Hydrological Controls on the Biogeochemistry of Polar Glacier Ice and its Meltwater

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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Abstract

Ice masses in the Antarctic, Greenland, and Canadian Arctic cover approximately 10% of the Earth's surface, contain approximately 70% of the Earth's freshwater, and are the top contributors to eustatic sea level rise. In recent years, these polar glacier systems have experienced significant increases in mass loss and melt rates, and the quantity of melt in these regions is expected to increase further under a warming climate. Existing research indicates that the physical, chemical, and microbial characteristics of these ice masses and the meltwater they produce are often distinct from those of other natural water sources. Their characteristics also show high temporal and spatial variability that may result from the combined presence of distinct and variable biogeochemical environments, particularly on the glacier surface and near the bed, and the strong variations in hydrological dynamics that often occur in glacial systems. This study examines glacier ice and meltwater from the Antarctic, Greenland, and Canadian Arctic to (1) investigate the variability in microbial assemblages and nutrient species/concentrations in the various biogeochemical environments that exist within and between polar glacier systems, and (2) evaluate how glacier hydrology influences the development and export of microbes and nutrients from these systems. Results of this study indicate that distinct biogeochemical environments exist in glacial systems, that they can function as sources and/or sinks for specific nutrients and microbes, and that the nutrients and microbes exported in glacial meltwater can vary according to the meltwater sources, flow paths, and residence times within the glacial system. Consequently, the biogeochemical characteristics of glacier ice and meltwater can differ between glaciers with different features, thermal regimes and/or hydrological systems, can change over the course of the melt season as the hydrological system within a glacier evolves, and can show different seasonal patterns for specific microbiological and nutrient parameters.

Preface

A version of Chapter 2 has been published [*Dubnick et al.*, 2017b]. I was responsible for field measurements and sample collection, data analysis and manuscript composition. J. Wadham and J. Orwin collaborated on the study design and field work and all authors (J. Wadham, M. Tranter, M. Sharp, J. Orwin, J. Barker, E. Bagshaw and S. Fitzsimons) contributed to manuscript edits.

A version of Chapter 3 has also been published [*Dubnick et al.*, 2017a]. I was responsible for study design, data collection and analyses and manuscript composition. J. Hawkings and A. Beaton collaborated on the study design, hydrology/chemistry fieldwork, and chemical analyses and S. Kazemi completed DNA extractions and contributed to microbial data analyses. S. Kazemi, M. Sharp, J. Wadham, J. Hawkings, A. Beaton, and B. Lanoil contributed to manuscript edits. Hydrology and chemistry field data were also published elsewhere [*Hawkings et al.*, 2016].

Chapter 4 is unpublished work. I completed the study design, field work, sample processing, data analyses and manuscript composition. B. Danielson assisted with field work and sampling and A. Saidi-Mehrabad completed DNA extractions. M. Sharp, M. Bhatia and J. Barker contributed to manuscript edits.

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Chapter 1: Introduction

1.1 Motivation

The Antarctic Ice Sheet (AIS), Greenland Ice Sheet (GrIS), and Canadian Arctic Archipelago (CAA) have experienced significant increases in mass loss and rates of glacial retreat in recent years [*Gardner et al.*, 2011] and the quantity of melt in these regions is predicted to continue to increase [*Radić et al.*, 2014]. Ice discharge from Antarctica was approximately 2000 Gt yr^{-1} in 2015, and increased by ~36 Gt yr^{-1} in 2013-2015 compared to 2008 [*Gardner et al.*, 2018]. Future increases in surface warming, basal ice shelf melting, and snowfall over Antarctica are predicted to increase ice discharge by up to three times by 2500 [*Winkelmann et al.*, 2012]. The GrIS, which currently discharges approximately 400 Gt yr^{-1} of freshwater to the Arctic and Atlantic oceans, is already experiencing rapid acceleration in mass loss and discharge is predicted to exceed 1000 Gt yr^{-1} by 2100 [*Fettweis et al.*, 2013]. The Canadian Arctic comprises approximately one-third of the global volume of land ice outside Greenland and Antarctica and is the next largest contributor to eustatic sea level rise, contributing 92 Gt yr^{-1} [*Gardner et al.*, 2011].

The increasing melt rates and mass loss from polar ice sheets, ice caps and glaciers translate to high and increasing seasonal fluxes of glacially-derived meltwater to downstream ecosystems. The Intergovernmental Panel on Climate Change estimates with high confidence that the future changes to glacial environments will affect downstream freshwater, riparian and near-shore marine ecosystems, but indicates that the biogeochemical processes and mechanisms that affect these ecosystems remain unclear and require further research [*Anisimov et al.*, 2007]. Understanding the biogeochemical characteristics of glacier meltwater is of global importance since downstream ecosystems support particularly high rates of primary productivity [*Rysgaard et al.*, 2012], contain genetically isolated populations [*Sköld et al.*, 2003], function as refugia for cold-water species

[*Węsławski et al.*, 2011], and are important feeding grounds and critical habitats for a number of marine mammals and seabirds [*Kuletz et al.*, 2003; *Mathews and Pendleton*, 2006; *Arimitsu et al.*, 2012].

