PHOTOCHEMICAL AND BIOLOGICAL DEGRADATION OF DISSOLVED ORGANIC CARBON IN THE MACKENZIE DELTA, NWT.

GAYLA WEEKS

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ABSTRACT

Circumpolar river deltas are a potential hotspot for the biogeochemical cycling of dissolved organic carbon (DOC) as it is leached from the surrounding landscape into deltaic river channels and eventually discharged to the near shore Arctic Ocean. The Mackenzie Delta, an intricate network of over 45,000 lakes in the western Canadian Arctic, is strongly dependent on both the flood dynamics and biogeochemical properties of the northward flowing Mackenzie River. This study examined the seasonal and spatial variability of photochemical and biological DOC degradation within select river channels and lakes of the Mackenzie Delta. The study revealed significant differences in DOC loss via photochemical (PCD) and biological degradation (BDOC) within lakes of differing flood regimes, while river waters showed only minor losses via BDOC, but significant photochemical degradation. In addition, incubation experiments indicate that BDOC is strongly enhanced through UV exposure.

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BDOC	Biological degradation of dissolved organic carbon
DOC	Dissolved organic carbon
PCD	Photo-chemical degradation of dissolved organic carbon
PE-BDOC	Photo-exposed biological degradation of dissolved organic carbon.
a_{330}	Absorbance coefficient at 330 nanometers
$S_{275-295}$	Spectral slope between 275 and 295 nanometers, where increasing values indicate decreasing molecular weight of dissolved organic carbon.
$S_{350-400}$	Spectral slope between 350 and 400 nanometers, where increasing values indicate decreasing molecular weight of dissolved organic carbon.
S_R	Slope ratio of the spectral slope between 275-295 nanometers and the spectral slope between 350 and 400 nanometers. An indicator for the molecular weight of dissolved organic carbon with higher ratios suggesting clearer waters with a lower molecular weight of dissolved organic carbon.
$SUVA_{254}$	Specific UV absorbency at 254 nanometers. an indicator for aromaticity of the humic fraction of dissolved organic carbon. Higher $SUVA_{254}$ values suggest more aromatic dissolved organic carbon within a sample. The molecular weight of DOC with higher ratios suggesting clearer waters with a lower molecular weight of dissolved organic carbon.

1.0 Background

The compounding effects of climate change have led to a compendium of research to increase our understanding of the dynamics and budgetary allowances of the carbon cycle within the global biosphere. Carbon exists in many forms within Earth's reservoirs including atmospheric CO_2, fossil carbon, inorganic carbon dissolved in oceans and lakes, terrestrial organic carbon within soils and vegetation, and particulate and dissolved forms of organic carbon within aquatic and marine environments. All of these forms of carbon contribute to the overall global carbon budget. Leading into the 21st century, anthropogenic perturbations of the carbon cycle have created unprecedented warming in the circumpolar Arctic (ACIA 2005; IPCC 2007) and produced broad scale effects within polar systems including changes to hydrological regimes (Beltaos *et al.* 2012), permafrost thaw (Vonk *et al.* 2013) and increasing UV intensity reaching the polar land surface (Erickson III *et al.* 2015).

Within the context of the Arctic carbon cycle there are a host of studies which focus on the duration of organic carbon storage within terrestrial environments (e.g. Spencer *et al.* 2009), the transport, transformation and storage of organic carbon within rivers and lakes (Tank *et al.* 2009; Holmes *et al.* 2012; Lesack *et al.* 2014), and the eventual discharge of organic carbon via riverine transport across the continental shelves to the Arctic Ocean (Bélanger *et al.* 2006; Déry *et al.* 2009; Manizza *et al.* 2011). Due to the overall complexity of the interactions between variable constituent processes within the carbon cycle, scientists direct their efforts towards particular aspects, or the transfer of carbon from one reservoir to another.

In accordance with these efforts, this study examined the fate of dissolved organic carbon as it moves through a major Arctic river delta (the Mackenzie), before it is discharged to the near shore region of the Beaufort Sea. Dissolved organic carbon is the most critical intermediary of the organic carbon pool and is subject to photochemical degradation through UV exposure, and/or biological degradation by bacteria. This work aims to address questions related to differences in the quantity of dissolved organic carbon that is measured between the entry point to major Arctic river deltas, and their outflow to nearshore coastal regions. One of the goals of this study is to explore the potential source of this differential flux of carbon within the lakes and rivers of the Mackenzie Delta with respect to photochemical and biological degradation of dissolved organic carbon. The specific aim of this background section is to inform the reader of the various elements and processes that contribute to the understanding of our study.

1.1 **Climate Change**

The effects of climate change have stressed, and consequently altered biogeochemical cycles of global ecosystems, perhaps none more significantly than the polar Arctic where surface temperatures have increased greater than twice that of more southern latitudes (ACIA 2005; IPCC 2007). On land north of 60^{o} N, surface air temperatures have increased 1.3^{o} C (Oct- Sept. 2015), relative to the annual mean calculated from 1981-2010, which represents an overall increase of 2.9^{o} C since the early 1900's (Arctic Report Card 2015).

This difference in surface temperatures is referred to in global climate models as Arctic amplification (Serreze & Barry 2011), and is caused by a change in albedo within polar

environments which includes loss of sea ice (Overland et. al 2011), and decreased precipitation as snowfall (Pithan & Mauritsen 2014). Contributing factors towards enhanced Arctic warming include anthropogenic forcing of atmospheric greenhouse gases including CO and CO_2 (IPCC 2007), primarily a result of the combustion of fossil fuels (Hansen *et al.* 2007; Solomon *et al.* 2009), and a thinning of the stratospheric ozone layer during the Arctic spring season (Manney *et al.* 2011; Erickson III *et al.* 2015).

Stratospheric ozone absorbs solar UV radiation in the upper atmosphere and limits the more intense UV-B radiation from reaching the earth surface (Schoeberl & Hartmann 1991). As the percentage of stratospheric ozone decreases, the amount of UV-B able to pass through the atmosphere increases. Together, these systemic changes have led to a series of positive feedbacks that have raised the potential for increased incoming net radiation on circumpolar lands and their associated watersheds.

Atmospheric stressors such as increased greenhouse gasses, decreased stratospheric ozone, and the resultant increase in net radiation, are related to observed changes in hydrological regimes such as increased Arctic riverine discharge through intensification of the hydrological cycle (Peterson *et al.* 2002; Walvoord & Striegl 2007; Rawlins *et al.* 2010; Holmes *et al.* 2012), and in terrestrial regimes including, deepening of the active layer within permafrost soils (McClelland & Frey 2009; Abbott *et al.* 2014), and the thawing of permafrost that surrounds rivers and lakes within the polar river deltas (Vonk *et al.* 2013).

Individually, these recent changes observed in northern regions do not produce a relationship for cause and effect in relation to climate change and the lability of organic carbon within

northern environments. However, the impacts of the collective change in dynamics of hydrological and terrestrial systems, due to warming surface temperatures and increasing solar radiation reaching the Earth's surface, may alter the cycling and distribution of organic carbon from land to the nearshore ocean.

1.2 What is Dissolved Organic Carbon?

Dissolved organic carbon (DOC) is a heterogeneous mixture of organic plant and animal detritus. In aquatic systems, DOC can be derived from production by microbes (phytoplankton, bacteria) and aquatic plants within the freshwater system, or as a result of the transport of organic carbon from land. Terrestrially derived organic carbon is typically subject to humification processes by microbes within soils (Pagano *et al.* 2014) before it is leached and transported into surrounding water bodies via surface runoff. Within DOC there are high molecular weight (HMW) humic and low molecular weight (LMW) fulvic acids as well as insoluble humin and non-humic compounds such as carbohydrates and proteins (Pagano *et al.* 2014). Water bodies with a high concentration of humic DOC tend to be darker in colour and thus have a greater photo-protective barrier which reduces UV penetration of the water column and acts as a sunscreen for aquatic organisms (Gareis *et al.* 2010).

The overall organic carbon pool referred to as total organic carbon (TOC), can be split into particulate (POC) and dissolved (DOC) forms of organic carbon (Pagano *et al.* 2014). The differentiating standard for categorizing DOC versus POC is largely based on the size of the respective molecule of organic carbon present within a sample. It is generally accepted that the measurement of DOC is defined as organic molecules in solution able to pass through a 0.45µm

filter, however 0.70µm and 0.20µm filters are also common (Pagano *et al.* 2014). In each case, the larger POC (>0.45 µm) is removed via sample filtration. For the purposes of this study, we concern ourselves solely with the properties and degradability of the DOC fraction of TOC within selected channel sites of the Mackenzie River and lakes within the Mackenzie Delta.

1.3 The Fate of DOC as it Passes from Land to Ocean in the Arctic System

There are six major circumpolar rivers that discharge into the Arctic Ocean including the Ob', Yenisey, Kolyma and Lena, on the Eurasian side of the Arctic, and the North American Mackenzie and Yukon Rivers (Holmes et al 2012). The Mackenzie River is the longest northward flowing river in Canada (1738 km), spanning four Canadian provinces and the Northwest Territories (Mackay 1963). The combined tributaries of the Mackenzie River drain an area of 1.8 M km², approximately one fifth of the Canadian landmass. Located at the end of the river is the Mackenzie Delta which is the second largest delta in the circumpolar Arctic behind the Eurasian Lena Delta (Mackay 1963; Emmerton 2007).

DOC was once presumed to pass from land to the nearshore ocean with little modification or degradation. Cole *et al.* (2007), refers to earlier work in fluvial geomorphology in which rivers were seen as "the gutters down which flow the ruins of the continents" (Leopold *et al.*1964). Within an Arctic context, more recent studies (Opsahl et al, 1999; Dittmar & Kattner; 2003, Kohler *et al.* 2003; Amon 2004), examined the potential for the lability of DOC within Arctic rivers and determined DOC to be recalcitrant – molecules that flow through rivers without being metabolized (Kaplan & Newbold 2003). The basis for this conclusion was largely determined through apparent conservative mixing behaviour of DOC across the continental

shelves (Opsahl et al 1999; Amon 2004), and was restricted to late summer sampling regimes when DOC was less labile (Kohler *et al.* 2003). Further studies regarding the lability of DOC (Moran & Zepp 1997; Cole et al 2007; Holmes et al 2008; Frey & McClelland 2009) were later conducted during the critical spring period following the annual spring flooding event and found that DOC was labile and reactive. In fact, DOC was actively degraded in rivers and lakes prior to discharge into the Beaufort Sea (Holmes *et al.* 2008). This newer information promoted a greater interest in the fate of DOC and the processes that altered its composition, as it flowed through, and among the rivers and lakes within major Arctic river deltas.

1.4 Photochemical and Biological Degradation of Organic Carbon

There are two main processes that enable the degradation of DOC within surface waters; photochemical and biological degradation of organic carbon. Photochemical degradation of DOC is the result of solar radiation absorbed by chromophores, the coloured, aromatic humic fraction inherent in DOC (Pagano *et al.* 2014). When solar radiation of a particular wavelength excites these molecules, energy is transferred and a suite of low molecular weight photoproducts are produced (Mopper & Kieber 2003). Chromophores within DOC are highly photo-reactive (Battin *et al.* 2008) and degrade over time due to prolonged exposure to solar radiation resulting in reduced chromophoric absorbance and loss of colour. This decrease in UV absorbance is commonly referred as “photo-bleaching” (Bricaud *et al.* 2012; Gonsior *et al.* 2013).

The photochemical degradation process alters the composition of the DOC molecule (Battin *et al.* 2008) and can enhance the bioavailability of the DOC pool via the production of organic

photo-products such as carbonyls, amino acids and sugars that are more readily used as a source of energy for heterotrophic bacteria (Bauer & Bianchi 2011). At the same time, direct photo-mineralization of DOC produces inorganic carbon gases including CO and CO_2. Biological degradation of organic carbon (BDOC) involves the transport of lower molecular weight compounds by heterotrophic bacteria across their cell membranes for growth and metabolism (Battin *et al.* 2008). Heterotrophic bacteria can preferentially take up smaller DOC molecules which can include the products of photo-mineralization, due to the lower amount of energy required to incorporate lower molecular weight DOC for growth efficiency (Battin *et al.* 2008). As a product of bacterial respiration, CO_2 and volatile organic carbons (VOCs) transformed to CO_2, contribute to the summation of inorganic carbons released to the atmosphere (Battin *et al.* 2008). Heterotrophic bacteria also serve as part of the base of the Arctic food web and contribute towards the critical growth and subsistence of higher trophic level organisms (Krumins *et al.* 2013; Kortsch *et al.* 2015). Although photochemical and biological degradation processes can occur in isolation, the combined effect of photochemical degradation and bacterial respiration may optimize the mineralization of organic carbon (Strome & Miller 1978; Bauer & Bianchi 2011).

One of the many reasons for exploring the lability of DOC within rivers and lakes of the Mackenzie Delta is to contribute to the understanding of the regional Arctic carbon cycle. A difference in the amount of carbon exists between the carbon measured within freshwater upper deltaic environments and the riverine discharge onto the nearby continental shelf (Alling et al 2010). One of the goals of this study is to determine whether a sink for this carbon occurs within the lakes of the Mackenzie Delta, where organic carbon is temporarily stored off channel

before it flows back into the river during the summer recession period and is ultimately discharged over the continental shelf.

2.0 Introduction

2.1 Arctic Rivers and Dissolved Organic Carbon (DOC)

Large north flowing rivers in the circumpolar Arctic mobilize an estimated 40 Tg per year of terrestrially derived organic carbon from land to the Arctic Ocean (Raymond et al 2007). The six largest Arctic rivers include the Yenisey, Ob', Kolyma and Lena that flow from Eurasia, and the Yukon and Mackenzie Rivers that discharge from North America to the nearshore environments of the Arctic Ocean. Relative to the global oceans, the Arctic Ocean is the smallest by volume and is surrounded by one fifth of the world's continental shelves which receive approximately 11 percent of freshwater discharge from deltaic circumpolar rivers (Holmes et al 2008). Thus, unlike other global oceans, the chemistry of the Arctic Ocean is greatly influenced by riverine freshwater discharge via circumpolar river deltas (Holmes et al, 2008; Déry *et al.* 2009; Alling *et al.* 2010; Manizza 2011; Holmes *et al.* 2012).

Several studies (Lobbes *et al.* 2000; Alling *et al.* 2010; Manizza 2011; Holmes *et al.* 2012) have researched the dynamics of the polar riverine carbon budget to gain an understanding of how constituents of the carbon pool are consumed, stored and distributed within circumpolar environments. A study by Alling *et al.* (2010) examined the removal of DOC from Arctic shelf waters and found significant amounts of terrestrially- derived organic carbon, measured at the outflow of north flowing rivers, is lost before it leaves the Arctic Ocean. Previous studies, (Lobbes *et al.* 2000; Manizza *et al.* 2009), have shown that the contribution of riverine DOC

along coastal regions far exceeds the concentration of DOC in the mid-Arctic Ocean. Each of these studies found significant differences between the riverine DOC measured from upstream locations of the delta or near shore environments and concentrations of DOC within the Arctic Ocean. Thus, large deltaic environments may be an important region for the decomposition of DOC as it moves from north- flowing rivers to the Arctic Ocean.

2.2 Large Arctic Rivers and Freshwater Discharge

Freshwater discharge from circumpolar rivers contributes to the dynamic flux of biogeochemical constituents such as DOC that has been leached from terrestrial sources and is then actively processed through major Arctic deltas to the receiving coastal environments, and ultimately discharged to the Arctic Ocean. A recent Arctic report indicates there has been an increase in circumpolar riverine discharge for the Eurasian polar rivers; a trend that has rapidly intensified since the beginning of the 21st century (Peterson *et al.* 2002; Arctic Report Card 2015). Previous studies (Marsh *et al.* 2002; Lesack & Marsh 2007; Lesack *et al.* 2014) had suggested that increased riverine discharges and warming surface temperatures (Yang *et al.*2014), may be the precursors to the earlier spring breakup of river-ice due to the formation of thinner ice over winter (Goulding *et al.* 2009). In addition, the reduction in albedo due to a decline in snow cover, particularly in the early spring may promote earlier ice decay (Lesack *et al.* 2014).

2.3 Circumpolar River Deltas

Circumpolar deltaic environments are key geographical regions for research into the lability of DOC within river channels and the associated delta lakes. Where river-mouth deltas occur in Arctic regions, the annual spring flooding regimes of polar rivers promotes temporary off-

channel storage of riverine waters within the vast number of surrounding delta lakes (>45,000 in the Mackenzie Delta; Emmerton *et al.* 2008). This temporary off-channel storage of river waters may optimize the potential for increased biogeochemical activity including photochemical (Gareis *et al.* 2010), and biological degradation of organic carbon (Cory & Kaplan 2012; Abbott *et al.* 2014).

This study had two key goals: First, to explore whether the temporary off-channel storage of water as it moves through polar deltas during the summer solstice period, could provide the mechanisms for the loss of carbon as measured by Alling *et al.* (2010), and the role of biological and photochemical degradation for this potential loss. The region of focus for this work is the Mackenzie Delta, where terrestrially derived organic carbon is transported by rivers via annual flood regimes resulting in the temporary off- channel storage of riverine DOC within the delta lakes. DOC is subject to photochemical and biological degradation processes that alter its composition, before it flows back into the river during the summer recession period and is ultimately discharged over the continental shelf region.

Second, this study aimed to investigate the seasonal variability of the degradation of DOC along the northerly flow gradient of the Mackenzie River from river channel sites near the entry point of the Mackenzie River into the Mackenzie River Delta, to an outflow site near the coast of the Beaufort Sea. Further, lakes in the mid- delta were examined for the variability of DOC degradation processes between Delta lakes that differed in their connection times to the Mackenzie River.

This study will connect previous assessments of the biogeochemistry of large, Arctic rivers including Holmes *et al.* (2012) whose authors examined the six major circumpolar rivers to quantify the total and seasonal flux of carbon, as well as other biogeochemical constituents. Other studies have focused on the flux of carbon from Arctic river deltas to the near-shore marine environments. Alling *et al.* (2010) examined changes in DOC concentration, and residence time within a Eurasian deltaic system, while Manizza *et al.* (2011) found that DOC concentrations decrease substantially during transport by rivers to the near-shore Arctic Ocean. Although several studies have examined the biological degradability of DOC from large Arctic rivers, (Mann *et al.* 2012; Wickland *et al.* 2012), fewer have examined the within-delta effects (Gareis *et al.* 2010) in response to climate change.

Enhanced climate change in northern environments continues to alter biogeochemical cycling, and processes within terrestrial, aquatic and marine ecosystems. Circumpolar deltaic river systems have the potential to be large processing centers for the modification and storage of carbon molecules that cycle between and within complex, interconnected carbon reservoirs. Intricate feedback effects that contribute to the lability of DOC include; destabilization of permafrost soils, the failure of thermokarst lakes through increased surface warming, and altered riverine discharge to sensitive biodiverse coastal environments and the Arctic Ocean.

