forms the observed high AOU water mass by late summer. As a result, the main aim of Chapter 4 was to examine microbial degradation of DOC in riverine and coastal southwestern and southeastern Hudson Bay waters using an incubation experiment approach. The study focuses on late winter, when river waters discharge under snow-covered land-fast sea ice, which is a dark environment in which photooxidation is not expected to occur. As a result of this study, I conclude that there is potential for significant microbial degradation of tDOC in Hudson Bay riverine-coastal waters in late winter fueled by a combination of moderate to high river discharge, high DOC concentrations in river water, and high degradability of the DOC being delivered at this time. Furthermore, the results of our experiments, suggesting that in late winter 20-50% of the tDOC deposited into Hudson Bay by southern rivers is biodegradable within a few weeks, somewhat support the hypothesis established in Chapter 3. However, the results of the incubation experiments also imply that southwestern and southeastern Hudson Bay significantly differ in the amount and lability of tDOC. For example, most of the Nelson River and Hayes River tDOC is probably degraded in the rivers and inner estuaries near the river mouths while most of the Great Whale River tDOC is probably degraded in the coastal ocean environment. Moreover, due to the difference in the concentration and lability of the tDOC, it is also expected that the Nelson/Hayes estuary would have a substantially higher CO_2 emission than the Great Whale River estuary when the ice comes off in spring.

The findings of these first studies of microbial degradation of terrestrial OC in Hudson Bay need to be validated with seasonal incubation experiments conducted from late winter till late summer. Furthermore, additional observations are needed to identify the source of the

organic carbon supporting the degradation I infer from the spatial AOU data analysis. The presence of the high-AOU water mass in eastern Hudson Bay WSML suggests that a significant amount of the tDOC deposited into the southern coastal waters, especially at James Bay, in spring-late winter accumulates in the eastern Hudson Bay WSML, where it ultimately gets degraded over a period of up to a year below the depth of 50 meters. This notion needs to be explored by assessing, first, the cumulative amount of the tDOC deposited into the SSML of the coastal Hudson Bay before it becomes a part of a newly formed WSML, and, second, biodegradability of the tDOC deposited by the Hudson Bay rivers, especially in James Bay. As a final remark, I expect my results would contribute to quantitative estimation of the degree of microbial degradation of tDOC in rivers and coastal ocean zone. My results will also be useful in modeling coastal ocean biogeochemistry dynamics as well as predicting its response to the on-going climate change in the Arctic Ocean.

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