The physical, chemical, and microbial characteristics of glacially-derived meltwaters are distinct from other natural water sources and may influence downstream ecosystem processes [*Battin et al.*, 2004] and biodiversity [*Wilhelm et al.*, 2013] and both the biogeochemistry [*Logue et al.*, 2004; *Battin et al.*, 2009; *Singer et al.*, 2012] and microbial ecology of fjord surface waters [*Gutiérrez et al.*, 2014]. Glacier meltwaters can transport high reactive suspended sediment loads and an abundance of bioavailable nutrients [*Telling et al.*, 2012; *Bhatia et al.*, 2013a, 2013b] and viable microbes [*Priscu and Christner*, 2004; *Hodson et al.*, 2008]. Glaciers can function as hot spots for bioavailable phosphorus [*Hawkings et al.*, 2016], iron [*Hawkings et al.*, 2014], nitrogen [*Petrone et al.*, 2006; *Lawson et al.*, 2014] and organic carbon [*Lafrenière and Sharp*, 2004; *Barker et al.*, 2006; *Hood et al.*, 2009; *Dubnick et al.*, 2010; *Pautler et al.*, 2012, 2013] that can be rapidly transformed in downstream freshwater and marine environments [*Fellman et al.*, 2010; *Nassry et al.*, 2013]. The microbes found in glacier ice and its meltwater are thought to be involved in a number of important nutrient producing and consuming reactions including heterotrophy [*Lawson et al.*, 2013], sulphide oxidation [*Skidmore et al.*, 2005], sulphate reduction [*Wadham et al.*, 2004], methanogenesis [*Wadham et al.*, 2012], nitrification, and nitrate-reduction [*Boyd et al.*, 2011].

While the physical, chemical and microbial characteristics of glacially-derived meltwaters are often distinct from those of other natural water sources, they can show high temporal and spatial variability. We expect that this variability results from the combined presence of (i) distinct and variable biogeochemical environments, particularly on the glacier surface (supraglacial environment) and near the bed (subglacial environment), and (ii) strong temporal and spatial

variability in hydrological dynamics within the glacial system, including flow rates, flow paths and residence times. Glacier hydrological systems are comprised of several sub-environments such as wet snow, cryoconite holes, supraglacial lakes, and streams on the surface of glaciers, to isolated cavities, thin films of water, water-saturated sediments, and large channels in the subglacial environments. Physical conditions differ greatly between these sub-environments including the availability of meltwater, its fluxes and residence times, ice and water temperatures, the presence/absence of light energy, the mineralogy/quantity/size distribution of sediment, redox conditions, and allochthonous sources of nutrients and microbes. Because of these physical differences, it is not surprising that distinct biogeochemical environments exist and that they produce vastly different mixtures of nutrients and microbes. The characteristics of bulk meltwater export are further complicated by the strong temporal and spatial variations in hydrological dynamics that occur in glaciated basins. Strong variations in flow rates, meltwater routing, and residence times along meltwater flow paths yield varying degrees of connectivity between different biogeochemical environments, and significant differences in the mixture of water sources that contribute to bulk meltwater export from glaciers.

1.2 Objectives and thesis outline

Although research over the past decade has advanced our understanding of both the biogeochemistry and hydrology of polar glaciers, it has yet to provide an integrated approach that investigates the links between glacier hydrology and biogeochemistry and evaluates biogeochemistry from both nutrient and microbial perspectives. The objectives of this research are to (1) investigate the variability in microbial assemblages and nutrient species/concentrations in the various biogeochemical environments that exist within and between polar glacier systems, and (2) evaluate how glacier hydrology influences the development and export of microbes and

nutrients from these systems. These objectives are explored via a series of studies that are presented in three main chapters.

The first study (Chapter 2) examines the distinct hydrological environments that occur along glacial-proglacial flow paths to evaluate whether they function as significant sources and/or sinks for dissolved macronutrients. It then explores how variations in glacier hydrology (e.g. meltwater routing and transit times through these environments) affect the export of dissolved macronutrients from the system as a whole. The second study (Chapter 3) examines how the seasonal evolution of meltwater sources and subglacial drainage system properties affect the character of microbial assemblages exported in glacial meltwater. The third study (Chapter 4) explores how basal temperature affects the biogeochemistry of basal ice and subglacial water. The results of these studies help to expand our knowledge of the distinct biogeochemical environments that exist in polar glacier systems, the mixtures of nutrients and microbes that they produce, and the controls on the biogeochemical processes and products of these systems.

1.3 Scientific background

Atmospheric aerosols and pollutants accumulate in the supraglacial snow pack of polar glaciers [*Laj et al.*, 1992; *Fischer and Wagenbach*, 1998] via wet and dry deposition. Solutes in glacier ice and snow are typically dominated by Na^+, Cl^-, and SO_4^{2-} and although there is usually a relative abundance of labile inorganic nitrogen (NH_4^+ and NO_3^-), organic matter is usually at low concentrations, of which a high proportion is microbial in origin [*Bhatia et al.*, 2013a; *Antony et al.*, 2014]. Microbes can also be deposited from the atmosphere and are typically at concentrations of 10^3-10^4 mL^{-1} in remote sites and at background atmospheric conditions [*Amato et al.*, 2007]. The snow surface can support autotrophic and mixotrophic algae communities [*Fogg*, 1967] that can be sites of carbon fixation and can provide nutrients to meltwater and downstream ecosystems

[*Lutz et al.*, 2014]. During the early stages of spring melt, when snowmelt is the main source of meltwater on glacier surfaces, elution processes release high concentrations of nutrients and solutes [*Hodson*, 2006; *Telling et al.*, 2014]. However, these waters often refreeze as they percolate through a cold snowpack in the early melt season, thereby delaying meltwater and nutrient delivery to downstream ecosystems until the snowpack warms and becomes isothermal, when lateral drainage can be established.