3.0 Study Area

The Mackenzie Delta encompasses an area over 13,000 km² and is comprised of an interconnected network of river channels, lakes and wetland areas in the continuous permafrost zone of the western Canadian Arctic (Figure 1; Mackay 1963; Emmerton *et al.* 2007). The ecological stability of the delta and associated coastal communities are sustained by the Mackenzie River, the longest northward flowing river in Canada (1738 km), spanning four Canadian provinces and the Northwest Territories (Mackay 1963). The combined tributaries of the Mackenzie River drain a vast carbon- rich area of 1.8 M km², approximately one fifth of the Canadian landmass. Located at the end of the river is the Mackenzie Delta, which is the second largest delta in the circumpolar Arctic behind the Lena Delta in Eurasia (Mackay 1963; Emmerton 2007). The course of the Mackenzie River is divided into five major anastomosing channels, the East, West, Peel, Reindeer and finally, the Napoiak that ultimately flow into the Arctic Ocean via the Beaufort Sea (Squires *et al.* 2009; Figure 1).

3.1 Catchment Area of the Mackenzie Delta

Water flow through the Mackenzie Delta is contributed by two main catchment basins, the Mackenzie and the Peel (Emmerton *et al.* 2007; Burn & Kokelj 2009; Lesack *et al.* 2014). The smaller Peel basin, drains an area of 70 000 km² from the northern regions of the Yukon Territory and the Northwest Territories where it transports organic matter and other materials throughout the trans-boundary 585 km reach of the Peel River (Burn &Kokelj 2009). The headwaters of the Peel River originate in the Ogilvie Mountains of the Yukon Territory. The Peel River flows eastward for 193 km, and then continues northward towards Fort McPherson in the

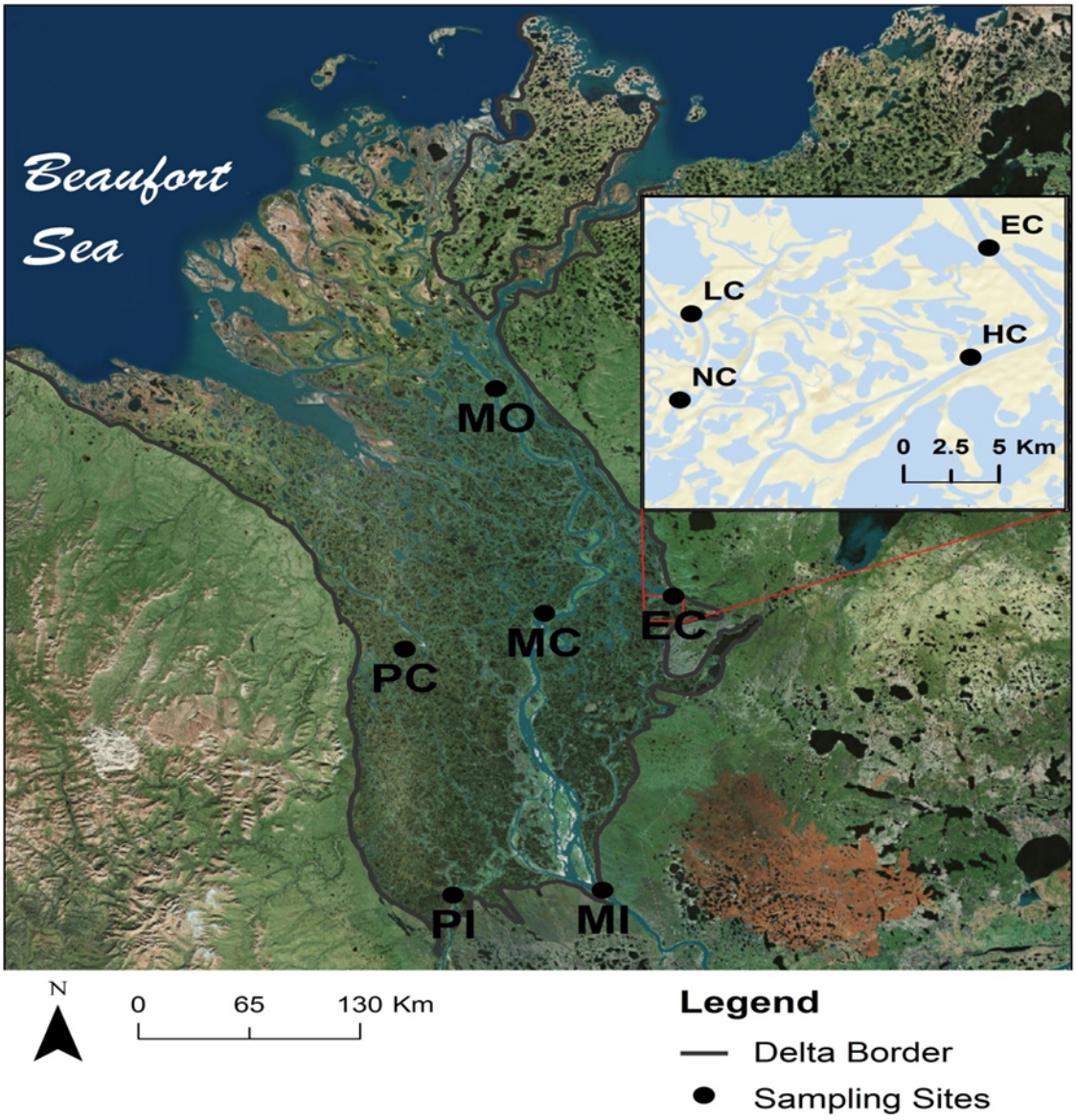

Figure 1: Sampling site locations for rivers in the Mackenzie Delta; Mackenzie Inflow (MI), Peel Inflow (PI), East Channel (EC) Middle Channel (MC), Peel Channel (PC) and Mackenzie Outflow (MO). Lake sampling locations are included in the Inset; No Closure (NC), Low Closure (LC), High Closure (HC) and the reference East Channel of the Mackenzie River (EC). *Image credit*: Google Maps 2013.

Northwest Territories where it eventually joins the confluence of the larger Mackenzie River, approximately 65 km south of Aklavik, NWT (MacDonald 1994).

Each of the catchment basins, (Mackenzie and Peel) have their own particular hydrology and riverine flow volume which may contribute to the overall concentration, and biogeochemical composition of their constituent organic matter that is leached from the surrounding landmasses. The Mackenzie Delta Hydrodynamic Model (Nafziger *et al.* 2009), quantified the percentage of the total monthly flow, split between various river channels of the Mackenzie Delta. The total monthly inflow of water flowing through the Mackenzie Delta was largest for the Middle channel (73.6%). The East Channel, near the origin of the delta carried 4.8%, while the East Channel near Inuvik was a mere 1.8% of total inflow. In addition to differing in the volume of water they carry, river channels vary in the degree to which they are influenced by the Peel and Mackenzie Rivers. The Peel Channel is largely influenced by the Peel River water while the Middle and East channels are intimately linked to the Mackenzie waters (Nafziger *et al.* 2009). An earlier study by Carson *et al.* (1999), found the largest proportion of sedimentary material (84%), originated from the Mackenzie River while the remainder was contributed via the Peel River.

3.2 Spring Break-up and Flooding of the Mackenzie Delta

The arrival of the spring melt season is accompanied by 24-hour daylight and warming surface temperatures. By late May to early June, a sharp rise in water levels (Figure 2) inundates the Mackenzie Delta with an average depth of 2.3 m of floodwaters (Emmerton *et al.* 2007), spread over 11,200 km^2 of the delta lakes, rivers and floodplain (Beltaos *et al.* 2012). There are two co-

occurring hydrological processes that contribute to the peak flow of floodwaters; 1) snow and ice pack that has accumulated over the winter season begins to melt and contributes to surface run off into nearby river channels; and, 2) ice jams that reflect regional climatic differences along the vast length of the Mackenzie River. Southern reaches of the Mackenzie River warm earlier in the spring season than more northerly regions, which cause southern meltwaters to encounter ice jams in the colder, more northerly regions. The resultant "javes", which are waves generated by the release of upstream ice jams (Beltaos *et al.* 2012), lead to overbank discharge along distributary channels. Taken together, these melt conditions contribute to peak water levels leading to the annual spring flood event (Lesack *et al.* 1998; Emmerton *et al.* 2007; Tank et al, 2011; Lesack *et al.* 2014).

The rapid rise in peak water levels (image 1, Appendix A) is followed by a long recession period where riverine floodwaters replete with nutrients and organic material, flows among variably connected lakes, that temporarily store the newly received floodwaters, and where DOC is acted upon by photochemical and biological degradation processes. As the floodwaters recede, the river waters gradually switch to a summer flow regime, on or about July 15th (Emmerton et al 2008) (Figure 2). Lake waters drain and eventually flow back into the river channels where it continues northward, discharging over the continental shelves and into the Arctic Ocean (image 2, Appendix A)

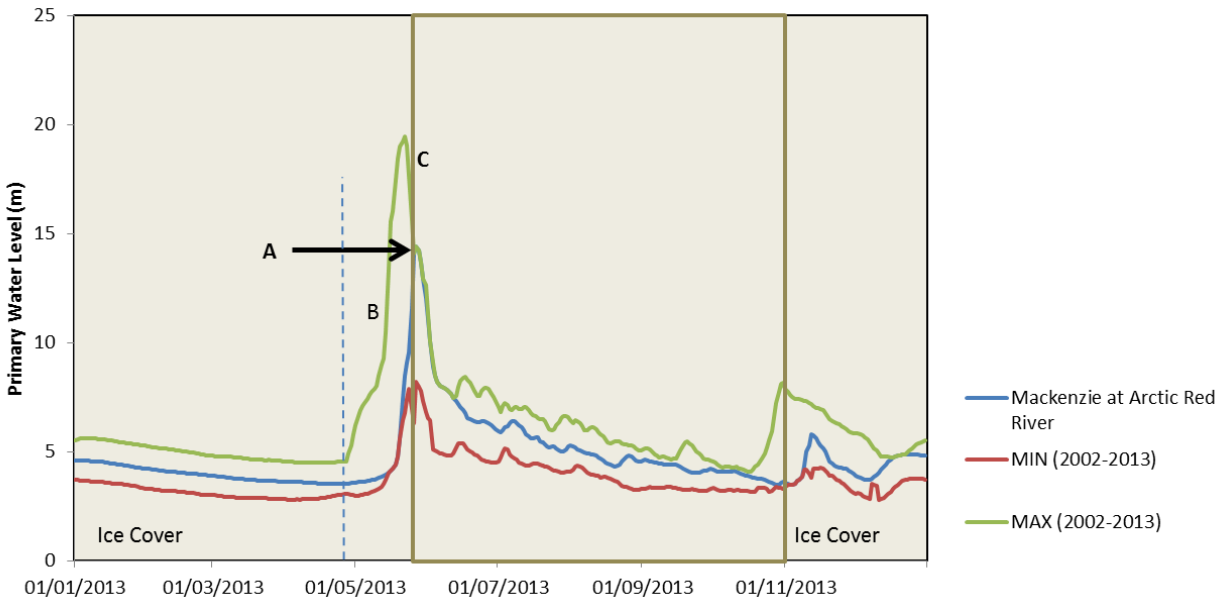

Figure 2: Flood stage waters of the Mackenzie inflow at the Arctic Red River with the long term mean, minimum and maximum water levels (2002-2013). A) Peak water level occurred on May 29th 2013 during the spring ice break up event, B) Sharp increase in primary water levels as the southern reaches of the rivers encounter ice in the northern reaches which causes a surge in primary water levels. C) Open water season in the Mackenzie River following the annual spring break up as floodwaters slowly recede and primary water levels return to base levels just prior to freeze up in mid to late November. *Image credit*: Historical data retrieved from the Water Survey of Canada.

3.3 Mackenzie Delta Lakes

The Mackenzie Delta is a biologically productive, lake- rich environment with over 45,000 lakes positioned throughout the landscape (Emmerton *et al.* 2007; Marsh & Lesack 2010). During the open water season (May to October), delta lakes have varying connectivity to the Mackenzie River through its distributary channels (Mackay 1963; Johnston & Brown 1964; Emmerton *et al.* 2007). Lakes within the delta are typically shallow with an average depth between 1.5-3 meters and are subject to differential flooding regimes based on their sill elevation relative to the river channel (Emmerton *et al.* 2007). Most of the lakes (33%) are located near the mid-delta region as the topography of the delta progrades northward to the Beaufort Sea (Emmerton *et al.* 2007). Smaller lakes tend towards the upper delta due to the region's high elevation (Marsh & Hey 1989), while larger lakes appear at the lower delta as a result of decreased river channel levees and incoming storm surges via the Beaufort Sea during the late summer season (Marsh & Schmidt 1993). Delta lakes exist in the zone of continuous permafrost but do not freeze to the bottom during the winter season (Marsh & Hey 1989). Taliks form beneath Arctic lakes where there is a zone of thermal energy created beneath lake waters, insulated by snow cover that actively prevents the intrusion of permafrost (Johnston & Brown 1964). However, permafrost soils surround the riparian edges of delta lakes (Johnston & Brown 1964).

Lakes within the delta are classified into three types based on their flood regime (Mackay 1963), which is regulated by connection times to the distributary river channel (Lesack *et al.* 1998; Emmerton *et al.* 2008; Tank *et al.*2009). No closure lakes (NC) are in a near constant connection to the river channel throughout the year. Low closure lakes (LC) are seasonally connected to the river channel during spring but not necessarily throughout the summer

(image 3, Appendix A) while high closure lakes (HC) flood infrequently due to their elevation above the river channel (Lesack *et al.* 1998). Some HC lakes are also classified as thermokarst lakes where meltwaters form in depressions caused by thawing permafrost (Mackay 1963; Marsh & Hey 1989; Lesack *et al.* 1998). In addition, lakes may also be defined by their sill elevation (Marsh & Hey 1989), which is given as the height of the thalweg (the entry point of riverine flow) between the lake and the river channel, or as in the case of high closure perched lakes, the elevation of the lake relative to the distributary channel. The classification of lakes based on their individual flood regimes and sill elevations help to determine the transport flow of carbon and other nutrients within river water to lakes within the delta (Lesack *et al.* 1998; Emmerton *et al.* 2008).

4.0 Methods

4.1 Sample Acquisition

Riverine water samples were collected on June 9th and July 23rd 2013 (Tables 1 and 2). Each sample set comprised of six sampling locations along a northerly flow gradient of the Mackenzie River from Point Separation, proximal to the entry of the Mackenzie River into the Delta, to the northernmost Middle Channel of the Mackenzie River near the Arctic Coast (Table 1; Figure 1). In addition, three lakes were chosen for study which included one lake from each of the three classes of lakes as defined by Mackay *et al.* (1963); no closure (NC), low closure (LC) and high closure (HC), (Table 2). Finally, one sampling site within the East Channel served as a reference point to enable comparison in trends between lake and river channel sites (Figure 1).

All lakes and the reference river site were sampled three times over the study period; June 12th following the spring freshet, June 28th post summer solstice, and July 15th when the river flow is

Table 1 : Geographical locations of river and lake sampling sites

	Latitude	**Longitude**
River Site		
Mackenzie Inflow (MI)	67.602^{o}	134.074^{o}
East Channel (EC)	68.336^{o}	133.705^{o}
Middle Channel (MC)	68.295^{o}	134.376^{o}
Mackenzie Outflow (MO)	68.843^{o}	134.629^{o}
Peel River Inflow (PI)	67.590^{o}	134.852^{o}
Peel Channel (PC)	68.207^{o}	135.103^{o}
Lake Site		
No Closure (NC)	68.182^{o}	133.511^{o}
Low Closure (LC)	68.194^{o}	133.508^{o}
High Closure (HC)	68.181^{o}	133.429^{o}
East Channel (EC)	68.337^{o}	133.705^{o}

Table 2 : Sample collection and incubation dates for river channels and lake sites

	T0	BDOC (T0 + 28 days)	T1-PCD (T0 + 3 days)	T2- PCD (T0 + 6 days)	PE-BDOC (T2 + 28 Days)
River Site					
R1-June 9					
MI-EC-MC-MO	Jun- 25	Jul -13	Jun- 28	Jul - 01	Jul- 29
PI- PC	Jun -27	Jul -25	Jun- 30	Jul- 03	Jul- 31
R2- Jul 23					
MI-EC-MC-MO	Jul- 26	Aug- 23	Jul- 29	Aug- 01	Aug- 29
PI- PC	Jul- 25	Aug- 22	Jul- 28	Jul- 31	Aug- 28
Lake Site					
R1- Jun- 12					
NC-LC-HC-EC	Jun- 15	Jul- 13	Jun- 18	Jun- 21	Jul- 19
R2- Jun- 28					
NC-LC-HC-EC	Jul- 05	Aug- 02	Jul- 08	Jul- 11	Aug- 08
R3- Jul- 15					
NC-LC-HC-EC	Jul- 17	Aug- 14	Jul- 20	Jul- 23	Aug- 20

re-set from a spring freshet regime to a summer flow regime (Lesack & Marsh 2007; Emmerton *et al.* 2008). Treatments for the percent loss of DOC were evaluated in relation to the selected lakes sill elevation, or connectivity to, the East Channel of the Mackenzie River near Inuvik, NWT. This sampling regime enabled us to provide insight into the potential gradient effect on the percent loss of DOC which included; 1) biological degradation of DOC (BDOC), 2) photochemical degradation (PCD) and, 3) coupled photo-exposed biological degradation, which we refer to as photo exposed biological degradation of DOC (PE-BDOC), (see Section 4.2).

River water samples were collected from the midpoint of the river channels via helicopter while lake water samples were accessed by boat, with sample waters collected from just below the surface of the deepest part of the lake, using five acid washed 1 L HDPE containers which were pre-rinsed with sample water. Collected samples were subsequently stored in a cool, dark location. At each collection site, measurements were taken for temperature, dissolved oxygen, specific conductivity and pH using a multi-probe YSI. Immediately on return to the laboratory at the Aurora Research Institute (Inuvik), all samples were filtered into site specific, pre-cleaned HDPE collapsible containers incorporating sequentially reduced and pre-rinsed capsule filters, (Geotech dispos-a-filter™ 10 µm to 0.45 µm and Pall Life Sciences, 0.2 µm). Employing the 0.2 µm filter ensured all bacteria was effectively removed from the sample. The filtering process enabled us to pool together all five of the one liter collected samples for laboratory analysis. Directly following filtration, samples from each site were stored in a refrigerated unit at 4^{o}C.