Once lateral drainage is established, snowmelt fills water storage sites in the supraglacial system, including the pore volume of snow and firn [*Fountain*, 1989], and ponds, lakes and stream channels both on the glacier surface [*Bartholomew et al.*, 2011] and along the margins of outlet glaciers (Figure 1-1). As the melt season progresses, the snow-line retreats up-glacier and the contributing drainage area expands. Bare ice is exposed at low elevations, and since it has relatively low albedo (0.3-0.5) relative to that of snow (~0.7), specific melt rates increase. These conditions generally lead to a progressive increase in the quantity of meltwater generated in the supraglacial environment over the course of the summer, although the effects of weather-related changes in surface melt rates are superimposed upon this well-defined seasonal runoff cycle.

Meltwater environments in the supraglacial system are generally exposed to light, atmospheric oxygen and carbon dioxide, and atmospheric/aeolian sources of nutrients and microbes. Consequently, they host microbial communities capable of photosynthesis and heterotrophy. Chemosynthetic organisms may also be present where wind-blown sediments are available. Cryoconite holes form where wind-blown sediment on the surface is heated preferentially relative to surrounding ice, causing accelerated melting of underlying/surrounding ice and result in water-filled cylindrical depressions. From a biogeochemical perspective,

cryoconite holes are the most well-studied of all supraglacial meltwater environments. They are considered hotspots for primary productivity [*Anesio et al.*, 2010; *Bagshaw et al.*, 2013, 2016a] and nutrient cycling [*Hodson et al.*, 2010b; *Telling et al.*, 2011; *Cameron et al.*, 2012; *Bagshaw et al.*, 2013]. Cryoconite holes host active microbial communities including heterotrophic bacteria, cyanobacteria, microalgae, microfungi and metazoans [*Wharton et al.*, 1981; *Säwström et al.*, 2002; *Christner et al.*, 2003] which utilize inorganic nutrients, and can generate high concentrations of dissolved organic carbon, nitrogen and phosphorus *[Stibal et al., 2008; Bagshaw et al.*, 2013]. The nutrients in cryoconite holes are often bio-available [*Stibal et al*., 2008; *Anesio et al.*, 2009; *Bhatia et al.*, 2010; *Bagshaw et al.*, 2013] and may feed downstream ecosystems if the cryoconite holes connect to surface or shallow subsurface meltwater streams.

In warm-based glacier systems, supraglacial meltwater enters the ice through crevasses and moulins, reaches the bed, and drains through the subglacial environment, where physical conditions are very different from those in the supraglacial environment. Basal ice is defined as ice that is chemically and/or physically altered by processes operating at or near the bed of glaciers such as bedrock or sediment erosion, melt-freeze effects, freezing of groundwater, or metamorphosis by thermal, strain and near-bed hydraulic conditions [*Knight*, 1997; *Hubbard et al.*, 2009]. The subglacial environment is characterised by large or variable amounts of (often very fine-grained) eroded debris, permanent darkness and low temperatures, and in some cases, limited availability of liquid water, which restricts the components of subglacial ecosystems to psychrotollerant and psychrophyllic prokaryotes that use chemotrophic and/or heterotrophic pathways. Although these conditions are not favourable for many prokaryotic species, studies have identified the ubiquitous presence of viable and active microbial populations in subglacial systems worldwide [*Sharp et al.*, 1999; *Foght et al.*, 2004; *Skidmore et al.*, 2005; *Lanoil et al.*, 2009; *Yde*

et al., 2010]. Subglacial microbial concentrations are positively correlated with sediment concentrations in basal ice and subglacial meltwaters [*Sharp et al.*, 1999] and are orders of magnitude higher in subglacial sediment than in basal or glacier ice [*Sharp et al.*, 1999; *Foght et al.*, 2004], suggesting that overridden soils and sediments may be a primary source of microbes and/or may support microbial growth by providing sources of carbon, and aqueous and particulate nutrients that are either attached to the sediment or suspended in ice or basal meltwaters [*Skidmore et al.*, 2000].

While basal ice is often thick and widespread at the base of glaciers, the subglacial drainage network is often more variable and includes both permanent elements, and elements that form, grow, and change structure over the course of a melt season, and then collapse over winter. "Distributed" or multi-thread drainage networks dominate the subglacial environment in the winter and early in the melt season, when runoff is commonly derived from basal melt (from geothermal or frictional heat), groundwater, small amounts of snowmelt and/or supraglacial meltwater stored in the subglacial system since the previous melt season. Such drainage networks typically lack large, well-defined channels, and water passes through them relatively slowly following "distributed" pathways where water is under high pressure [*Fountain et al.*, 1998]. These pathways include water films, the pore volume of water-saturated till, and poorly inter-connected networks of water-filled cavities that develop on the downstream side of bedrock bumps or boulders on the glacier bed where ice separates from the bed during flow by basal sliding [*Tranter et al.*, 2005].

Water and microbes in "distributed" drainage networks typically have ready access to supplies of freshly comminuted, reactive minerals, such as carbonates and sulphides, that are released from bedrock during subglacial erosion. In the presence of oxygen, biogeochemical

processes utilize oxygen as an electron acceptor, typically via sulphide oxidation coupled to carbonate dissolution (Equation 1-1), sulphide oxidation coupled to silicate dissolution (Equation 1-2), and/or oxidation of organic matter (Equation 1-3) [*Tranter et al.*, 2005]. Because distributed drainage networks are relatively isolated from the atmosphere, oxygen is only supplied to these areas from the release of air bubbles when ice melts *in situ*. Therefore, if reaction rates are higher than rates of oxygen supply, biogeochemical processes can drive some areas of the subglacial system towards sub-oxic or anoxic conditions. In such conditions, alternative electron acceptors may be utilized in biogeochemical reactions, such as NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, S, or CO_2 [*Skidmore et al.*, 2000; *Bottrell and Tranter*, 2002; *Tranter et al.*, 2002; *Wadham et al.*, 2004, 2008, 2012; *Wynn et al.*, 2006; *Boyd et al.*, 2010, 2011; *Stibal et al.*, 2012a].

Equation 1-1: Sulphide oxidation coupled to carbonate dissolution

$$4FeS_{2(s)} + 16Ca_{1-x}Mg_xCO_{3(s)} + 15O_{2(aq)} + 14H_2O_{(l)}$$

$$\leftrightarrow$$

$$16(1-x)Ca^{2+}_{(aq)} + 16xMg^{2+}_{(aq)} + 16HCO^{-}_{3(aq)} + 8SO^{2-}_{4(aq)} + 4Fe(OH)_{3(s)}$$

Equation 1-2: Sulphide oxidation coupled to silicate (feldspar) dissolution

$$4FeS_{2(s)} + 16Na_{1-x}K_xAlSi_3O_{8(s)} + 15O_{2(aq)} + 86H_2O_{(l)}$$

$$\leftrightarrow$$

$$16(1-x)Na^{+}_{(aq)} + 16xK^{+}_{(aq)} + 8SO^{2-}_{4(aq)} + 4Al_4Si_4O_{10}(OH)_{8(s)} + 32H_4SiO_{4(aq)} + 4Fe(OH)_{3(s)}$$

Equation 1-3: Oxidation of organic carbon

$$C_{org(s)} + O_{2(aq)} + H_2O_{(l)} \leftrightarrow CO_{2(aq)} + H_2O_{(l)} \leftrightarrow H^+ + HCO^-_{3\,(aq)}$$

Equation 1-4: Carbonation of carbonate

$$Ca_{1-x}Mg_xCO_{3(s)} + CO_{2(aq)} + H_2O_{(l)} \leftrightarrow (1-x)Ca^{2+}_{(aq)} + xMg^{2+}_{(aq)} + 2HCO^{-}_{3\,(aq)}$$

Equation 1-5: Carbonation of feldspar

$$CaAl_2Si_2O_{8(s)} + 2CO_{2(aq)} + H_2O_{(l)} \leftrightarrow Ca^{2+}_{(aq)} + 2HCO^{-}_{3\,(aq)} + H_2Al_2Si_2O_{8(s)}$$

As the flux of surface-generated meltwater delivered to the glacier bed increases over the melt season, large channels develop and become incised into either the overlying ice (tunnels) or underlying sediments (canals). These tunnels and/or canals comprise a more efficient "channelized" drainage system that receives meltwaters from both the supraglacial system and distributed areas of the bed, and they allow relatively rapid meltwater drainage to the glacier terminus. Efficient hydrological connectivity with the supraglacial environment (through crevasses and moulins) allows channelized drainage to experience weather-related or diurnal discharge-related fluctuations in water pressure which can result in reversals of the pressure gradient between the channelized and distributed drainage systems and bi-directional exchange of water between the two systems.

Reactive minerals are often exhausted in distributed drainage networks, so channelized drainage networks generally lack access to sulphides to drive weathering reactions. Instead, the dissolution of atmospheric CO_2 supplies these waters with protons for weathering, including the carbonation of carbonate (Equation 1-4) and feldspar (Equation 1-5) [*Tranter et al.*, 2005]. Since transit through the channelized system is quick relative to flow through distributed drainage systems, reactions with fast kinetics dominate solute acquisition by these waters.

On cold-based glaciers that are frozen to the bed, supraglacial waters bypass the subglacial system and are routed directly from the supraglacial environment to either an un-channelized ice-marginal zone or a well-defined proglacial stream. Like the better-studied subglacial environment, the ice-marginal environment is an area in which dilute supraglacial meltwater comes into contact with abundant sediment, some of which is likely freshly comminuted. Also like the subglacial environment, the ice-marginal environment may contain a complex drainage network that includes thin films of water, water-saturated till, and poorly inter-connected ponds with various residence times, flushing rates, and degrees of rock-water contact. The main difference between the ice-marginal zone in cold based glaciers and the subglacial system in warm-based glaciers is that ice-marginal streams and pools are in full contact with the atmosphere and have access to a continuous supply of atmospheric CO_2 that can fuel weathering processes. These areas are also exposed to light and diurnal/seasonal fluctuations in weather and may therefore support different microbial communities and biogeochemical processes. Regardless, the chemical characteristics of meltwater are likely to undergo rapid and dramatic change in both settings.