4.2 Experimental Design

4.2.1 Photochemical Degradation (PCD)

Filtered water samples were pumped into UV transparent Tedlar bags using a peristaltic pump outfitted with clean, acid washed and pre-rinsed tubing. Each bag was filled, taking care to minimize the headspace, with 400 ml of sample water and placed in an outdoor UV incubation chamber which was filled with ~ 100 L of water to a depth of 0.3 meters. Each of the incubation set-ups consisted of two control (T0) replicates which were immediately processed, six UV light-exposed replicates, and three replicates for dark control samples. Dark samples were triple wrapped in a dark opaque material to prevent UV penetration. Following three days of UV exposure (T1), three light bags were removed and processed for analysis. Following six days of UV exposure (T2), the remaining three light bags and the remaining three dark bags were removed from the incubation chamber and similarly processed. Both UV-A + UV-B (Apogee SU 100™) and temperature (Type T thermocouple), sensors were attached to a Campbell Scientific CR 1000 data logger, and placed on a planar surface near the chamber which measured incoming UV, (Wm^{-2}) and temperature, (^{o}C) every 10 minutes for the duration of the experiment. Riverine sample waters were collected on June 9th and July 23rd (Table 2). For each of these collection dates, riverine incubations were conducted over two time periods; the incubation time period for the Mackenzie influenced sample waters began (T0) on June 25th and July 26th, for the second incubation time period (Table 2). The time periods for the Peel influenced samples waters began with incubations starting on June 27th and July 25th (Table 2). Differences in the start date for the incubations of the Mackenzie, and Peel influenced waters was to assess whether there were differences in the amount of PCD between the two sub-

basins (Mackenzie and Peel) of the Mackenzie River. Lake water samples were collected on June 12th, June 28th and July 15th (Table 2). For each of the sample collection dates, lake water incubations were conducted over one time period, beginning (T0) on June 15th, July 5th, and July 17th, respectively (Table 2).

4.2.2 Biological Degradation (BDOC) and Photo-Exposed BDOC (PE-BDOC)

To compare the importance of BDOC relative to PCD, bacterial inoculate was prepared by filtering raw sample waters from each of the lake/river sites. 60 ml of water was withdrawn and subsequently filtered with a Whatman™ GF/C filter (nominal pore size 1.0 µm) into an acid washed 40 ml glass vial which had been previously muffled at 450^{o} C. Once prepared, inocula were refrigerated at 4^{o} C, until required for the incubation experiments. For each sample site at T0, duplicate 30 ml samples of 0.2 µm-filtered (i.e., bacteria-free) water was added to 40 ml glass vials into which, 300 µL of GF/C-filtered bacterial inoculate was added. These samples were capped loosely to allow air flow to circulate, and incubated at 20^{o}C for a period of 28 days. Following completion of the incubation period, samples were re-filtered back into the existing 40 ml vials through a GF/F filter outfitted onto a 60 ml syringe. The syringe was rinsed once with the sample water prior to re-filling the vial. Following filtration, the samples were acidified to pH 2 with concentrated 11M hydrochloric acid to ensure no further bacterial degradation could occur within the samples. In addition to the incubated samples, duplicate, non-irradiated 30 ml samples were processed immediately at T0, to act as controls for the experiment. These samples were treated identically to the terminated samples that had undergone the incubation treatment (see above), and were refrigerated for later analysis, and comparison as a T0-BDOC sample. Finally, at T=6 days post irradiation, one 30 ml sample from

each light-exposed bag (n=3 per site) was incubated via the same process as the non-irradiated (T0) incubations, to allow for an examination of rates of BDOC on photo-exposed samples.

4.3 Laboratory Analyses

4.3.1 DOC concentration

For photochemical degradation (PCD) samples, 30 ml of water from each Tedlar bag was transferred to 40 ml glass vials into which a few drops of concentrated 11M hydrochloric acid was added to reduce the pH < 2. Samples were subsequently stored at 4 ^{o}C until they were transported to the lab at York University. Concentrations of DOC from PCD samples together with incubation treatment samples for biodegradation of DOC and PE-BDOC were analyzed as non-purgeable organic carbon (NPOC), as determined by a Shimadzu TOC- L CPH/CPN analyzer. A calibration curve was generated from a 1000 mg C L^{-1} standard solution that was initially diluted to 20 mg L^{-1}. A series of caffeine standards (10 mg L^{-1}) were inserted into the sample carousel between each of a ten vial count of DOC samples to assess for catalyst degradation, and maintain the quality of analyses. Each injection from the sample vials was sparged with CO_2-free air for a period of seven minutes at a flow rate of 10 ml min^{-1} to effectively eliminate inorganic carbon from the sample output measurement. The best three out of five injections per sample vial were averaged to obtain the true DOC concentration value for each DOC sample.

4.3.2 Absorbance (a_{330})

PCD samples for absorbance from each Tedlar bag were transferred into 60 ml acid washed HDPE containers, taking care to minimize headspace. Following refrigeration and transport to the lab, duplicate room temperature samples were scanned for absorbance between 250-750

nm using a Genesys 10 UV- VIS spectrophotometer with a 0.05 m quartz cuvette. Absorbance measurements were converted to absorption coefficients by multiplying by 2.303 and then dividing by the path length of the cuvette (Helms *et al.* 2008). Calculations for analysis included specific UV absorbance ($SUVA_{254}$; Weishaar *et al.* 2003), which was determined by dividing the UV absorbance at 254 nm by the concentration of DOC (mg L^{-1}). In addition, the spectral slope of each absorbance spectra ($S_{275-295}$ and $S_{350-400}$), was acquired by obtaining the log linear fits for each of the selected wavelengths (Helms *et al.* 2008). Finally, the spectral slope ratio (S_R) was calculated as a ratio between the slope of short ($S_{275-295}$) and long wave ($S_{350-400}$) absorbance spectral regions (Helms *et al.* 2008). Chromophores within the humic fraction of DOC are capable of absorbing light greater than 200 nm while the absorption spectra of simple aromatic carbons are less than 300 nm (Braslavsky 2007). In addition, within the short wavelength UV spectrum stimulated light photons are only able to promote organic molecules over wavelengths between 200 and 400 nm (Braslavsky 2007; Helms *et al.* 2008; Hansell *et al.* 2014). The greater the energy released by photons within UV light that is absorbed by chromophores within DOC, the steeper the curve output for the spectral slope.

4.4 **Statistical Analyses**

One way ANOVAs for DOC percent loss were used to determine whether there were significant differences between treatments for photo-degradation and biological degradation of dissolved organic carbon within river and lake samples. Post-hoc Tukey tests were performed to detect differences between treatments, following significant ANOVA results. In addition, one way ANOVAs were used to assess the effect of photo-degradation on spectral absorbance variables including a_{330}, $S_{275-295}$, $S_{350-400}$, S_R and $SUVA_{254}$.

5.0 Results

5.1 UV and Temperature

5.1.1 River Sites

Downwelling UV and ambient air temperature data sensors showed a marked diurnal trend for both the Peel and the Mackenzie influenced river water incubations, despite continuous 24-hour daylight (Figures 3 and 4). UV and temperature data for the first incubation period for river water collected on June 9th was lost. For river waters collected on July 23rd, the incubation period for the Peel influenced waters was from July 25th through to July 31st 2013 while the Mackenzie influenced waters were incubated from July 26th through to August 1st. Values recorded via data sensors every ten minutes were averaged over three hour intervals followed by a daily averaged value over a 24- hour period, beginning at the start time of the incubation period and continuing until the end of the incubation period. Cumulative daily UV radiation (UVR) values were then used to assess total UVR exposure over each of the sampling intervals; three days solar incubation (T0-T1), and six days solar incubation (T0-T2). Due to differences in the initial day of incubation, small differences in the cumulative values for UVR were attained for each river set i.e., Mackenzie or Peel influenced river waters.

Average UVR for the incubation of the Peel influenced waters from July 25th through to July 28th (T0-T1, three day average) was 148.28 Wm^{-2} and from July 25th to July 31st (T0-T2, six day average) was 130.12 Wm^{-2} while the Mackenzie influenced water incubations showed a three day average (T0-T1) of 121.78 Wm^{-2} between July 26th and July 29th and 124.24 Wm^{-2} between July 26th and August 1st (T0-T2, six day average)

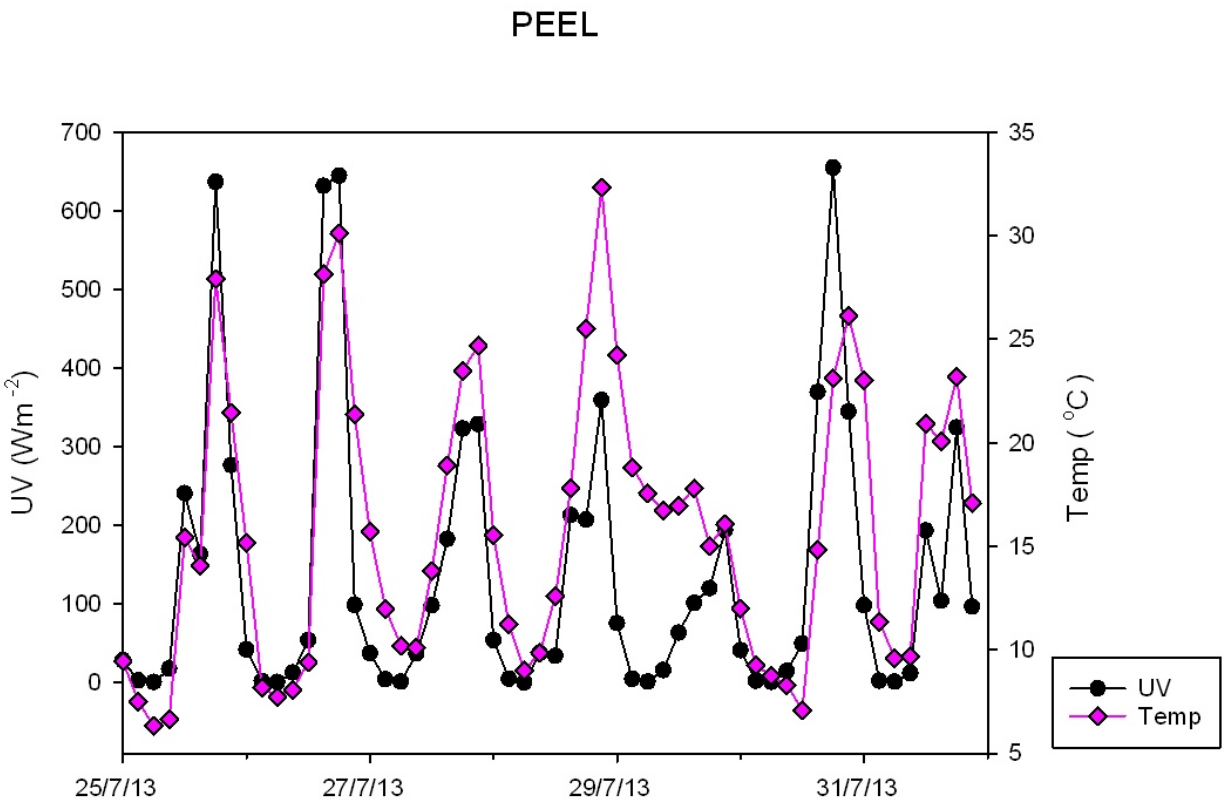

Figure 3: Averaged daily logged UV (Wm^{-2}) and temperature (^{o}C) for incubations of the Peel influenced river channels, the Peel inflow (PI) and the Peel Channel (PC) which were retrieved from UV and temperature sensors in association with solar incubations over the late summer period (July 25th through to August 1st).

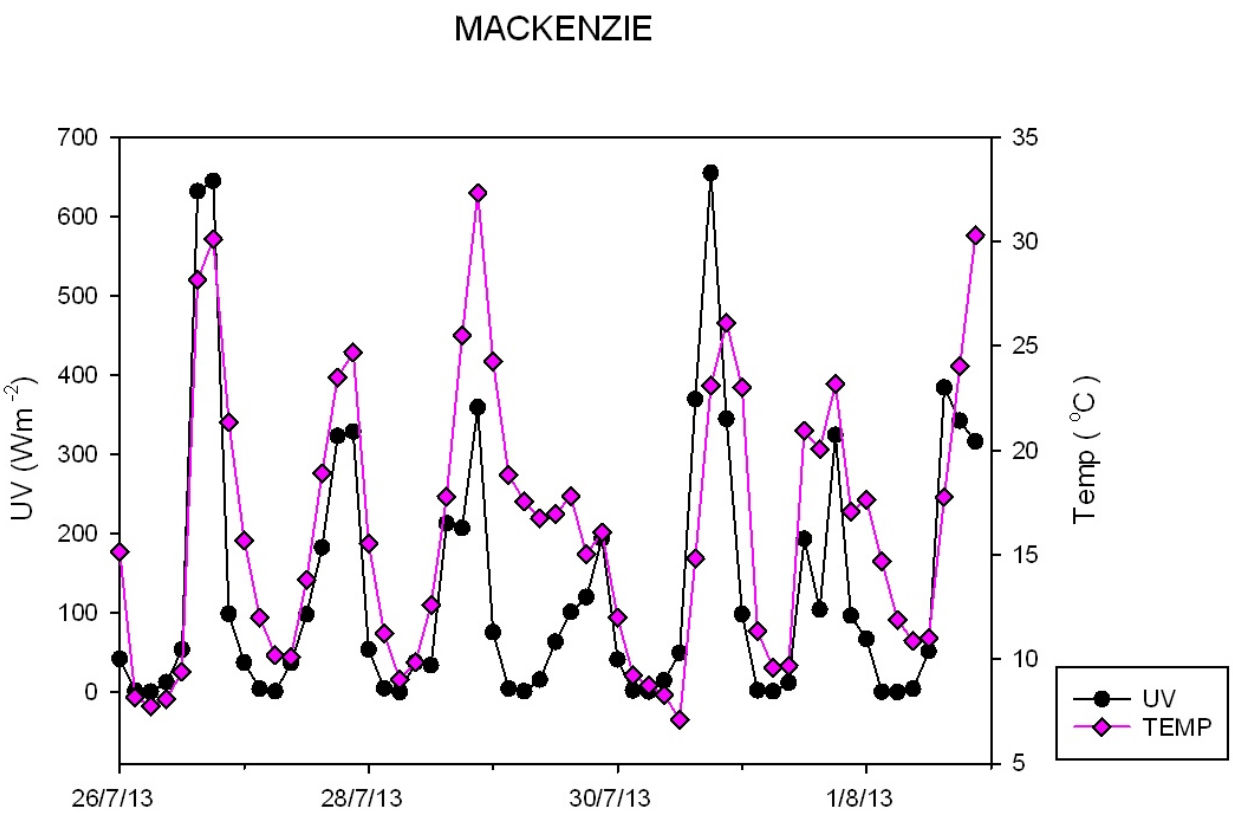

Figure 4 : Averaged daily UV and Temperature data retrieved from UVA/UVB (Wm^{-2}) and temperature (^{o}C) sensors attached to the solar incubator for incubations of the Mackenzie influenced river sites, specifically the Mackenzie inflow (MI), middle channel (MC) and the Mackenzie outflow (MO) from July 26th through to August 2nd.

5.1.2 **Lake Sites**

As previously stated for the river water incubations, there was a strong diurnal trend in UV and ambient air temperature during the incubations of lake waters of differing sill elevations despite the presence of 24- hour daylight throughout the summer period (Figures 5 and 6). In general, peak UV times are between 1500h and 1900 hrs while UV minimums occur in the early morning hours (Figures 5 and 6). For the most part, changes in temperature are closely aligned to changes in UV (Figures 5 and 6). The average total cumulative UV was calculated for incubation intervals of three (T0-T1) and six days (T0-T2) during each of the incubation periods. The first data set was lost, however the June 28th sample found a UV average of 217.07 Wm^{-2} over the three day T0-T1 interval and 201.75 Wm^{-2} throughout the full six day, (T0-T2) incubation. The final incubation for the sampling period of July 15th showed a three day UV average of 195.32 Wm^{-2} from July 17th to July 20th (T0-T1), while 213.03 Wm^{-2} was the calculated six day UV average for July 17th to July 23rd inclusive (T0-T2).

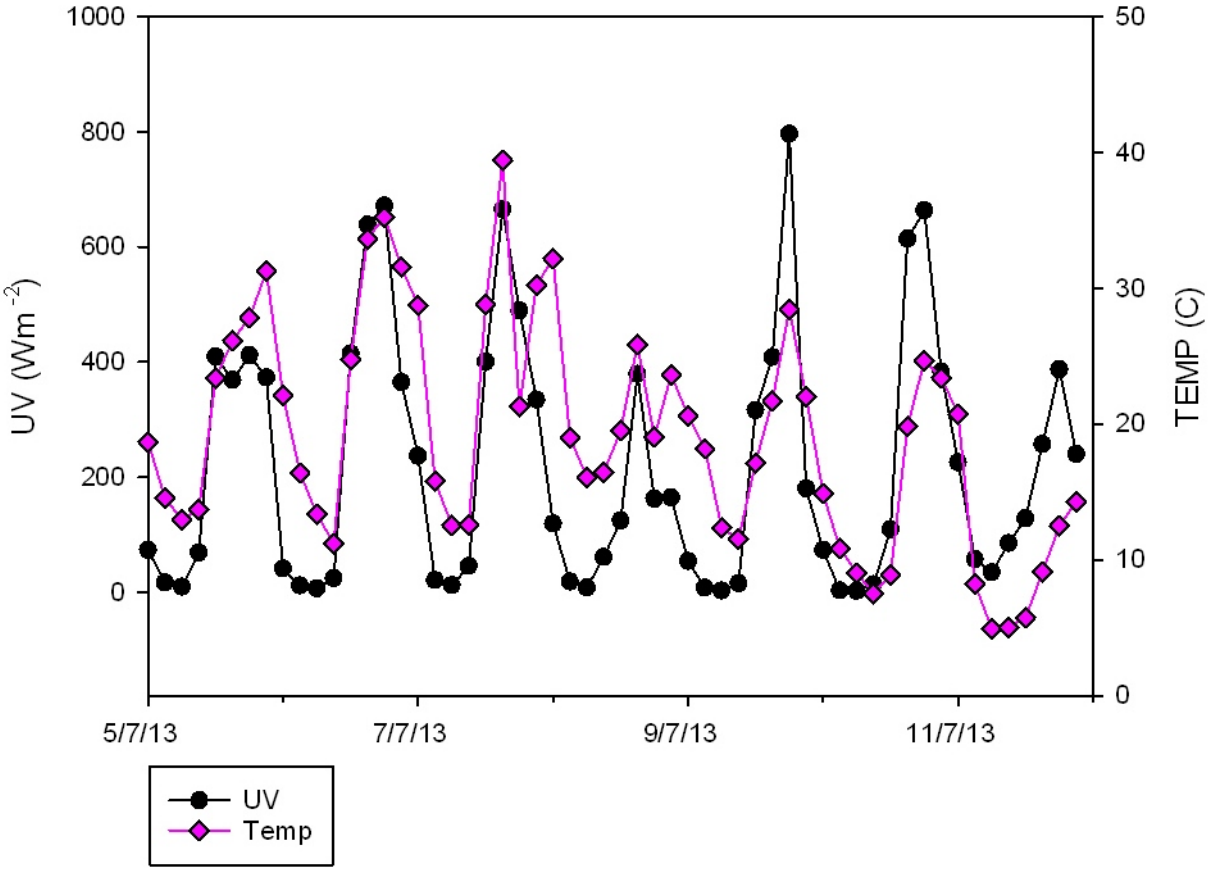

Figure 5 : Averaged daily UV and Temperature data retrieved from UV (Wm^{-2}) and temperature (^{o}C) sensors attached to the solar incubator for incubations of water from the sampled lake sites , no closure (NC), low closure (LC) and high closure (HC) during the July 5th to July 14th incubation period

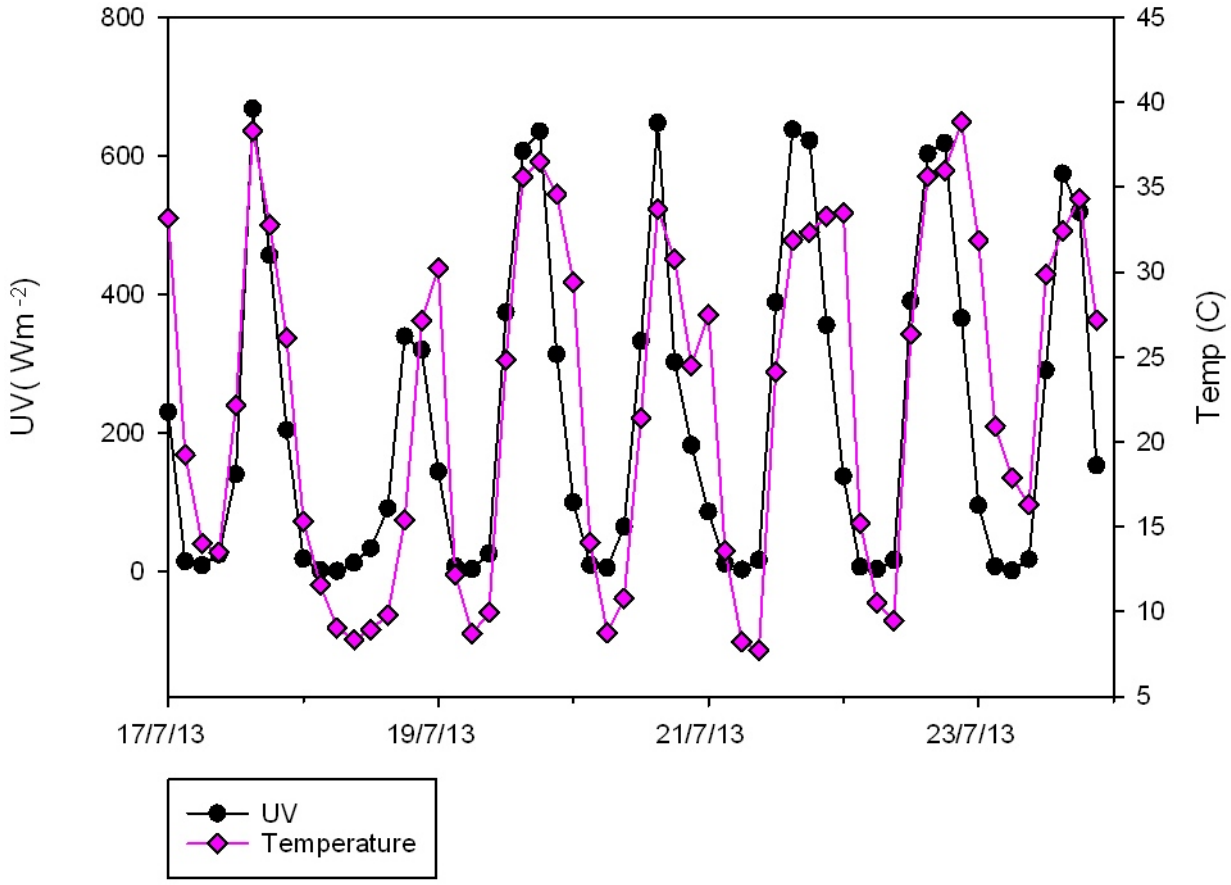

Figure 6 : Averaged daily UV and temperature data retrieved from UVA/UVB (Wm^{-2}) and temperature (^{o}C) sensors attached to the solar incubator for incubations of water from the sampled lake sites, no closure (NC), low closure (LC) and high closure (HC) during the July 17th to July 24th incubation period.

5.2 DOC Percent Loss

5.2.1 River Sites

In all but a few cases, our river channel degradation treatments resulted in a significant loss of DOC (Figure 7). Overall, DOC loss via photochemical degradation (PCD) was significantly greater than the percent loss of BDOC with the exception of the Mackenzie Outflow (MO) for both sampling periods (June 9th and July 23rd) (Figure 7; Table 3). Within the Mackenzie influenced sites, (MI), (MC), (EC) and (MO), percent loss of BDOC was low and showed only minor variability between the two study periods. Conversely, the Peel influenced channel sites, (PI and PC), revealed a greater percent loss of BDOC during both of the sampling periods. In general, BDOC declined gradually from the southern inflows, MI and PI, across the mid delta, and into the northernmost MO (Figure 7). Within the Mackenzie- influenced waters, photochemical degradation (PCD) was greater than percent loss of BDOC, particularly in the Mackenzie Inflow (MI), and the East Channel (EC), while the Middle Channel (MC) showed PCD > BDOC only during the June sampling period (Figure 7; Table 3). In regards to the Peel influenced waters, degradation rates tended to be larger than that of the Mackenzie; however significant differences only existed between PCD and BDOC at the Peel Channel (PC) during the June sampling period (Figure 7; Table 3).

Overall, the strongest response for percent loss occurred within treatments where samples of the individual river sites were subject to six days of UV exposure followed by a 28 day bacterial incubation, or photo-exposed biodegradation of organic carbon, (PE-BDOC). This effect was most evident immediately following the spring freshet where significant losses via PE-BDOC

were found for MC and EC (Figure 7). Prominent differences appear to exist between the Mackenzie and Peel River influenced sites for the coupled percent loss of PE-BDOC which was most evident during the June 9th sampling period. In the Mackenzie influenced waters (MC and EC) there were significant DOC losses for treatments of PCD and PE-BDOC (Table 3). Overall loss rates at the PC site were greater than the percent loss rates observed for the PI, however, there were no significant differences between PCD and PE-BDOC incubations in the Peel influenced waters (Figure 7). It is notable that the most significant losses occurred within the mid- delta sites (PC, MC and EC), for all three treatment types (Figure 7; Table 3), as the central delta contains the largest percentage of lakes which provide temporary off-channel storage of the river waters. Along the South-North gradient of the Mackenzie influenced river flow, BDOC showed a consistently minor percent loss at the head of the delta for both sampling periods, which continued steadily downstream towards the Mackenzie Outflow. There was no significant percent loss for BDOC at the Mackenzie Outflow (MO) in the June sampling period and only a minor significant loss during the July sampling period (Figure 7).

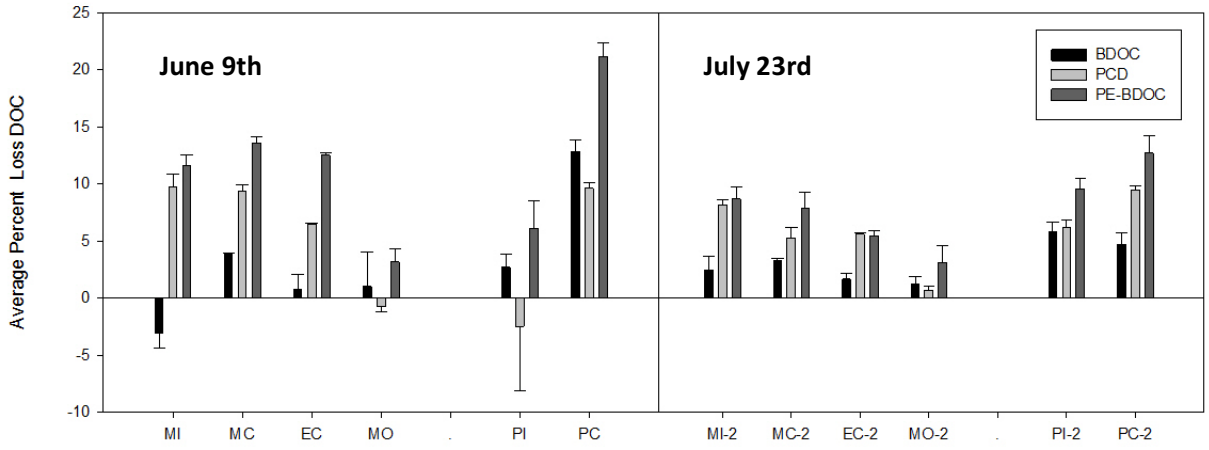

Figure 7 : Average percent loss of DOC for treatments of bacterial degradation of DOC (BDOC), photochemical degradation of DOC (PCD) and photo- exposed bacterial degradation of DOC (PE-BDOC). MI, MC, EC and MO are the Mackenzie influenced sites, while PI and PC are the Peel influenced sites. Error bars represent 95% confidence intervals. (See Table 1 for specific abbreviations).

Table 3 : Treatment results for percent loss of DOC within a) river channels and b) lake sites which show F critical and significant results where $p < 0.05$. Comparisons were conducted using a Tukey post hoc analysis test. Significant differences between treatments are indicated by different alphabetical letters. Non -significant results are denoted with an asterisk

	R1 Jun 9					**R2 Jul 23**				
	F	P	Contrasts			F	P	Contrasts		
a) RIVERS			BDOC	PCD	PE-BDOC			BDOC	PCD	PE-BDOC
MI	45.67	0.00	A	B	B	13.66	0.00	A	B	B
EC	109.78	0.00	A	B	C	31.98	0.00	A	B	B
MC	77.80	0.00	A	B	C	7.17	0.20	*	*	*
MO	2.07	0.22	*	*	*	1.94	0.21	*	*	*
PI	1.40	0.37	*	*	*	6.07	0.03	A	AB	B
PC	40.61	0.00	A	A	B	10.67	0.02	A	AB	B

	R2 Jun 28					**R3 Jul 15**				
	F	P	Contrasts			F	P	Contrasts		
b) LAKES			BDOC	PCD	PE-BDOC			BDOC	PCD	PE-BDOC
NC	101.58	0.00	A	B	C	201.68	0.00	A	A	B
LC	330.48	0.00	A	B	A	113.55	0.00	A	B	C
HC	1665.69	0.00	A	B	C	0.03	0.97	*	*	*
EC	*	*	*			6.96	0.02	A	AB	B

5.2.2 **Lake Sites**

Replicate samples for June 15th were not available; however, the concentrations of DOC were assessed for individual sample treatments processed during this sampling period (Figure 8). Lake-water samples from the connected lakes (NC and LC), and the riverine sample waters from the reference site (EC) showed a higher initial (T0) concentration of DOC than the HC lake-waters. However, all three lake classes (NC, LC and HC) showed DOC loss via PE-BDOC was greater than DOC losses associated with PCD (Figure 8). During the second sampling period following the summer solstice (June 28th), BDOC showed a greater percent loss than PCD in all three of the lakes that were assessed (Table 3; Figure 9). The BDOC sample for EC was lost and unavailable for comparison (Figure 9). Both NC and HC lakes showed a significantly greater percent loss for PE-BDOC as compared to PCD (Table 3; Figure 9).

Towards the end of summer (July 15th), there was a dramatic shift in response to treatments for DOC degradation as BDOC decreased sharply within lake classes, and at the reference EC site when compared to the previous incubation period (Figure 9). In addition, the treatment for PE-BDOC showed an outcome that differed among lake classes where NC and LC lakes showed a large percent loss while HC and EC sampling locations were starkly reduced (Figure 9). As opposed to the gradual reduction in PE-BDOC loss revealed during the June 28th sampling period, degradation rates decreased abruptly with increasing sill elevation. Perhaps the most notable difference between these two sampling periods was that of the HC lake which showed significant variability between all three treatments following the June summer solstice, together with a much higher percent loss for PDC and PE-BDOC. Conversely, during the final

sampling period in mid-July, none of the treatments were significant and DOC losses were minor (Figure 9; Table 3).

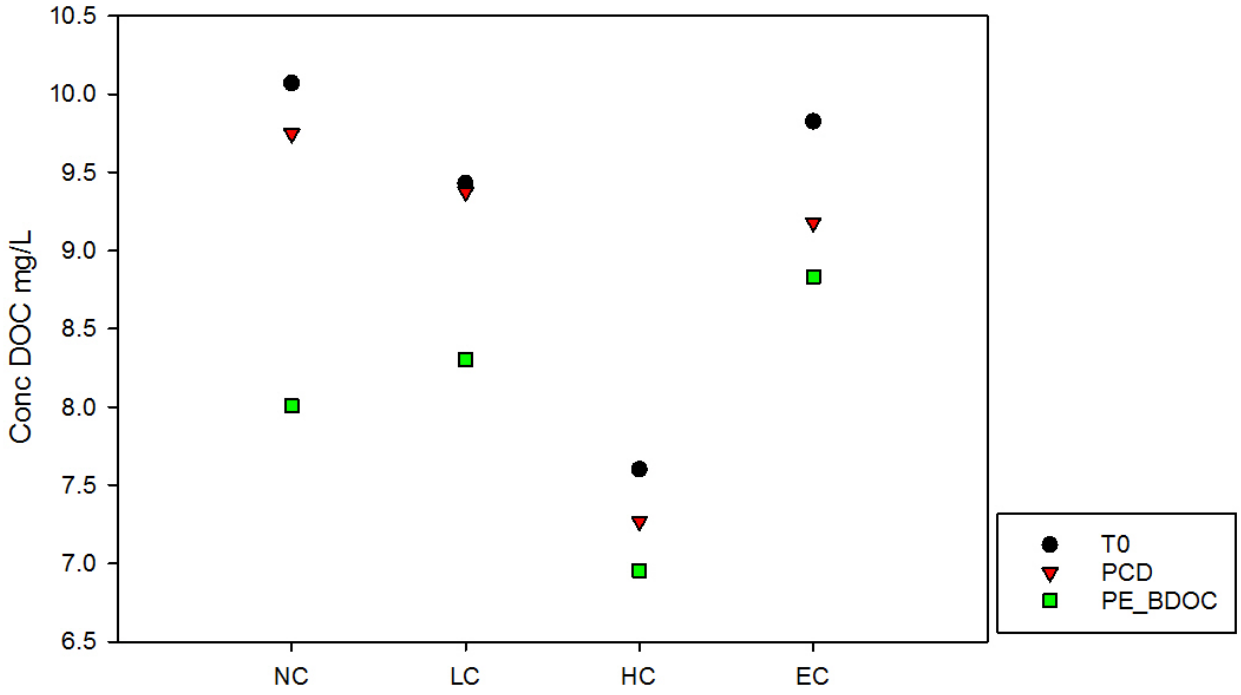

Figure 8 : Concentration of DOC for no closure (NC), low closure (LC) and high closure (HC) lakes along with the reference sampling site within the East Channel (EC) of the Mackenzie River during the June 12th sampling period. Experimental treatments for photochemical degradation of DOC (PCD) and photo-exposed biological degradation of DOC (PE-BDOC) are shown in relation to the initial concentration of DOC (T0).

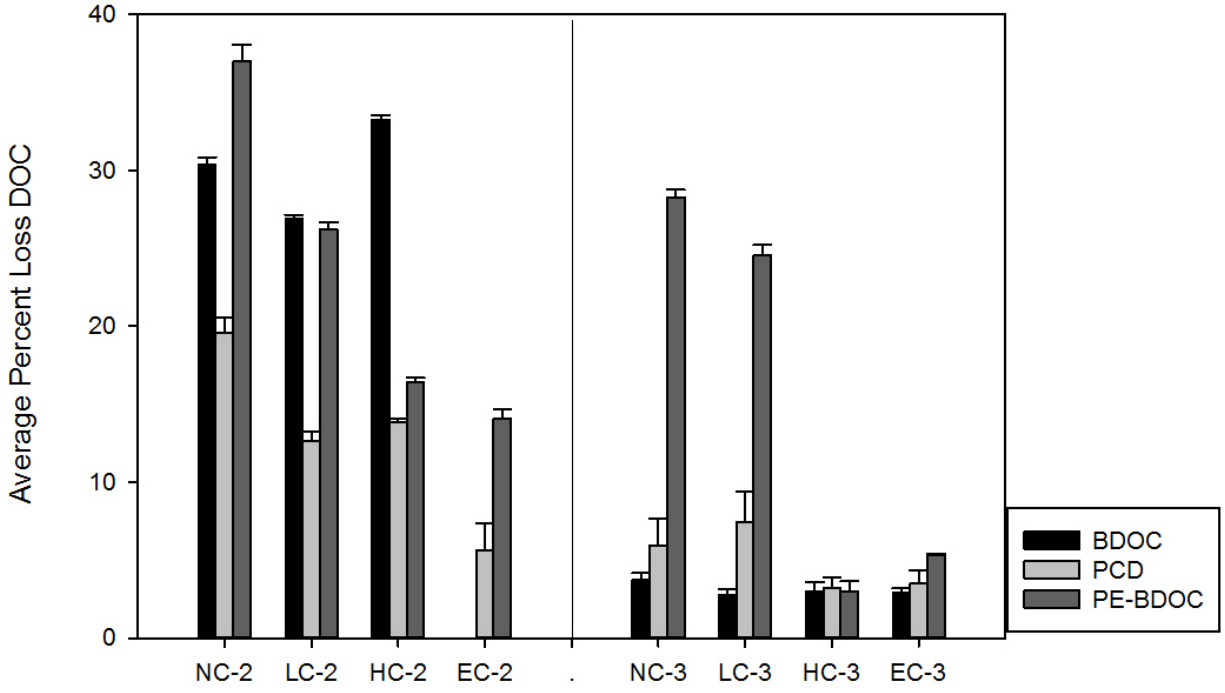

Figure 9 : Average percent Loss of DOC for lake sites with experimental treatments of biological degradation of DOC (BDOC) photochemical degradation of DOC (PCD) and photo exposed biological degradation of DOC (PE-BDOC). NC-2, LC-2, HC-2 and EC-2 represent the June 28th sampling period. NC-3, LC-3, HC-3 and EC-3 represent the July 15th sampling period. Error bars represent 95% confidence intervals.

5.3 Absorbance

5.3.1 River Sites

5.3.1.1 a_{330}

The absorption coefficient (a_{330}) is a measure of how strongly the humic fraction of DOC absorbs UV light at 330nm and provides a good indicator of the potential for solar photo-bleaching of the humic portion of the DOC molecule (Vähätalo & Wetzel 2008). During the June 9th sampling period immediately following the spring freshet, a_{330} values for all river sites decreased rapidly following three days of solar incubation. The highest initial (T0) values were measured at the inflow sites while the lowest measured values occurred at the Mackenzie outflow site (Figure 10a). After a period of six days incubation (T2), measurements for a_{330} decreased further, however to a lesser degree (Figure 10a). Meanwhile, the dark sample measurements were statistically identical to the initial (T0) measured values; therefore, we can assume we were successful in blocking UV activity in the dark control (T2D) samples, and that there was no microbial activity during the incubations (Table 4).