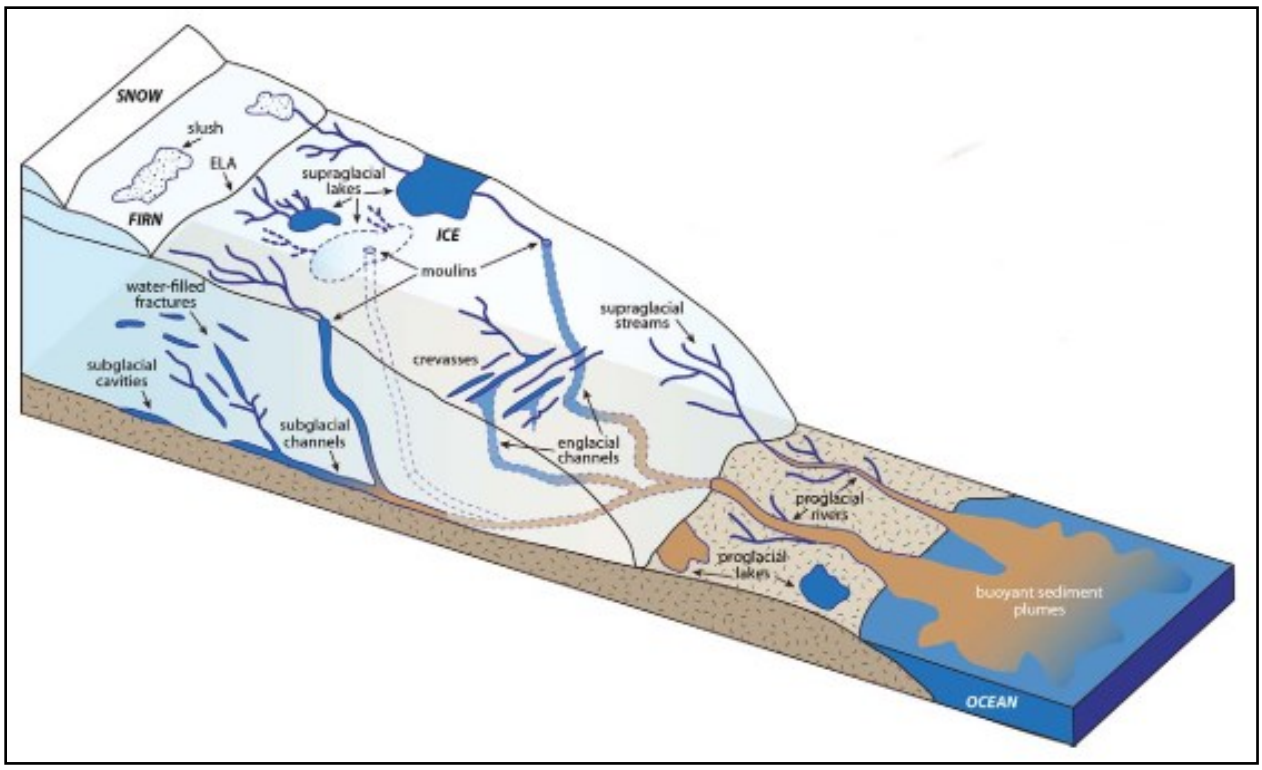

Figure 1-1: Hydrology of a warm-based, polar glacier (Source: Chu [2014])

Chapter 2: Trickle or treat: the dynamics of nutrient export from polar glaciers

2.1 Abstract

Cold-based polar glacier watersheds contain well-defined supraglacial, ice-marginal, and proglacial elements that differ in their degree of hydrologic connectivity, sources of water (e.g. snow, ice, and/or sediment pore water), meltwater residence times, allochthonous and autochthonous nutrient and sediment loads. We investigated 11 distinct hydrological units along the supraglacial, ice marginal, and proglacial flow paths that drain Joyce Glacier in the McMurdo Dry Valleys of Antarctica. We found that these units play unique and important roles as sources and/or sinks for dissolved inorganic nitrogen (DIN) and phosphorus (DIP), and for specific fractions of dissolved organic matter (DOM) as waters are routed from the glacier into nutrient-poor downstream ecosystems. Changes in nutrient export from the glacial system as a whole were observed as the routing and residence times of meltwater changed throughout the melt season. The concentrations of major ions in the proglacial stream were inversely proportional to discharge, such that there was a relatively constant "trickle" of these solutes into downstream ecosystems. In contrast, NO_3^- concentrations generally increased with discharge, resulting in delivery of episodic pulses of DIN-rich water ("treats") into those same ecosystems during high discharge events. DOM concentrations/fluorescence did not correlate with discharge rate, but high variability in DOM concentrations/fluorescence suggests that DOM may be exported downstream as episodic "treats", but with spatial and/or temporal patterns that remain poorly understood. The strong, nutrient-specific responses to changes in hydrology suggest that polar glacier drainage systems may export meltwater with nutrient compositions that vary within and between melt seasons and watersheds. Since nutrient dynamics identified

in this study differ between glacier watersheds with broadly similar hydrology, climate and geology, we emphasize the need to develop conceptual models of nutrient export that thoroughly integrate the biogeochemical and hydrological processes that control the sources, fate and export of nutrients from each system.