Initial measurements for a_{330} during the July 28th sampling period showed a clear decrease in the initial absorbance values relative to the first sampling period (June 9th) earlier in the open water season (Figure 10a and b). All river sites showed a steady, albeit shallow decrease in absorptivity throughout the six day incubation experiment (Figure 10b; Table 4). As with the June 9th solar incubation, a $_{330}$ declined significantly in all cases over the course of the experiment, while the dark control samples (T2D) did not differ from initial (T0) measurements (Figure 10b; Table 4)

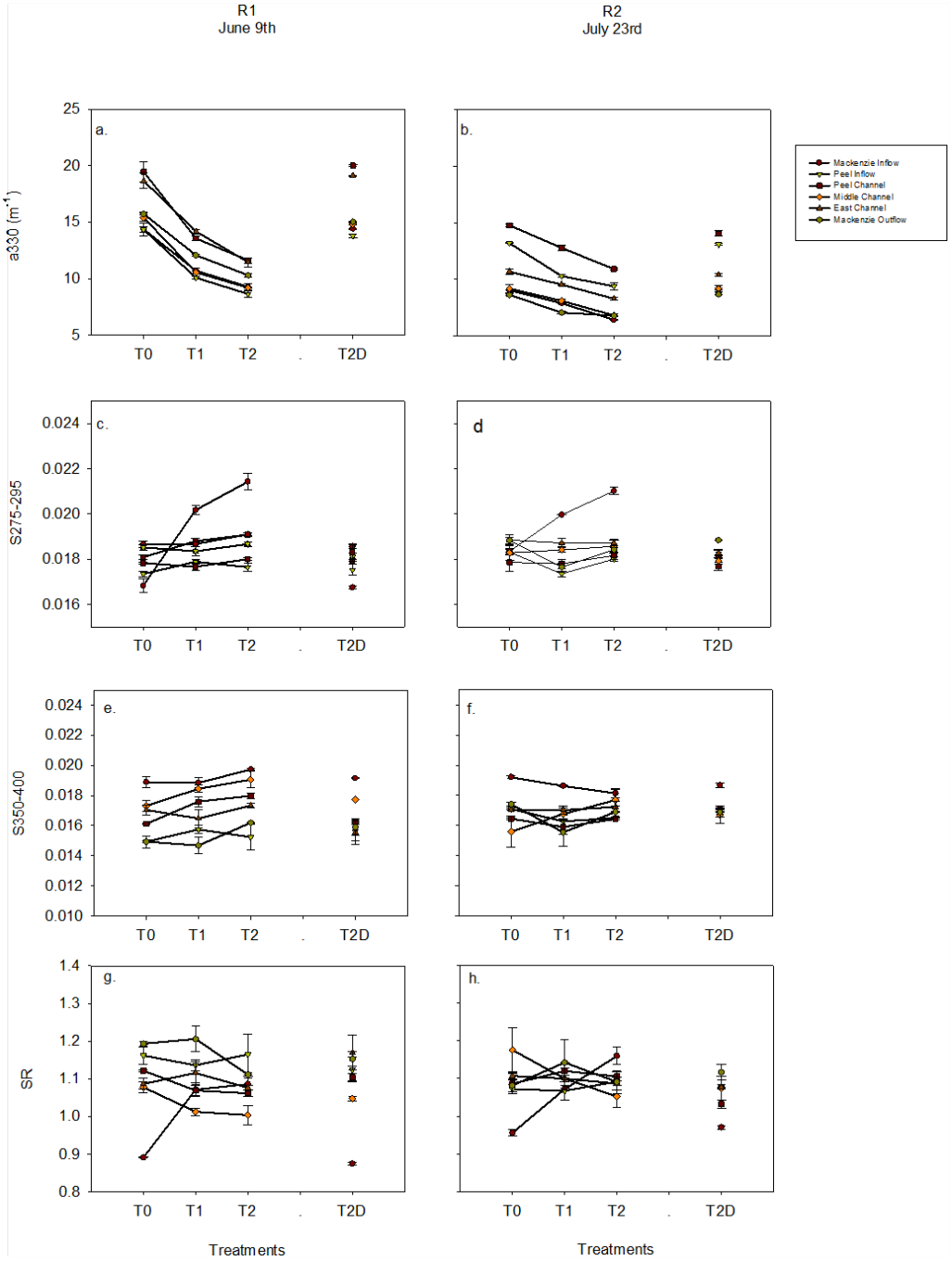

Figure 10 : Spectral absorbance of DOC for riverine sample waters over the June 9th (a, c, e and g), and July 23rd (b,d,f and h) sampling periods. T0 control samples are plotted against treatments for three days UV exposure (T1) and 6 days UV exposure (T2). Dark samples, represented as "T2D" were double wrapped in a black plastic material for a period of six days, hence equal to the time duration of the exposed T2 samples. Masking of the dark samples effectively blocked exposure to the effects UV solar radiation acting on the DOC within the treated samples (T1 and T2). Error bars represent 95% confidence intervals.

Table 4 : Spectral absorbance contrasts for river sites showing *F* critical and significant outcomes where $p < 0.05$. Comparisons were conducted using a Tukey post hoc analysis test. Significant differences between treatments are indicated through different alphabetical letters. Non -significant results are denoted with an asterisk.

	R1 Jun 9						R2 Jul 23					
	F	P	Contrasts				F	P	Contrasts			
a330 (m^{-1})			T0	T1	T2	T2D			T0	T1	T2	T2D
MI	85.56	0.00	A	B	C	A	909.04	0.00	A	B	C	A
EC	120.45	0.00	A	B	C	A	65.58	0.00	A	B	C	A
MC	411.88	0.00	A	B	C	A	22.07	0.00	A	A	B	A
MO	457.95	0.00	A	B	C	D	232.84	0.00	A	B	B	A
PI	146.23	0.00	A	B	C	A	82.82	0.00	A	B	B	A
PC	161.84	0.00	A	B	C	A	60.94	0.00	A	B	C	A
Shortwave (S275-295)												
MI	84.71	0.00	A	B	C	A	215.87	0.00	A	B	C	A
EC	2.21	0.18	*	*	*	*	2.54	0.14	*	*	*	*
MC	5.55	0.03	AB	AB	B	A	1.67	0.26	*	*	*	*
MO	1.79	0.24	*	*	*	*	19.22	0.00	A	B	A	A
PI	1.35	0.33	*	*	*	*	9.88	0.00	A	B	AB	A
PC	37.06	0.00	A	B	B	A	1.01	0.44	*	*	*	*
Longwave (S350-400)												
MI	3.28	0.09	*	*	*	*	4.56	0.05	A	AB	B	AB
EC	2.03	0.20	*	*	*	*	0.22	0.88	*	*	*	*
MC	4.46	0.05	A	AB	B	AB	1.40	0.32	*	*	*	*
MO	3.05	0.10	*	*	*	*	1.84	0.23	*	*	*	*
PI	0.32	0.81	*	*	*	*	2.70	0.13	*	*	*	*
PC	14.82	0.00	A	B	B	A	3.26	0.09	*	*	*	*
Slope (S_R)												
MI	63.52	0.00	A	B	B	A	47.73	0.00	A	B	C	A
EC	1.85	0.23	*	*	*	*	1.40	0.32	*	*	*	*
MC	3.82	0.07	*	*	*	*	1.99	0.20	*	*	*	*
MO	4.05	0.06	*	*	*	*	0.47	0.72	*	*	*	*
PI	0.29	0.83	*	*	*	*	0.50	0.69	*	*	*	*
PC	6.61	0.19	*	*	*	*	5.21	0.03	AB	B	AB	C
$SUVA_{254}$												
MI	66.4	0.00	A	B	B	C	38.72	0.00	AB	B	C	A
EC	30.99	0.00	AB	B	C	AB	4.09	0.06	*	*	*	*
MC	27.72	0.00	A	B	B	A	4.83	0.04	A	A	A	A
MO	47.54	0.00	A	B	B	B	2.06	0.19	*	*	*	*
PI	8.59	0.01	A	AB	B	AB	16.46	0.00	A	B	BC	CA
PC	59.88	0.00	A	B	B	A	1.95	0.21	*	*	*	*

5.3.1.2 Shortwave and Longwave Spectral Slopes

Spectral slope (S) is calculated over a range of UV wavelengths that can provide information on the characteristics of dissolved organic matter within a sample. Further, spectral slopes calculated over a range of wavelengths can be used as a proxy for the molecular weight of the humic fraction within DOC (Helms *et al.* 2008; Guéguen & Cuss 2011).

During the June 9th incubation period, light exposure produced steeper curves (greater slope values) between $S_{275-295}$ nm for MC, PC and particularly, MI (Figure 10c; Table 4). A similar effect was observed during the July 28th incubation series where MI showed a pronounced increase in slope values relative to PI and MO (Figure 10d). During the June 9th incubation, $S_{350-400}$ tended to increase slightly with light exposure, the PC showed a significant increase, while the increase in MC was only moderately significant (Figure 10e, Table 4). During the July 28th incubation a significant increase in $S_{350-400}$ was observed only for MI (Figure 10f). Once again, initial values for both $S_{275-295}$ and $S_{350-400}$ were not significantly different than the values of the dark control samples (T2D) (Figure 10c, d, e and f).

5.3.1.3 Slope Ratio

Slope ratio (S_R) can be used as an indicator for the molecular weight of DOC with higher ratios suggesting clearer waters with a lower molecular weight of DOC, while a lower S_R suggests more organic rich waters and thus, a higher molecular weight of DOC (Helms *et al.* 2008). The June 9th incubation series revealed most river sites at T0 tended towards a lower S_R - organic rich waters, suggesting the molecular weight of DOC was largely similar among the river channels (Figure 10g). Results for the June 9th incubation were largely insignificant with the exception of the MI where there is a clear increase in slope over time (Figure 10g; Table 4).

During the July incubation, MI again shows a strongly significant rise in slope which suggests decreasing molecular weight in the humic portion of the DOC molecule. In addition, the PC site also shows moderate significance for increased S_R over time.

5.3.1.4 $SUVA_{254}$

$SUVA_{254}$ is generally used as an indicator for aromaticity of the humic fraction of DOC within aquatic environments. Higher $SUVA_{254}$ values suggest more aromatic organic matter (Weishaar *et al.* 2003) and in the Mackenzie Delta system tend to be highest following the spring freshet (Tank *et al.* 2009). In our incubation experiments, $SUVA_{254}$ values fell rapidly following three days of UV exposure followed by a smaller further decrease in values after six days UV exposure within the incubation chamber (Figure 11a). Our results show this trend was significant for all sites during the June 9th incubation series (Table 4). During the incubation treatments in late July, decreases in $SUVA_{254}$ were significant for the Mackenzie inflow (MI) and the Peel Inflow (PI) sites (Figure 11b; Table 4).

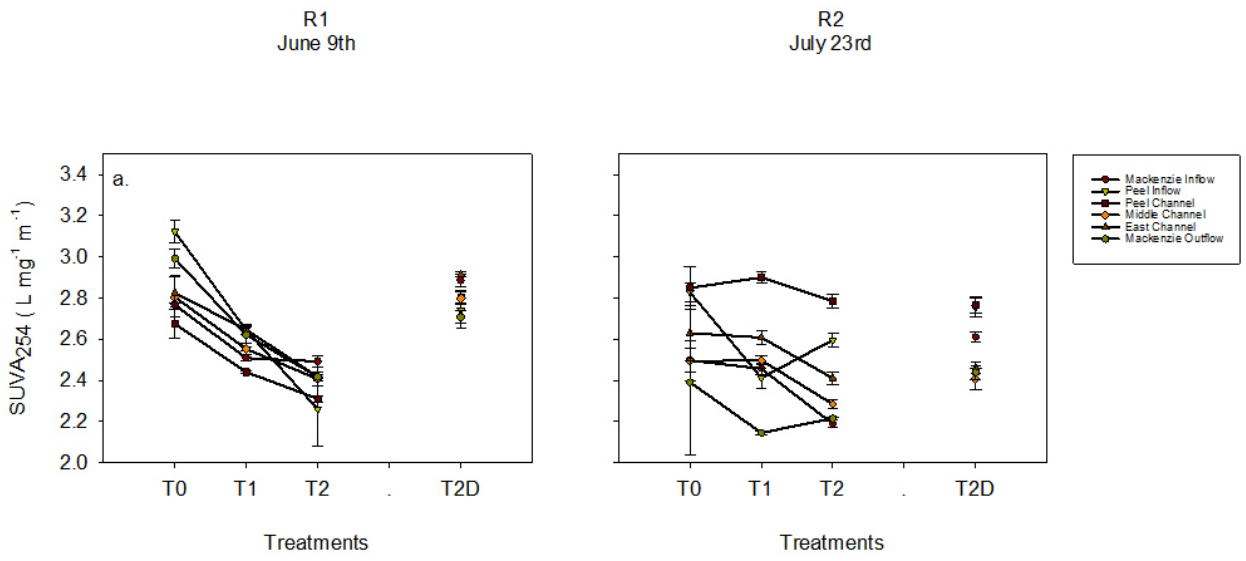

Figure 11 : Spectral absorbance of DOC from riverine sample waters over the June 9th (a), and July 23rd (b) sampling periods. T0 control samples are plotted against treatments for three days UV exposure (T1) and 6 days UV exposure (T2). Dark samples, represented as "T2D" were double wrapped in a black plastic material for a period of six days, hence equal to the time duration of the exposed T2 samples. Masking of the dark samples effectively blocked exposure to the effects UV solar radiation acting on the DOC within the treated samples (T1 and T2). Error bars represent 95% confidence intervals.

5.3.2 **Lake Sites**

Statistical analyses were not performed for the June 12th sampling period as there were limited replicates to complete the data set. In addition, dark samples for this experimental period were not available. However, when two samples per treatment were available, these samples were averaged to include in our figures. In the event that only a single sample was available, the true concentration of that sample was also included in our figures (Figures 12 a, d, g; Figures 13 a, d). We have chosen to represent these results together with our June 28th and July 15th incubation periods as they help to show the seasonal trend for the absorbance spectral analyses.

5.3.2.1 **Absorbance (a_{330})**

During the June 28th and July 15th incubation periods, all sites showed significant photo-bleaching effects of the humic portion of the DOC molecules within our samples (Table 5). In general, T0 values of samples were similar to values for T2D samples (Table 5). The HC lake showed consistently lower values for a_{330} as compared to other lake sites (Figure 12 a, b and c). Patterns for the June 12th lake- water samples were similar to the statistical results obtained for the June 28th and July 15th incubation periods.

5.3.2.2 **Shortwave and Longwave Spectral Slopes**

During the June 28th and July 15th incubation periods, all sites showed a significant increase in $S_{275\text{-}295}$ (Table 5). Each of the incubation periods, which include the June 12th incubation, showed a rapid response to incoming UV following three days of light exposure (Figure 12e and f). Overall, the HC lake consistently showed greater $S_{275\text{-}295}$ values than the other lake sites (Figure 12 d, e and f). In contrast to the $S_{275\text{-}295}$ results, $S_{350\text{-}400}$ showed no significant response to

irradiation among the lake sites for the June 28th incubation period (Figure 12h; Table 5), while the July 15th showed a significant increase in values for LC and EC (Figure 12i; Table 5).

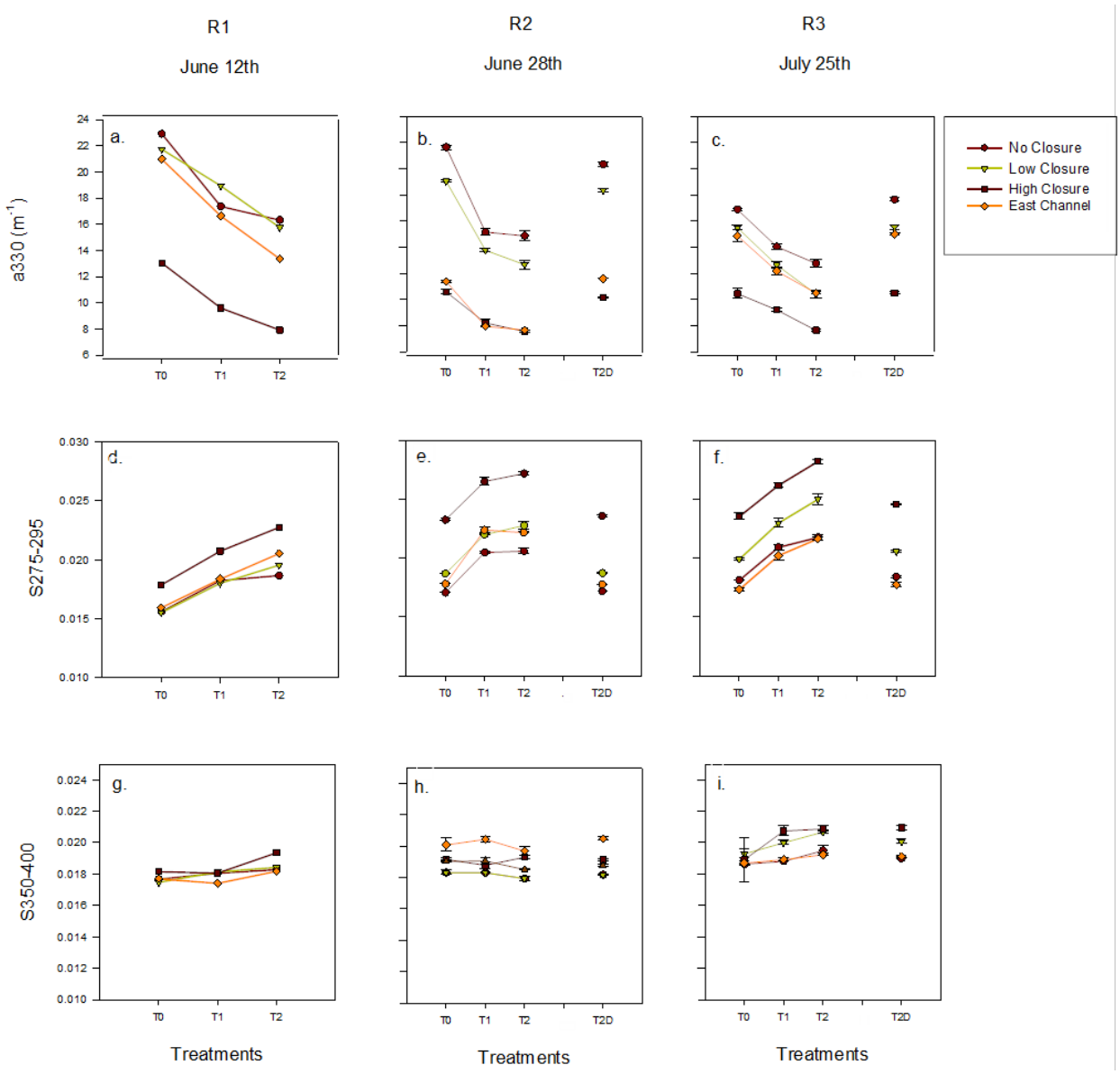

Figure 12 : Measurements of spectral absorbance of DOC within no closure (NC), low closure (LC) and high closure (HC) lakes, in comparison to the reference river channel (EC) site. Each experimental period is shown at the top of each column (R1- June 12, R2- June 26th and R3- July 15th). Seasonal changes over time can be seen left to right. Parametrics include a330 (a, b, and c), $S_{275-295}$ (d, e, and f) and $S_{350-400}$ (g, h, and i). T0 control samples are plotted against treatments for three days UV exposure (T1) and 6 days UV exposure (T2). Dark samples, represented as "T2D" were double wrapped in a black plastic material for a period of six days, hence equal to the time duration of the exposed T2 samples. It is important to note that there are cases where the individual averaged values for lake sites overlap each other. Error bars represent 95% confidence intervals.

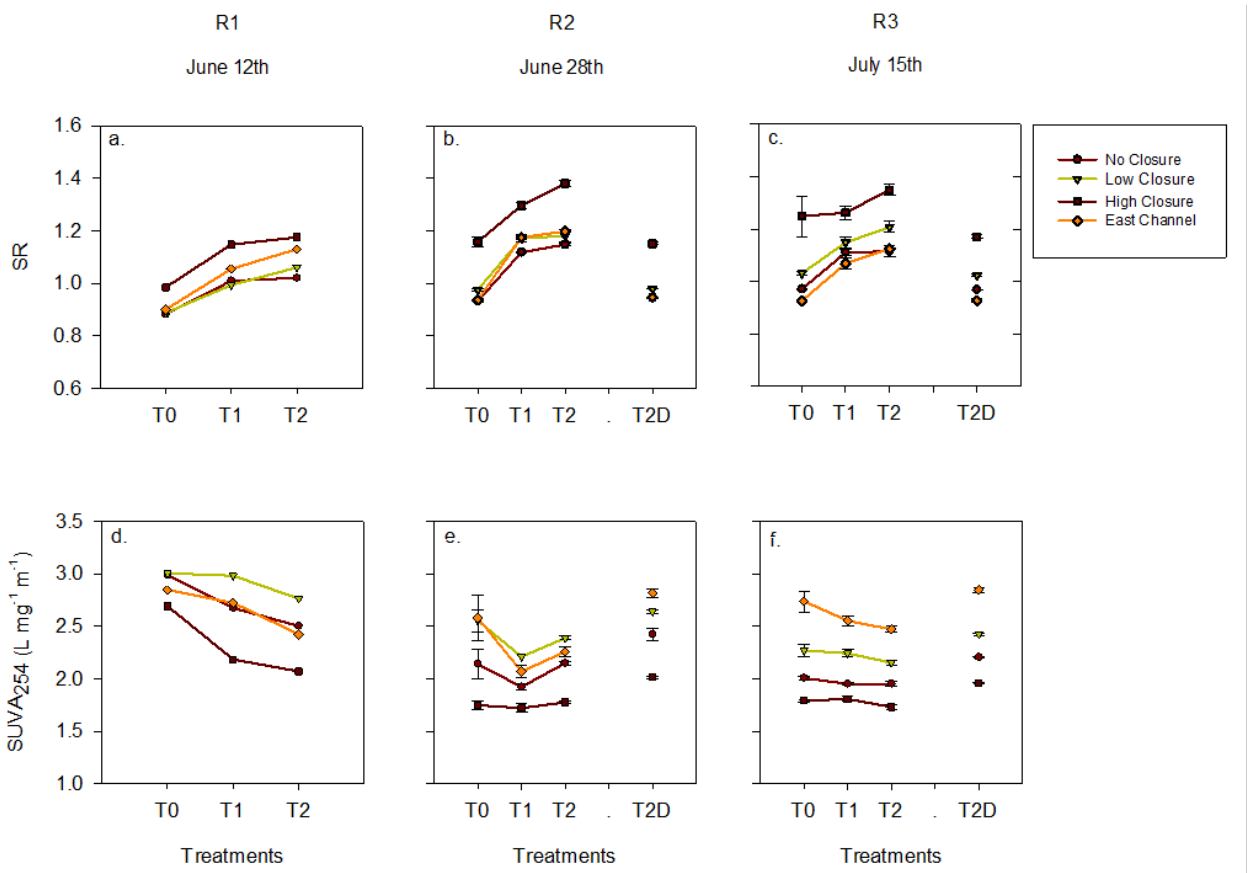

Figure 13 : Measurements of spectral absorbance of DOC within no closure (NC), low closure (LC) and high closure (HC) lakes in comparison to the reference river channel (EC) site. Each experimental period is shown at the top of each column (R1- June 12, R2- June 26th and R3- July 15th). Seasonal changes over time can be seen left to right. Parameters for absorbance shown here are S_R (a, b and c) and $SUVA_{254}$ (d, e and f). Error bars represent 95% confidence intervals.

Table 5 : Spectral absorbance contrasts for lake sites showing *F* critical and significant outcomes where p < 0.05 . Comparisons were conducted using a Tukey post hoc analysis test. Significant differences between treatments are indicated by different alphabetical letters. Non -significant results are denoted with an asterisk.

	R2 Jun 28						R3 Jul 15					
	F	P	Contrasts				F	P	Contrasts			
a330 (m^{-1})			**T0**	**T1**	**T2**	**T2D**			**T0**	**T1**	**T2**	**T2D**
NC	154.60	0.00	A	B	B	C	113.98	0.00	A	B	C	A
LC	224.33	0.00	A	B	C	A	93.04	0.00	A	B	C	A
HC	71.80	0.00	A	B	B	A	67.42	0.00	A	B	C	A
EC	3748.37	0.00	A	B	C	D	90.03	0.00	A	B	C	A
Shortwave (275-295)												
NC	186.34	0.00	A	B	B	A	87.78	0.00	A	B	B	A
LC	147.81	0.00	A	B	B	A	47.89	0.00	A	B	C	A
HC	111.51	0.00	A	B	B	A	115.57	0.00	A	B	C	D
EC	338.65	0.00	A	B	B	A	56.81	0.00	A	B	C	A
Longwave (350-400)												
NC	3.28	0.89	*	*	*	*	4.18	0.05	A	AB	B	AB
LC	2.22	0.17	*	*	*	*	13.63	0.00	A	B	B	B
HC	2.66	0.13	*	*	*	*	2.92	0.11	*	*	*	*
EC	4.00	0.06	*	*	*	*	6.04	0.02	A	AB	B	B
Slope (S_R)												
NC	753.08	0.00	A	B	C	A	38.49	0.00	A	B	B	A
LC	60.53	0.00	A	B	B	A	30.05	0.00	A	B	B	A
HC	96.07	0.00	A	B	C	A	5.85	0.03	AB	AB	B	A
EC	527.42	0.00	A	B	B	A	64.72	0.00	A	B	B	A
$SUVA_{254}$												
NC	12.73	0.00	AB	A	AB	B	81.53	0.00	A	A	A	B
LC	5.02	0.04	A	A	A	A	13.9	0.00	A	A	A	B
HC	29.80	0.00	A	A	A	B	32.91	0.00	A	A	A	B
EC	2.71	0.13	*	*	*	*	14.09	0.00	AB	BC	C	A

5.3.2.3 Slope Ratio

Contrary to results calculated for the river sites, all lake sites showed significant increases in S_R with increasing irradiance (Table 5, see also Table 4 for comparison). The June 28th sampling period showed initial ratios that were higher than the June 12th sampling period. This increase in S_R suggests clearer waters as the summer progressed, with lower molecular weight DOC (higher S_R values) that was especially notable for HC (Figure 13a, b and c). Initial S_R values during the July 15th incubation period showed little change from the previous June 28th incubation period, however all sites showed a significant response to irradiation (Table 5). In addition, statistical comparisons between T0 and T2D samples showed no difference existed between initial control values and dark samples (Figure 13b and c and Table 5).

5.3.2.4 $SUVA_{254}$

$SUVA_{254}$ showed significant variation as a result of incubation, with the exception of EC in the June 28th sampling period (Table 5). During the June 28th sampling period, humic content decreased (decreasing $SUVA_{254}$) following three days exposure (T1) and then increased slightly post six days exposure (T2) (Figure 13e). In addition, dark samples did not reflect initial T0 values (Figure 13e). During the July 15th sampling period, the humic content appears to decrease slightly however, once again dark (T2D) samples are marginally increased over T0 values (Figure 13f).

6.0 Discussion

The composition and structure of terrestrially derived DOC within the Mackenzie Delta is modified as a result of photochemical and biological degradation processes that occur within river channels and lakes of this deltaic region. The results of our study suggest the degradation pathway for DOC is strongly influenced by the seasonal variation in DOC composition that occurs as a result of changing hydrological processes, including peak water flow during the annual spring flood event, and the gradual return to base flow during the lengthy summer recession period. In addition, lakes within the delta support different degradation processes that modify the structure of DOC based on their flood regimes and connectivity to nearby river channels.

In this study, continuous 24-hour daylight, gradually increasing UV, and warming surface temperatures during the spring season provides the potential for rapid degradation of DOC, concurrent with peak seasonal discharge within river channels following the spring freshet. This is particularly true for lake sites, where riverine sediments entrained within the turbid river flow, fall out of suspension when they are channeled into the reduced flow of the lake environments. Ultimately, these clearer lake waters permit a greater amount of UV exposure acting on DOC and an increased depth of penetration for UV degradation processes (Gareis *et al.* 2010).

Looking towards the future, enhanced warming due to climate change and decreasing stratospheric ozone may increase the intensity of solar radiation that is available to be absorbed by terrestrial organic carbon (Erickson III *et al.* 2015). In addition, permafrost thaw may alter the concentration and lability of DOC within freshwater environments (Emmerton *et*

al. 2007; Vonk *et al.* 2013; Lesack *et al.* 2014). Changes to the hydrological cycle due to earlier ice break up and declining water level peaks (Lesack & Marsh 2007) and the increasing volume of riverine discharge (Peterson *et al.* 2002) may result in changes to degradation rates that support the ecological stability of the Mackenzie Delta. A few of these changes include, a larger amount of sediment transported by river channels due to melting permafrost and soil erosion (Vonk *et al.* 2013; Lesack *et al.* 2014), and shorter water resident times of DOC in freshwater environments (Catalan *et al.* 2015). In addition, positive feedbacks may exist including, increased bacterial productivity which would lead to a greater amount of CO_2 to the atmosphere as a by-product of bacterial respiration. In addition to bacterial degradation of DOC, direct photo-mineralization of DOC via stimulation of chromophores by UV also produces CO_2 to the overlying atmosphere as a by-product of photolysis.

This work suggests that one potential mechanism for the amount of carbon lost between the upper deltaic river channels and the nearshore coastal environments (Alling et al 2010), is through decomposition processes within the lakes of the Mackenzie Delta where DOC is temporarily stored before it flows back into the river during the lengthy summer recession period. In the following sections, specific results for biological and photodegradation of DOC in river and lake sites are discussed in detail.

6.1 Rivers

6.1.1 Seasonal Variation in the Lability of DOC

During the Arctic spring freshet, surface runoff of organic carbon from catchment soils is leached and transported to nearby river channels producing an organic rich environment with high riverine discharge (Lesack *et al.* 1998; Emmerton *et al.* 2007; Tank et al, 2011; Lesack *et al.*

2014). The resultant sediment load within the Mackenzie River also creates a photo-protective barrier that restricts UV from penetrating the water column *in situ*. In our study we examined the degradation potential for DOC when it is subject to a sediment poor environment. Our filtered results showed that DOC loss due to PCD and PE-BDOC was greater during the spring (June 9th) relative to the summer period (July 23rd). This higher decomposition occurs at the same time as newly derived terrestrial organic carbon is mobilized into the riverine environment as highly aromatic DOC (Figure 7).

Our first collection of river water samples was undertaken shortly following the spring freshet (June 9th) when DOC was highly aromatic and protected by the sediment load from UV exposure within the rivers, while the late summer collection (July 23rd) occurred once DOC had been continuously exposed to 24 hour daylight as the river waters gradually declined post freshet, and became more dilute within the river channel. Thus the DOC within our July 23rd sample waters was likely significantly photo-bleached prior to our incubation treatments. Further, some of the post freshet DOC originates from deeper soil layers that have thawed during the warm summer period and are less aromatic as compared to the earlier spring DOC from soil surface horizons (Vonk *et al.* 2013).

The chromophoric (humic) fraction of DOC absorbs incoming UV radiation that contributes to the PCD- enabled degradation of DOC through photolysis and mineralization of DOC (see next section 6.1.2; percent loss photo-chemical degradation of DOC). At the same time, photo-products including carbonyls, amino acids and sugars are produced via PCD (Bauer & Bianchi 2011). Within our PE-BDOC samples, photo-products were available for uptake over the 28 day

bacterial incubation period. Our results showed the percent loss for PE-BDOC was greater than our non-irradiated BDOC control samples in both incubation periods (June 9th and July 23rd; Figure 7). In addition, most sample sites (MI, PC, MC and EC) showed significantly lower DOC loss as BDOC, when compared to PCD and PE-BDOC during the June 9th incubation period (Figure 7; Table 3). However, the PC site in particular showed a greater loss from BDOC than the Mackenzie influenced sites. We suggest this may be due to the source and composition of DOC from the Peel sub basin relative to that of the larger Mackenzie catchment (see section 6.1.5 Mackenzie and Peel influenced river waters).

During the July 23rd incubation BDOC again showed significantly lower percent loss for the MI and EC, while comparatively, both of the Peel influenced sites (PI and PC) showed a larger percent loss (Figure 7; Table 3). Later in the summer, riverine discharge is considerably reduced along with the contribution of sedimentary material during the recession period as waters from the delta drain towards the coastal environment (Emmerton *et al.*2008; Beltaos *et al.* 2012). In addition, DOC aromaticity is similarly reduced through photo-bleaching of the humic component of the molecule, as a result of continuous UV exposure near the river surface. Thus the seasonal variability of DOC percent loss occurring within our riverine incubations likely reflect the aromatic content (the amount/concentration of humic material within DOC) as it is modified by UV processes throughout the open water season.

6.1.2 Spectral Characteristics of Riverine DOC

Our results showed photo-bleaching occurred rapidly following three days of UV exposure (T1) for all river sites in both incubation periods (June 9th and July 23rd). There was a marked decrease in the absorptivity of UV light at 330 nm (a_{330}), particularly during the June incubation

period (Figure 10a). During the July incubation period this same pattern emerged albeit to a much reduced extent, with a gradual decline in absorptivity over the six day incubation period (Figure 10b). This seasonal difference suggests newly released DOC following the spring freshet had greater aromaticity relative to the sample waters obtained for the July incubation. Chromophores within DOC are highly photo-reactive and degrade over time with continued exposure to UV light which ultimately results in reduced absorbance referred as "photo-bleaching" (Bricaud *et al.* 2012; Gonsior et al 2013). Following the spring freshet run-off regime, and the turn-around to a summer flow regime in mid- July (Emmerton *et al.* 2008), continuous UV exposure would likely cause a reduction in DOC aromaticity and thus a lower affinity for absorption of light at 330nm. In addition, river waters collected for the July sampling period were more dilute with respect to the concentration of DOC and thus, showed a lowered total humic content relative to the spring incubation (June 9th). Finally, as mentioned previously in Section 6.1.1; differences in the source of DOC (deeper soil layers) may also result in reduced aromaticity.

Assessing the a_{330} results in concert with the slope ratio (S_R) data suggests that DOC molecular weight and the humic fraction within the DOC molecule was much higher in the June incubation relative to the July incubation, particularly for the MI (Figures 10g and h). Further, initial $SUVA_{254}$ values decreased rapidly during the June incubation following three days' exposure to UV while the July incubation showed a much smaller change over the same period of exposure (Figure 11a and b). Weishaar *et al.* (2003) showed that higher $SUVA_{254}$ is indicative of more aromatic dissolved organic matter, while Tank *et al.* (2009) found these values tend to be highest following the spring freshet within the Mackenzie Delta.

6.1.3 **Photo- exposed Biological Degradation of Riverine DOC (PE-BDOC)**

As previously stated, DOC loss via BDOC, in the absence of irradiation, was consistently low in river water samples. However, PE-BDOC incubations often showed degradation rates that were significantly greater than those for BDOC alone, particularly during the June sampling period (Figure 7). Through the process of PCD, the absorption of UV photons by chromophores within DOC modifies the DOC molecule producing lower molecular weight photoproducts including carbonyls, sugars and amino acids. Heterotrophic bacteria can transport these lower molecular weight photoproducts across their cell membranes for growth and metabolism (Battin *et al.* 2008). Previous studies (Strome & Miller 1978; Bauer & Bianchi 2011) suggest that PE-BDOC may augment the mineralization of organic carbon to CO_2 while others (Moran *et al.* 2000) suggest that DOC photo-bleaching can promote bacterial uptake by 6-12%, when compared to non-irradiated DOC. Miller & Zepp (1995) found that bio-reactivity (BDOC) increased with irradiation in freshwater systems that were largely composed of terrestrially derived DOC, and a contrasting decreasing effect on bio-reactivity was found for plankton derived DOC through UV exposure . However, the precise mechanism for these effects remained unclear.

It is possible that BDOC rates within the Mackenzie River Delta are much lower in relation to other major circumpolar river deltas because groundwater inputs are higher in the Mackenzie and a contributing factor to DOC mobilization in this system (Walvoord & Striegl 2007). Vonk *et al.* (2015) found that permafrost extent had an effect on BDOC processing. Rivers in the zone of continuous permafrost (Kolyma River) have shallower hydrological flowpaths that impede water flow and contributes to the degradation of organic carbon. DOC sources of the Kolyma River originate in shallow soil depth and surface litter which result in increased BDOC in surface

waters (Vonk *et al.* 2015). Permafrost DOC tends to be well preserved in frozen soils and is rapidly degraded once it is leached into the aquatic environment during thaw conditions (Wickland *et al.* 2012; Abbott *et al.* 2014; Spencer *et al.* 2015; Vonk *et al.* 2015). Furthermore, rates for BDOC in Arctic Rivers tend to be much reduced in late summer when compared to the early summer/late spring. Arctic river waters are colder in the spring which restricts the bio-mineralization of organic carbon within soils (Striegl *et al.* 2005; Spencer *et al.* 2015). Thus, the chemical nature, or source of riverine DOC is critical to DOC degradation via BDOC.

In this study, the Mackenzie Delta is a region underlain by continuous permafrost and the results showed that riverine BDOC was limited throughout the study period (Figure 7; Table 3a). An exception exists for the PC which was somewhat greater than the other river sites during the June 9th incubation period and decreased substantially during the July 23rd incubation period (Figure 7; Table 3a) In addition, during the July 23rd incubation period, there appears to be a significant increase in BDOC for the PI (Figure 7; Table 3a).