2.2 Introduction

Glaciers are a primary water source in many polar watersheds and are an important source of macronutrients, including nitrogen (N), phosphorus (P) and carbon (C) [*Bagshaw et al.*, 2013; *Bhatia et al.*, 2013a; *Hawkings et al.*, 2016]. Most glacially-derived meltwater originates on the glacier surface (supraglacial environment) and in cold-based glacier systems in the McMurdo Dry Valleys of Antarctica (and many other glacier systems world-wide), this environment contains a number of discrete and relatively well-studied biogeochemical systems including snow, glacier ice, cryoconite holes, cryolakes, and supraglacial streams. The physical differences between these systems result in differences in both allochthonous and autochthonous sources/sinks for nutrients. Atmospheric aerosol deposition and *in situ* biogeochemical processes and microbial activity in supraglacial snowpacks [*Hodson*, 2006] can lead to the release of meltwaters with high concentrations of dissolved inorganic nitrogen (DIN; Tranter *et al.*, 1993; Hodson *et al.*, 2005) and labile organic matter [*Barker et al.*, 2006, 2009; *Dubnick et al.*, 2010]. Microbial activity in cryoconite holes can generate high concentrations of dissolved organic carbon (DOC), nitrogen (DON) and phosphorus (DOP) [*Stibal et al.*, 2008; *Bagshaw et al.*, 2013], even in Blue Ice areas of the East Antarctic ice sheet where DIN may accumulate and is recycled by the cryoconite microbial community [*Hodson et al.*, 2013]. These nutrients may be bio-available [*Stibal et al.*, 2008; *Anesio et al.*, 2009; *Bhatia et al.*, 2010; *Bagshaw et al.*, 2013] and can feed downstream ecosystems [*Foreman et al.*, 2004] if the meltwaters connect to streams that transport them across

the glacier surface. Surface streams are one of the least favourable biological habitats in the supraglacial system and are characterised by low concentrations of NO_3^- and low nutrient processing rates, but nitrification and dissolved organic matter (DOM) uptake have nonetheless been observed [*Fortner et al.*, 2005; *Scott et al.*, 2010].

On cold-based glaciers that are frozen to the bed, supraglacial streams transport meltwater across the glacier surface to either an un-channelized ice-marginal zone or a well-defined proglacial stream. This ice-marginal environment has geochemical similarities with the subglacial environments in warm-based and polythermal glaciers since it can host a complex drainage network that includes thin films of water, water-saturated till, and poorly inter-connected ponds. It is also the location where dilute supraglacial meltwater first comes into contact with abundant sediment, some of which may be freshly comminuted, and hence is an area of potentially high geochemical activity [*Anderson et al.*, 2000]. Unlike many subglacial regions, the ice-marginal environment is exposed to atmospheric sources of solutes and atmospheric gases (e.g. O_2 and CO_2) that can fuel weathering processes.

Studies of the form, availability, and cycling of glacially-derived nutrients highlight the importance of nutrients in supporting downstream ecosystems (e.g. Hood *et al.*, 2009; Bhatia *et al.*, 2013a; Lawson *et al.*, 2013, 2014; Hawkings *et al.*, 2015). This is particularly evident in the polar desert watersheds of Antarctica's Dry Valleys [*Moorhead et al.*, 1997, 2005; *Foreman et al.*, 2004; *Mcknight et al.*, 2004; *Barrett et al.*, 2007; *Bate et al.*, 2008] where glacier runoff is effectively the only source of water and downstream lakes are among the most nutrient-limited aquatic ecosystems on Earth [*Parker and Simmons*, 1985; *Priscu*, 1995; *Foreman et al.*, 2004; *Dore and Priscu*, 2013]. The fluxes and timing of nutrient delivery, especially of limiting nutrients,

to depauperate downstream ecosystems may play an important role in controlling the rates and timing of primary production in those systems [*Bagshaw et al.*, 2013].

To date, there has been no integrated study of the distinct sources/sinks of macronutrients in Dry Valley watersheds and the nutrient cycling that occurs as waters flow en route to downstream proglacial ecosystems. Joyce Glacier in the Garwood Valley of Southern Victoria Land, Antarctica, provides a unique opportunity to study these processes. Its watershed includes distinct and accessible supraglacial, ice-marginal and proglacial hydrological units that exhibit variability in flow rates, water levels, and water residence times over the course of a melt season. These hydrological units differ in their degree of hydrologic connectivity, sources of water (e.g. snow, ice, and/or sediment pore water), meltwater residence times, allochthonous and autochthonous nutrient and sediment loads.

This study has two objectives. The first is to evaluate whether/how the distinct hydrological environments encountered by meltwaters passing through Joyce Glacier's supraglacial, ice-marginal and proglacial drainage systems function as sources and/or sinks for dissolved macronutrients (N, P, and C). We predict that each hydrological environment will play a unique role in the meltwater and nutrient dynamics of the whole drainage system because they differ in terms of the degree of contact that occurs between water, geological material, the atmosphere, biotic communities, and allochthonous nutrient sources. We expect nutrient export from the whole system to be sensitive to the fraction of water that passes through each environment, and to the amount of time that water spends in each of them. Our second objective is therefore to evaluate how variations in the routing and transit times of meltwater passing through the combined supraglacial, ice-marginal, and proglacial drainage system affect the export of macronutrients from

the system as a whole. Specifically, we seek to determine whether nutrient delivery to downstream ecosystems occurs as a steady "trickle" or as a series of episodic "treats".