Following the spring freshet, the amount of sedimentary material flowing through the Mackenzie River is high relative to later in the summer (Marsh & Lesack 2007; Holmes *et al.* 2008; Lesack *et al.* 2014). Our results showed BDOC was less than 5% for percent loss DOC while PE-BDOC showed a percent loss between a low of ~ 8 % for EC and a high of > 20% for the PC during the June 9th incubation (Figure 7). During the late summer incubation, BDOC remained near 5% and PE-BDOC showed a reduced loss (7-12%) when compared to the previous incubation, for all of the riverine sample locations (Figure 7). Other studies have demonstrated that DOC loss via BDOC within Arctic river waters varies seasonally from a high of

40 % following the spring freshet to a low of 10 % during the summer flow regime (Holmes *et al.* 2008; Mann *et al.* 2012).

In general, it is understood that BDOC and PCD act on distinct substrates within DOC (Obernosterer & Benner 2004). However, previous studies suggest it is possible that a competition may exist between the direct photochemical oxidation of photo-products to CO_2 and bacterial uptake of these same low molecular weight photo-products for growth and subsequent respiration to inorganic carbon (*e.g.* CO_2). Obernosterer & Benner (2004) conducted two related experiments to determine the potential for fractions of DOC that were simultaneously bio-reactive and photo-reactive. A sequential experiment was conducted where DOC was subject to artificial UV light while measurements for absorbance (a_{330}) were calculated at regular intervals. Following irradiation, these samples were inoculated with bacteria from the same aquatic environment and incubated for a period of 240 days and DOC loss was recorded over time.

The second related experiment used an alternating approach to PCD and BDOC by first inoculating the sample waters with bacteria from the respective sites, followed by an incubation period that ended when DOC concentration appeared to stabilize (near 240 days). These samples were then filtered and exposed to UV for a period of six days. Following irradiation, the sample waters were re-inoculated with bacteria and kept in the dark for a period of 99 days. The results of this experiment, and the experiment discussed above, indicate that 15% of DOC is susceptible to both PCD and BDOC and that each of these degradation processes compete for the same substrates.

Obernosterer & Benner (2004) suggest that the chemical composition of DOC and the intensity and duration of exposure to UV may influence the outcome of the competition for substrates. In addition, the study found near 50% of terrestrially derived DOC that was biodegradable, is also susceptible to PCD, but only 30% of DOC that may be potentially photodegraded was also biodegradable. Thus, through the process of photo-mineralization of DOC, a fraction of bio-labile constituent carbon within the DOC molecule may be removed, thus limiting its availability to microbial communities, and may restrict increases in bacterial decomposition following irradiation.

The results of our study suggest it is possible that the higher percent loss for PE-BDOC in both incubation periods relative to PCD and BDOC may be based on competitive processes between PCD and BDOC where the biolabile component of DOC may be removed through UV exposure (Obernosterer & Benner 2004). However, it is also possible that a portion of the bio-labile fraction of DOC is enabled by UV exposure (Figure 7) which may result in increased bacterial production or respiration (Strome & Miller 1978; Obernosterer & Benner 2004; Bauer & Bianchi 2011). The results for DOC loss indicate that the average combined DOC losses for BDOC+ PCD are greater than PE-BDOC for the MI, MC, PI and PC during the June 9th incubation period and for the MI, MC, EC, PI and PC during the July 23rd incubation which suggests that there is evidence for competition and that biodegradable DOC may be enabled by UV exposure (Figure 7). Overall, the outcome of the competition between degradation processes may be dependent on the intensity and duration of UV exposure (Obernosterer & Benner 2004; Reader & Miller 2014) and whether the DOC is sourced from terrestrial or plankton materials (Obernosterer & Benner 2004). In our study PE-BDOC showed a greater DOC loss during the spring incubation

(June 9th) as compared to the late summer incubation (July 23rd) when the summer riverine flow regime (Emmerton *et al.* 2007) had returned, and DOC within the system was likely to be more photodegraded. Increased exposure to UV radiation in the lakes draining into the river channels may have reduced the biological and photo-reactivity of DOC. In addition, the sources of DOC remaining in the system may be from deeper soil layers including thawing permafrost which had been previously processed by microbes before being leached into the surrounding river surface waters (Vonk *et al.* 2015).

6.1.4 Comparisons between the Mackenzie and Peel influenced River Waters

There appears to be a greater percent loss of DOC via BDOC within the PC during the June incubation and for both the PI and PC during the July incubation, relative to the Mackenzie influenced waters (Figure 7). In addition, both incubation periods showed a greater percent loss of PE-BDOC for the Peel influenced waters when compared to the Mackenzie influenced waters for each of the incubation periods (June and July; Figure 7). UV and temperature data during the July incubation for the Peel influenced waters (Figure 3) and the Mackenzie influenced waters (Figure 4) showed similar diurnal fluctuations. However, the average cumulative UV was consistently higher for the Peel influenced waters relative to the Mackenzie influenced waters (see results, UV and temperature) particularly over the three day (T1) solar incubation. It is possible this small difference (13%) in cumulative UV for the Peel influenced waters may account for the greater PE-BDOC within the PI and the PC during the July incubation.

Differences in BDOC between the Peel and the Mackenzie influenced waters may be related to other potential variables including local climate, hydrological regimes and the composition of soil and vegetation within the Peel sub basin. As a result, the origin and chemical composition

of DOC may contribute to large differences for both PCD and BDOC (Moran & Zepp 1997; Mopper & Kieber 2003). We suggest that DOC within the Peel sub basin may be chemically and compositionally distinct from the DOC of the larger Mackenzie basin, and thus present unique characteristics for the bio- and photo-lability of DOC when compared to the Mackenzie influenced river sites.

6.2 Lakes

6.2.1 River to Lake Connectivity

During the annual spring break up event, NC and LC lakes within the Delta are recharged with river waters from the spring freshet while HC lakes may only receive river waters when the flood water levels are unusually high. For the past few decades (since 1964), peak flood water levels within the Mackenzie Delta have declined (Lesack & Marsh 2007), while riverine discharge has remained at a near constant volume during the spring break up period (Lesack *et al.* 2014). As discussed previously in section 3.3, NC lakes are in near constant connection with deltaic river channels during the open water season (average > 120 days; Lesack & Marsh 2007) while LC lakes are connected to the river channels during the spring freshet, but not necessarily throughout the full summer season (average 17-120 days; Lesack & Marsh 2007). Finally, HC lakes may go several years between spring recharge events (Lesack & Marsh 2007). These differences in river- to- lake connection types provide a basis for understanding the lake's biogeochemical characteristics and thus the potential effect of degradation processes for DOC.

An endmember analogy with lakes that vary across a habitat continuum was suggested by Lesack & Marsh (2010) as an argument against the potential for "alternative states" within shallow lakes (Bayley & Prather 2003). The alternative states postulate suggests that lakes

within the delta could be construed as having two possible states; a “stable state” when lakes are recharged by their connection to the river during the open water season, and a “quasi-stable state” when they are not. Instead, Lesack & Marsh (2010) suggest a “habitat variability continuum” for large river floodplain lakes such as those of the Mackenzie Delta.

Lesack & Marsh (2010) proposed an analogy for the diversity of lake types within the Mackenzie Delta on the basis of connection times to the river and the biogeochemical state of the associated delta lakes. Lakes that are rarely flooded during the spring period and have short connection times to the river channels produce a subset set of lakes that are highly distinct from one another, as exemplified by the Mackenzie Delta’s HC lakes. Lesack and Marsh (2010) refer to this subset of lakes as a snowflake class endpoint. The second endpoint represents lakes that receive near continuous (NC lakes), or variable (LC lakes) river-to-lake connection times and/or, multiple recharges through the open water season. These lakes are classified as a cookie endpoint. This increased lake- to- river connection causes these lakes to be more similar to each other with respect to their biogeochemical composition and thus, a “cookie-like” in relative composition. This analogy is a more precise descriptor for the Mackenzie Delta lakes rather than the “alternative states” that allow for only two possible states within shallow lakes.

6.2.2 Potential Sources for Within-Lake DOC

DOC within lakes of the Mackenzie Delta is chemically complex and can be derived from several sources (Tank *et al.* 2009; Gareis *et al.* 2010). Unlike riverine DOC which is largely terrestrially derived via surface runoff, within- lake DOC in the Mackenzie system can also be derived via thermokarst activity beneath, and active layer deepening at the margins of HC lakes (Tank *et al.* 2009; Cory *et al.* 2012) and through the exudates of aquatic plants, which are abundant in many

lakes in this system (Tank *et al.* 2009). Aquatic plant derived DOC is non-chromophoric (less aromatic), which may result in macrophyte-rich lakes (typically HC and LC lakes) with greater water clarity at a given level of DOC, as opposed to lakes that receive a more continuous flow of terrestrially derived DOC- rich waters from the river channels (typically NC lakes). Although LC lakes are connected to the river channel for part of the summer, the variability of the DOC source and thus, biogeochemical signature within the lake may change from year to year based on flood- water levels and connection time to the river channel (Lesack & Marsh 2010).

Throughout the study period, the waters within the HC study lake remained clear despite an increase in the concentration of DOC from an initial concentration (T0) of 7.8 mg C L^{-1} for the June 15th incubation (Figure 8) to an initial (T0) concentration of 12.7 mg C L^{-1} for the July 5th incubation. DOC then remained high at an initial (T0) concentration of 12.0 mg C L^{-1} for the July 23rd incubation period, which suggests the presence of non-chromophoric DOC with a lower UV absorbance potential (Tank *et al.* 2009). Our HC lake did not flood during the 2013 spring freshet and is undergoing thermokarst activity which suggests thermokarst and permafrost derived DOC may also contribute as DOC sources within this lake as they tend to be less aromatic than terrestrially derived riverine DOC.

An additional potential source of DOC within Delta lakes is DOC that was transported to lake waters through previous years' flooding regimes. Lesack & Marsh (2010) refer to this difference in the timing since delivery of flood waters, and the biogeochemical effects that these residual waters from previous years may have on the current year's lake-water biogeochemistry, as "legacy effects".

Although NC lakes are generally fully flushed each year, LC and HC lakes may contain residual waters from previous years' flooding events. Thus, lakes within the Mackenzie Delta have many potential sources of DOC including contributions of terrestrially derived DOC via the Mackenzie River catchment, within-lake DOC that is derived from macrophytes or thermokarst activity, and previously exposed DOC that continues to exist in lakes that do not fully flush each year, as a result of legacy effects.

6.2.3 Percent Loss of DOC across Lakes of Varying Sill Elevations

6.2.3.1 No closure lakes

NC lakes exchange water flow continually throughout the open water season with the river channels. This continuous exchange of flow allows the NC lake to receive continual pulses of riverine DOC through its connection to the EC. Although our NC study lake receives DOC from the larger Mackenzie catchment, within- lake DOC (algal and macrophyte derived DOC) and terrestrially derived DOC from the lake's immediate catchment also contributes to the overall DOC within the NC lake (Tank *et al.* 2009).

During the June incubation period, it is likely that the large BDOC percent loss is related to the larger source of aromatic riverine DOC within the lake, relative to the DOC source from within the lake's immediate catchment. Our late summer incubation (July 15th) showed a much lower BDOC percent loss as compared to the June 28th incubation period which may be a result of reduced aromaticity within DOC and other changes in the composition of DOC (Figure 9). In addition to BDOC percent loss, our results show that PE-BDOC remained high for the early (June 28th) and late summer (July 15th) incubation periods (Figure 9). High molecular weight DOC during the early summer tends towards greater UV absorbency which may promote the lability

of DOC to bacterial communities (Bauer & Bianchi 2011) while competitive processes for DOC degradation (discussed previously in Section 6.1.4) together with sustained UV exposure (Obernosterer & Benner 2004; Reader & Miller 2014) may enable greater PE-BDOC percent loss during the July incubation period.

6.2.3.2 Low closure lakes

LC lakes act similarly to NC lakes with respect to BDOC percent loss, however there is the exception that there is no continuous exchange of river waters from the EC throughout the summer period. LC lakes may not completely flush during the spring recharge period and may include "legacy effects" from previous years' flooding regimes (Lesack & Marsh 2010) that affect the overall biogeochemical signature of these lake waters and thus, the photochemical and biological degradability of DOC.

Newly delivered DOC from the present year which is of higher molecular weight and UV absorbency is more likely to be rapidly degraded via PCD while lower molecular weight photoproducts may quickly be made available to the bacterial community (Bauer & Bianchi 2011). These degradation processes occur coincident with the ongoing loss of DOC from previous years that may be of lower quality (reduced photo-absorbency and lower molecular weight).

The timing of the riverine inflow of DOC to the LC lake may play a role in the higher loss of DOC through BDOC when compared to PCD (Figure 9). Riverine DOC that remained from the previous year may be more degraded versus that of the current year's newly released riverine DOC. Potentially, the DOC with a longer residence time within the lake would be more easily

taken up and mineralized by bacterial communities due to its long term exposure to UV, and lower molecular weight. Therefore, LC lakes may present as a carbon source to the overlying atmosphere via bacterial respiration of CO_2 during the spring/ early summer.

As the lakes drain the overflow waters back into the river channel the lake eventually becomes cut off from the main river channel. Organic rich waters transition to more clear waters as the humic portion of DOC is mineralized by UV and photo products including carbonyls are consumed by bacteria while submerged aquatic plants develop through the increased availability of solar radiation into the water column. Lake waters in LC lakes were appreciably clearer by late summer (July 25th incubation period).

Previous work by Tank *et al.* (2011) discussed the loss of sediment from the water column within the lakes that are cut off from the river channel for at least part of the summer, which increases the depth of UV penetration as water clarity increases. In addition, DOC generated via macrophytes root exudates, and the degradation of senesced aquatic plants contribute non-chromophoric DOC to lakes (Tank *et al.* 2009; Gareis *et al.* 2010), and may be partially responsible for the relative clarity of this class of lake in late summer as opposed to the connected NC lakes, where the waters continuously exchange flow with the river channel throughout the open water season. We suggest there may be a temporal change in the source of lake DOC between early spring and late summer. During the early spring/summer riverine sourced high molecular weight (HMW) terrestrially derived DOC may be the major constituent for degradation processes, particularly for NC and LC lakes that receive annual inputs of DOC from the larger catchment of the Mackenzie River. Conversely, within-lake contributions, and

riverine sourced DOC with reduced aromaticity (Tank *et al.* 2011) together with greater UV penetration as photosynthetically active radiation (PAR) into the water column of lakes, are more critical variables during the late summer period (Gareis *et al.* 2010).

In the spring and early summer when the LC lake is connected to the river channel and run off from the surrounding landmass is delivered to the lake, terrestrially derived DOC is of high molecular weight (HMW) promoting a higher absorption rate of UV, as the chromophores are highly photo–reactive and eventually the humic material within the DOC molecule becomes photo-bleached. The overall process of PCD leads to two results, 1) LMW photoproducts are available for BDOC and, 2) increased PAR through the water column promotes photosynthesis in developing submerged aquatic plants. By late summer (July 15th), the lake waters are remarkably clear and PE-BDOC is substantial for the NC and LC lakes (Figure 9). Surface bacterial biomass could potentially reap the benefits of increased water temperature, UV penetration and availability of photo-products. Taking all this into consideration, it is possible the seasonal source for DOC may change from terrestrially derived to macrophyte derived DOC within LC lakes (Tank *et al.* 2009).

6.2.3.3 High closure lakes

The results for percent loss DOC in the HC lake were considerably different than the NC and LC lakes, particularly in regards to the seasonal variation of potential pathways for percent loss DOC between the incubation periods. In the early spring, the concentration of DOC was substantially lower in the HC lake than in either of the NC or LC lakes (Figure 8). Apart from river water contributions from previous flooding regimes, water renewal contributions to HC lakes occur as localized run off from the surrounding landscape, ice melt and precipitation in the

form of rainfall during the summer (Lesack & Marsh 2007; Tank *et al.* 2009; Gareis *et al.* 2010). In addition, HC lakes are infrequently flooded and some may show signs of thermokarst activity (Marsh & Lesack 2007; Gareis *et al.* 2010). As permafrost thaws along the riparian edges of these lakes it causes slumping of the lake margins and the surrounding vegetation may include "drunken" trees whose roots are destabilized by permafrost thaw/meltwater intrusion (Vonk *et al.* 2015). Thermokarst features generally form on lake shores and may persist for several years (Abbott *et al.* 2014) and can result in an increase in lake area and potentially alter the internal processing of DOC within these HC lakes (Cory & Kaplan 2012; McGuire *et al.* 2015).

Following the summer solstice (June 28th) the active thermokarst HC lake in our study showed significant BDOC, over and above either the PCD or PE-BDOC (Figure 9). It is possible that this high BDOC is related to legacy effects from previous flood regimes where there is a large constituent of previously exposed DOC. Previous studies found that as much as 60% of the waters in HC lakes may be legacy waters (Lesack & Marsh 2010; Tank *et al.* 2011). In addition to legacy effects and within-lake DOC, a portion of the total terrigenous DOC within HC lakes may include DOC released from thawing permafrost. The age and thus, aromaticity of permafrost derived DOC may be a considerable factor for degradation pathways and percent loss of DOC.

Depending on the aromaticity and age (the amount of time since burial) of the newly released permafrost DOC in the HC lake, it may explain why percent loss BDOC is much greater following the summer solstice when surface temperatures are increased and the active layers of permafrost soils surrounding the HC lake are seasonally thawed. Even if the age of the DOC is modern, it does not necessarily speak to the aromaticity of the DOC. Assuming the DOC is

modern in age then it is possible it may have been previously exposed prior to burial within permafrost soils. Hence the aromatic content may not reflect a higher molecular weight DOC.

Recent studies have suggested that the DOC within permafrost soils of the North Slope of Alaska has greater biodegradability than DOC derived through surface runoff (Abbott *et al.* 2014). The potential mechanisms include recalcitrant hydrophobic carbon species that are strongly absorbed within permafrost soils are released during permafrost thaw into the lake waters. This permafrost DOC may have a larger potential for biodegradability as bioavailable constituent compounds were previously filtered by the mineral soil. In addition to these potential mechanisms, Abbott *et al.* (2014) found when permafrost DOC was exposed to sunlight it resulted in a 40% increase in the microbial conversion of DOC to CO_2 which suggests that DOC released from permafrost is rapidly mineralized when exposed to sunlight (Cory *et al.* 2012).

6.2.4 Seasonal Variation of Spectral Absorbance within Different Classes of Lakes

6.2.4.1 Early spring June 12th incubation period

Immediately following the spring freshet, initial a_{330} values were high for NC, LC and the EC and steadily decreased over the six day incubation period (Figure 12a). Similarly, initial values for $S_{275\text{-}295}$ suggests that waters in these river- associated systems had high molecular weight DOC which decreased almost linearly with UV exposure during the incubation period. This is shown graphically as an increase in slope values over the six day incubation period (Figure 12 d).

It is likely that the highly aromatic DOC from the Mackenzie catchment post freshet influenced the absorbency of shorter wavelength UVB within the photo-reactive chromophores of DOC. Both the NC and LC lakes within our samples suggest newly released DOC would have both a

higher molecular weight and an increased affinity for UV absorption. In addition, $SUVA_{254}$ values remained relatively high during the post freshet incubation as compared to incubations later in the summer season (Figure 12e and f), which suggests sample waters for the NC and LC lakes retained a rather large humic fraction within the DOC molecule early in the season (Figure 12d). Conversely, the HC lake showed lower absorbance values relative to the NC and LC lakes which may be a result of lowered aromaticity of DOC within the HC lake (Figure 8). The reduced spectral absorbance may suggest a differential source of DOC within the HC lake including within- lake DOC from thermokarst or macrophyte sources (Tank *et al.* 2009; Gareis *et al.* 2010; Cory *et al.* 2012). The legacy effects common to HC lakes (Lesack & Marsh 2010) may also cause DOC in these systems to be much less aromatic.

6.2.4.2 Early Summer June 28th incubation period

Shortly following the summer solstice when incoming UV is most intense, the initial (T0) values for a_{330} remained high for the NC and LC lakes (Figure 12b). However, a_{330} for the EC fell in comparison to the June 9th values, as the pulse of earlier spring run- off contributions from the Mackenzie catchment subsided and became more dilute (Figure 12 a and b). Absorbance declined sharply for NC and LC lakes with radiation, particularly following the first three days of UV exposure, while the slope values for the shorter wavelengths ($S_{275\text{-}295}$) increased during the same period of exposure (Figure 12e). This inverse relationship of declining a_{330} and increasing $S_{275\text{-}295}$ suggests decreasing aromaticity and an associated lower molecular weight of the humic portion of DOC. Additionally, both of the NC and LC lakes showed similar initial (T0) $S_{275\text{-}295}$ values during the June 9th and June 28th incubations which suggests the molecular weight of DOC remained relatively high prior to the June 28th incubation treatment. Thus, the

composition of DOC from NC and LC lakes is chemically altered by UV exposure, due to photo-bleaching that potentially decreases the photo-reactivity of DOC.

Although DOC concentrations increased in the HC lake between the June 12th and June 28th sample period, initial (T0) absorbance values declined significantly, while $S_{275\text{-}295}$, and S_R parameters increased, and $SUVA_{254}$ declined. Taken together, these results suggest that the composition of DOC changed significantly in the HC lake, with a movement towards lower molecular weight, less aromatic carbon. Previous work by Gareis *et al.* (2010) also found that the concentration of DOC within this HC lake increased over the summer period. However, as in our results for this current study, the authors found that a_{330} values were lower in comparison to other lake types (NC and LC). Gareis *et al.* (2010) suggest that the lowered values may indicate a considerable amount of non-chromophoric or less aromatic DOC exists within this HC lake. Another consideration for the increase in DOC concentration within HC thermokarst lakes is through lake-water evaporation. Tank *et al.* (2011) found that DOC concentration was strongly linked to lake elevation rather than macrophyte biomass. This correlation was highest in thermokarst HC lakes that were isolated from the influence of river waters.

Similar to the a_{330} and slope ratios results discussed above, $SUVA_{254}$ values showed that initial DOC aromaticity for the NC and LC lakes was substantially greater and rapidly decreased following three days UV exposure as compared to the HC lake which slowed little variability over the six day incubation period (Figure 13e). The clearer waters of the HC lake suggest either a lower humic fraction of DOC remained and /or, the source of the DOC was from either

permafrost or macrophyte DOC which does not have a large humic fraction within the DOC molecule.

Finally, the slope ratio (S_R) results showed the molecular size of the DOC molecule decreased rapidly for the NC and LC lakes, especially over the first three day interval of UV exposure. This was followed by a much lower response in the latter three days as the molecular size of DOC stabilized to the new photo-chemically altered environment within the sample (Figure 13b). The S_R of the HC lake also showed a decrease in DOC molecular size however, it was a significantly less pronounced than either of the NC or LC lakes. In addition, the initial (T0) S_R value for the HC lake indicates the molecular size of the HC lake was already much smaller that the NC and LC lakes.

6.2.4.3 Late summer July 25th incubation period

Our results showed there was a marked decrease in the initial a_{330} values for the late-summer (July 25th) incubation period relative to the initial values for the June 28th incubation period (Figure 12b and c). This decrease suggests there was less photo-reactivity within the chromophores and the composition of DOC within delta lakes was likely altered through sustained UV exposure (Vähätalo & Wetzel 2008).

Spectral slope in the shorter UV wavelength ($S_{275-295}$) showed an almost linear decrease in the molecular weight of DOC throughout the six day incubation period for the NC and LC lakes classes and the EC (Figure 12f). This decrease in molecular weight suggests increasing photo-mineralization of DOC over time by converting organic carbon to lower molecular weight inorganic carbon (i.*e*. CO_2). The results for all three of the lake classes are largely similar to the

previous incubation on June 28th which showed a large decrease in DOC molecular weight (Figure 12e and f).

Finally, our $SUVA_{254}$ results showed initial (T0) values for aromaticity within the EC during the July 25th incubation had increased slightly from the previous June 28th incubation (Figure 13e and f). This may be a result of the timing of our sample water collection period later in the season which may have had a higher aromatic content via episodic precipitation that percolated through surrounding soils and was delivered to the river channel as DOC. The subsequent leaching of organic material into the EC may have produced a temporary pulse of organic rich DOC. However, following three days UV exposure, there is a clear decrease in DOC aromaticity (Figure 13f).

7.0 Conclusion

The seasonal lability of DOC within the Mackenzie Delta is strongly dependent on climatic and hydrological variables that promote biological and photochemical mineralization of organic carbon. During the spring freshet a thin layer of floodwaters together with 24 hour continuous daylight promotes the absorption of UV radiation via the photo-reactive chromophores within the DOC. During the annual spring freshet, newly released terrestrially derived DOC from the large Mackenzie catchment is transported by the Mackenzie River to delta lakes where it is temporarily stored until the primary water levels gradually recede during the open water season. Differences in the biogeochemistry of delta lakes are largely dependent on their connection times to the river channel. In addition, DOC within the lake waters may be more susceptible to degradation processes depending on the composition and aromaticity of the DOC source. Further, UV exposure of DOC may either increase BDOC as suggested for the riverine sample waters, particularly during the spring incubation period (June 9th; Figure 9), and into the early summer season in the lake waters (June 28th; Figure 7) or, strip the biolabile component of DOC through competitive processes between PCD and BDOC for the same substrate. Finally, during the late summer season, DOC within the river channels and lakes becomes increasingly photo-bleached which translates to losses in UV absorbance, aromaticity and molecular weight.

7.1 Carbon Loss within the Mackenzie Delta

Alling *et al.* (2010) examined differences in DOC loss within the discharge of the Lena River as it flows eastward across the Eastern Siberian Arctic Shelf (ESAS), and before it leaves the Arctic Ocean. At the Lena River mouth the DOC concentration was 500 µM and declined to 50-80µM

among two sampling sites along the ESAS, corresponding to an 84-90% DOC loss across the shelf region. The Lena River is the primary source for terrestrially derived DOC to the ESAS, while other potential sources of DOC along the shelf region are mainly due to coastal erosion (chromophoric), and to a lesser extent, via primary productivity (non-chromophoric). Alling *et al.* (2010) conclude that DOC loss in the near-shore Arctic Ocean may be substantial, and that this mineralized DOC is released to the overlying atmosphere as CO_2 via bacterial respiration and photo-mineralization within riverine discharge along the Arctic shelf regions.

The results of this study suggest that a partial loss of DOC may occur within the connected lakes of the Mackenzie Delta. The most intense DOC degradation appears to occur shortly following the spring freshet when 47% of the Mackenzie River flow is diverted off channel, and temporarily stored in the lakes of the Mackenzie Delta (Emmerton *et al.* 2007). The abundance of connected lakes within the mid- delta (31% of Delta lakes - Emmerton *et al.* 2007), 24 hour daylight and the gradual release of modified DOC from lake-waters that drain back into the river channels during the summer recession period may support the large difference in the measurement of carbon loss between the reaches of the upper delta and the lower deltaic environment.

Our study showed a marked difference in DOC loss for all the experimental treatments (BDOC, PCD and PE-BDOC), between the river inflow sites (MI, PI) and the outflow site (MO) (Figure 7) which suggests incoming DOC from the larger Mackenzie River catchment is highly aromatic and thus more susceptible to degradation. However, contrary to the findings of Alling *et al.* (2010) DOC decreases in aromaticity as it is transported out of the system towards the Delta

outflow, thus there is a greater potential for DOC degradation within the Mackenzie Delta versus waters that are leaving the deltaic system.

It is reasonable to conclude that temporary lake storage/processing of riverine DOC and within lake DOC represent compositionally distinct sources of DOC that are variably subject to uptake via BDOC and PCD. For example, in the case of BDOC, while our lake DOC may be susceptible to BDOC during the spring and early summer (Figures 8 and 9), our study shows there is minimal BDOC within the river channel waters for both incubation periods (Figure 7). Moreover, riverine DOC appears more susceptible to PE-BDOC within river channels (Figure 7). In either case, it appears that river channels and the associated Delta lakes create a source of CO_2 through photochemical processes and biological respiration, particularly following the spring freshet when DOC aromaticity is high, followed by a shift to a carbon sink along with the progression of the summer growth season. Clearly this dynamic flux in carbon within the delta lakes would need to be taken into account for the overall carbon measured between the upper deltaic environment, and before it discharges into the Arctic Ocean.

7.2 Lakes as Processing Centers of Riverine DOC

The challenge of this study was to reconcile how the mineralization of DOC via photochemical and biological degradation pathways within the river channels is associated with the loss of DOC within the delta lakes. We conducted two experiments, the first of which was to evaluate the potential for DOC loss by biological and photochemical degradation within river and lake waters, while in a related experiment we analyzed the results for the absorbance spectra of DOC to assess the quality (aromaticity) and lability of DOC with respect to UV exposure. Lakes

play an integral role in the processing of DOC within the Mackenzie Delta through the temporary storage of riverine floodwaters within the connected lakes.

Our study lakes showed significant percent loss of BDOC during the early summer which is not reflected within any of our river channel sites throughout the study period. Each class of lake (NC, LC and HC) has a different flood regime which contributes to the biogeochemical characteristics of the associated lakes. It appears reasonable that within- lake sources of DOC contribute to the mineralization of DOC during the critical spring period, although the mechanisms for degradation may not only be seasonally variable, but significantly variable between the different classes of lakes and may largely depend on the source and composition of within- lake DOC. In addition, legacy effects from previous flood regimes (Lesack & Marsh 2010) may influence the higher percent loss through BDOC, as previously exposed DOC would have a lower molecular weight and would promote the bacterial uptake and mineralization of DOC, particularly within our LC lake as the NC lakes are known to completely flush each year and are therefore not affected by legacy effects.

Our results for the late summer incubation period (July 15th) showed that PE-BDOC was the major pathway for degradation of DOC within the NC and LC lakes. It could be suggested that the increased residence time for DOC within the river channels contributed to a dilution effect via photo-bleaching, and as suggested by previous studies (Obernosterer & Benner 2004; Reader and Miller 2014), may be a result of a competition where biolabile components of the DOC molecule that were essentially hijacked/ selected in favor of photochemical processes.

Sustained UV exposure during the incubation treatment may have caused increased photo-mineralization of DOC which ultimately led to a higher percent loss for PE-BDOC.

Overall, the results of this study suggest that NC and LC lakes are processing centers for the degradation of riverine DOC, particularly during the spring and early summer. Aided by the continuous 24 hour daylight, a significant portion of DOC within lakes is degraded via bacterial and/or, photochemical processes (Figure 9). BDOC during the spring could be largely related to legacy effects from photo-primed and overwintered DOC from the previous year, while PE-BDOC may be an outcome of competitive processes for both photo and biolabile components of the newly released DOC. As lakes drain and the river channel returns to a summer flow regime near July 15th (Emmerton et al 2008) (Figure 2) there is a rapid decline in the quality of DOC available for PCD due to decreased aromaticity.

7.3 **Climate Change**

Increasing regional temperatures and decreasing precipitation as snow have large implications for the flooding regime and the cycling of carbon within river channels and lakes of the Mackenzie Delta. Lesack *et al.* (2014) suggest warmer springtime conditions and declining snowfall during the month of April may alter the timing of the spring ice break-up as a result of faster snow melt and reduced albedo due to declining snow on the river ice (Hicks *et al.* 2009). Earlier ice break up is occurring throughout the delta with declining spring peaks in water levels (Lesack *et al.* 2014) which affect river to lake connection times by reducing the off channel flow of the Mackenzie River to the associated lakes within the Delta. In addition, a related increase

in base flow water levels in the river channels of the Mackenzie Delta is largely a result of reduced ice extent near the coastal Beaufort Sea (Lesack & Marsh 2007; Lesack *et al.* 2014).

Although riverine discharge and the timing of the spring freshet have not changed within the Mackenzie Delta, other circumpolar river deltas (Déry *et al.* 2009) have shown an earlier arrival of the spring freshet and increased riverine discharge due to the intensification of the Arctic hydrological cycle and positive water- vapor feedbacks that are the direct result of global warming (ACIA 2005). The full extent of these changes, and others, including the potential loss of many HC lakes, partially due to declining flood water peaks, (Emmerton *et al.* 2007; Lesack *et al.* 2014) will likely lead to compounding effects within the Mackenzie Delta, and the associated coastal environment, remain unclear. However, it is likely they will impact the biodiversity (Lesack & Marsh 2007; Emmerton *et al.* 2007; Gareis *et al.* 2010), the range of habitats for wildlife within the inland lakes of the delta (Usher *et al.* 2005; IPCC 2007), and biological productivity on the nearshore environment of the Beaufort Sea (IPCC 2007).

Another potential issue related to the future warming of spring temperatures in polar regions is the decline in spring time stratospheric ozone that increases the intensity of shorter wavelength UVB reaching the earth surface and affects the biogeochemical cycling of carbon, among other elements (Bais *et al.* 2015; Erickson III *et al.* 2015; Hader *et al.* 2015). Potential impacts on the Mackenzie Delta may include enhanced mineralization of DOC as a result of changes to coupled UV influenced hydro-climatic conditions such as increased surface runoff and soil erosion (Erickson III *et al.* 2015), intensified photo-bleaching of DOC through UV exposure which would allow greater penetration of UV into the water column, exposing

organisms to harmful UVB (Hader *et al.* 2015). Finally, changes to the timing and duration of snow and ice cover may create a shift in the community structure of photosynthetic organisms and heterotrophic bacteria due to increasing PAR and UVB respectively (Clark *et al.* 2013).

We have only discussed a few of the many rapid changes occurring in the Mackenzie Delta, which may impact the lability of DOC together with the contributing effects on the larger carbon cycle. Complex interactions and feedback mechanisms between and among carbon reservoirs make deltaic environments a challenging, yet critical area for continued research. Although this study examined potential differences in riverine DOC contribution between the Mackenzie-influenced river channels and the Peel-influenced sub basin of the Mackenzie River, future studies should consider a more detailed assessment of the contributions of DOC from each of these systems. Another potential area for research may include a study to model decreasing spring time stratospheric ozone, and the effects of this change on the aromaticity of riverine DOC and the potential impacts on coastal biodiversity.

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APPENDIX

Images

Image 1: An example of the water levels attained during the annual spring flood event (late May/early June) in the Mackenzie Delta.

Image 2: Terraced river banks along the East Channel of the Mackenzie River. Riverine floodwaters slowly subside and lake waters gradually drain towards the Mackenzie Outflow of the Mackenzie Delta

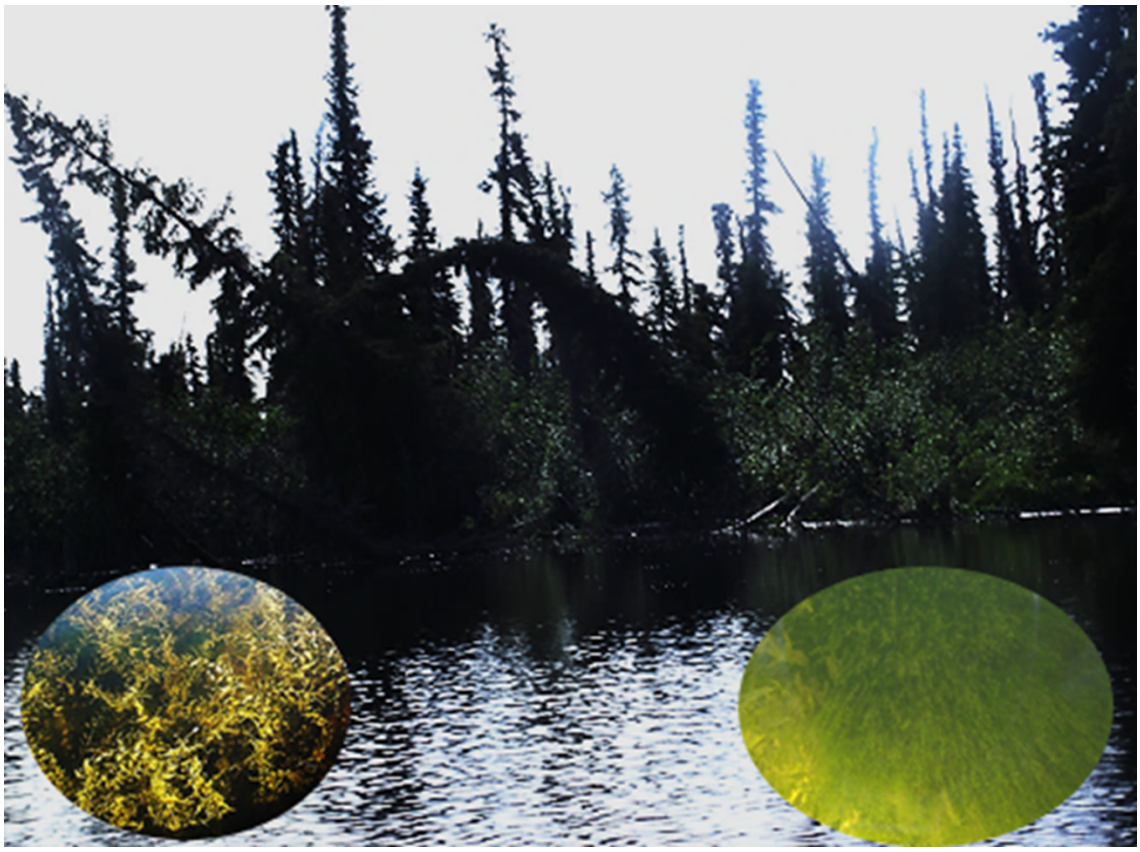

Image 3: Low Closure lake with insets showing the water clarity and production within this lake. On the shoreline of the lake you can see the “drunken” trees leaning towards the lake waters. July 15 2013.