2.3 Methods

2.3.1 Study site

The Garwood Valley in Southern Victoria Land, East Antarctica, extends east-west between the East Antarctic Ice Sheet and the Ross Sea (78°1'S, 163°51'E). The area is considered a polar desert with high winds and very low precipitation, almost all of which falls as snow. The surficial geology of the Garwood Valley consists largely of calcareous aeolian and fluvial sediments and glacial moraines, with exposures of dolomite, granite, and metamorphosed bedrock. Basement rocks are dominated by impure calcareous rocks, with a mineral composition that includes calcite, calc-silicates, phlogopite, pargasite and chondrodite [*Williams et al.*, 1971]. Mafic and felsic rocks are also present, and include amphibolites and rocks containing quartz-feldspar-biotite [*Williams et al.*, 1971].

Joyce Glacier, located at the western end of the Garwood Valley, feeds proglacial Holland Stream (Figure 2-1), which flows along the north-east margin of the glacier and into proglacial Lake Colleen, approximately 750 m from the glacier terminus. This 1 km long lake is permanently ice-covered but develops a moat several meters wide and an outlet channel during the melt season. The outflow of Lake Colleen (Garwood Stream), flows along the terminus of the Garwood Glacier, and enters the Ross Sea ~10 km downstream.

Meltwaters are routed into the Holland Stream via one of two dominant flow paths. Water following the primary flow path originates from supraglacial ice and snow melt, and passes through cryoconite holes, cryolakes, and small supraglacial streams before draining into the ice-marginal environment via gullies along the glacier margin. It then flows through multiple small,

poorly-defined streams and/or via shallow subsurface pathways until it reaches the Holland Stream (Figure 2-1).

Considerably less water follows the second flow path to the proglacial stream. Most of this water originates as ice melt from either the terminal cliffs of Joyce Glacier or the apron of calved ice blocks at their foot. These waters drain through moraines via shallow subsurface pathways and collect in a small proglacial pond that fills and discharges intermittently (typically when melt rates are high) into proglacial Holland Stream via a well-defined channel.

2.3.2 Data collection

2.3.2.1 Discharge monitoring

Holland Stream stage was measured from January 7-31, 2010 at 15-minute resolution using a non-vented HOBO U20-001-04 Water Level Logger (range of 0 to 4 m and accuracy of ± 0.3 cm). The stage data were barometrically compensated using data from a CS100 Setra barometer installed at the Joyce Glacier weather station (see below). Manual flow measurements, made almost daily between January 7th and January 31st, 2010, were used to estimate discharge using the USGS mid-section method, with velocity measured at 0.6 of water depth in each segment of the cross-section [*Turnipseed and Sauer*, 2010] using a Marsh-McBirney Flo-Mate 2000.

Stage-discharge relationships were established using the *Rating Curve* toolbox in the AQUARIUS™ software suite, using 21 manual discharge measurements. Shift corrections were applied to the stage-discharge rating curve after January 17th to account for the effects of sediment aggradation on the hydraulic geometry. Due to difficulties in generating a stable rating curve, the magnitude of the calculated discharge values should be treated with caution.

2.3.2.2 Meteorological monitoring

Meteorological conditions on Joyce Glacier were recorded using a Campbell Scientific weather station powered by a solar panel. Measurements were logged every 5 minutes and stored as 15-minute averages in a Campbell Scientific CR1000 data logger and include air temperature and relative humidity (HMP45C sensor), incoming and outgoing short plus long wave radiation (CNR1 net radiometer), and wind speed and direction (RM Young 5103 sensor).

2.3.2.3 Sampling

A total of 154 water samples were collected from the supraglacial (cryoconite holes/cryolakes, supraglacial streams), ice-marginal (gullies and pond outflow) and proglacial (upstream, lake and downstream) environments between January 6 and February 2, 2010 (Table 2-1). The samples probably do not represent the full range of spatial or temporal variability in water chemistry that exists within each environment. Since the focus of our study is on nutrient dynamics in the proglacial stream, we targeted our sampling of the supraglacial and ice-marginal systems from multiple sites during conditions of high hydrological connectivity/export (between ~11:00 and 18:00) and interpret our results in the context of other studies that more fully capture the temporal and spatial variability of similar environments. We compare daily samples collected in the proglacial (Holland) stream in 2010 with samples from the source areas, as well as samples collected at 2-hour intervals over a 24-hour period on December 9-10, 2008.

Water samples were collected in 1-L plastic Nalgene bottles after rinsing three times with sample. Ice samples were collected using an ethanol-bathed and flame-sterilized steel chisel and were melted in the field in sterile Whirlpak bags. An aliquot of sample was filtered through sterile 0.7 μm GF/F syringe/filters (rinsed three times with sample prior to use). Two 28-mL universal glass vials were each rinsed three times with filtered sample before being filled and frozen (for

dissolved organic carbon (DOC), dissolved organic matter (DOM), and total nitrogen (TN) analyses). This procedure was also followed using 0.45 µm cellulose nitrate filters to fill two 50-mL plastic Nalgene bottles (for major ions) and two 1.5-mL dry glass chromacol vials (for $\delta^{18}O$ and $\delta^{2}H$) for each sample.

2.3.3 Laboratory analyses

Concentrations of major ions (Ca^{2+}, K^{+}, Na^{+}, NH_4^{+}, SO_4^{2-}, NO_3^{-}, and Cl^{-}) were determined using a Dionex (DX-500) ion chromatograph (IC) equipped with a GP50 gradient pump and an autosampler with 5 mL polypropylene polyvials (as described by Lawson *et al.*, 2013). For anion analyses, we used an IonPac AS11-HC Hydroxide Selective Anion-Exchange Column (4 x 250 mm) and IonPac AG11-HC Guard Column (2 x 50 mm) with an ASRS (4mm) suppressor, operated in 100 mA AutoRegen mode with 30 mM sodium hydroxide eluent. For cation analyses, we used an IonPac CS12A Cation-Exchange Column (4 x 250 mm) with CSRS ULTRA II 4 mm suppressor, operated in the 50 mA AutoRegen mode with 20 mM MSA eluent. Detection limits were: Ca^{2+} = 2.0 µeq L^{-1}, K^{+} = 0.26 µeq L^{-1}, Na^{+} = 3.0 µeq L^{-1}, NH_4^{+} = 0.55 µeq L^{-1}, SO_4^{2-} = 2.1 µeq L^{-1}, NO_3^{-} = 0.48 µeq L^{-1}, and Cl^{-} = 2.8 µeq L^{-1} and accuracies were c. 5%. HCO_3^{-} concentrations were taken to be equal to the charge balance error for each sample. Concentrations of PO_4^{3-}, DSi, NO_2^{-} were analyzed using a Bran and Luebbe continuous segmented-flow AutoAnalyser (AA3) based on principles of colorimetry. Detection limits for each ion were: PO_4^{3-} = 0.42 µeq L^{-1}; DSi = 3.2 µM, NO_2^{-} = 0.26 µM, and accuracies were c. 10%.

Total dissolved P was determined using a sulphuric acid/persulphate digestion step [*Johnes and Heathwaite*, 1992]. The samples were autoclaved with an oxidizing solution containing potassium persulphate, boric acid and sodium hydroxide. The samples were then measured colorimetrically on a Shimadzu UVmini-1240 spectrophotometer for total dissolved phosphorus.

The detection limit was 1.6 µM and accuracy was <5%. Non-purgeable organic carbon and total nitrogen (TN) concentrations were determined by high temperature combustion (680°C) using a Shimadzu TOC-VCSN/TNM-1 Analyzer equipped with a high sensitivity catalyst. The detection limit for DOC was 17 µM (accuracy of ca. 10%) and 0.7 µM (accuracy of < ca. 5%) for TN. DON was subsequently calculated by subtracting corresponding NO_3^- and NH_4^+ concentrations from TN.

The spectrofluorescent properties of DOM were determined using a Horiba Fluorolog-3 spectrofluorometer equipped with a xenon lamp as an excitation source. Frozen samples were thawed and warmed to room temperature immediately prior to analysis in a sample-rinsed quartz glass cuvette with a 10 mm path length. Synchronous scans were completed by measuring the fluorescence intensity at 1 nm intervals over emission wavelengths between 218 and 618 nm, with an excitation offset of 18 nm, an integration time of 0.5 s, and 10 nm slits. Internal and dark corrections were applied to the results.

2.3.4 Data processing and statistical analyses

Data were processed in Matlab R2015a. One-way analysis of variance (ANOVA) was used to assess the significance of differences in the concentrations of nutrients between sampling environments (e.g. cryoconite holes vs supraglacial streams). For chemical nutrients with concentrations that were below the analytical detection limit in most samples (i.e. NH_4^+ and PO_4^3), Fisher Exact Tests (FET) were used to evaluate the significance of between-environment differences in the frequency of detection. Where concentrations of a given constituent were above the detection limit in all samples taken from a specific environment, 2-sample T-tests were used to evaluate the statistical significance of concentration differences between environments. Spearman Rank correlations were used to evaluate the significance of dependency between variables within an environment. We acknowledge that because samples were not collected

randomly (in space or time), p-values may not accurately reflect the true significance of the differences that exist within or between the hydrological environments sampled in this study. Nonetheless, a p-value of <0.05 was judged to indicate a significant difference for all statistical tests that were applied to the spatially and/or temporally clustered sample data that form the basis to this study.

The spectrofluorescence data were processed and modelled using Principal Components Analysis (PCA) to decompose the complex multivariate signals into linearly independent components [*Persson and Wedborg*, 2001; *Barker et al.*, 2009], which characterize the variance in the dataset and are interpreted as specific fractions of DOM. Due to the limitations associated with classifying individual components of DOM via fluorescence spectroscopy, particularly when using synchronous scans that cover only a small transect of the total optical space, we characterize DOM components broadly as being either protein-like (emission peak <350 nm) or humic-like (emission peak >350 nm) [*Carstea*, 2012].

Relationships between nutrient concentrations and coincident discharge rates (typically measured within 1 hour of sampling) were developed using Locally Weighted Scatterplot Smoothing (LOWESS) with a span of 0.7. Confidence intervals were calculated as ± two times the standard deviation of 1000 LOWESS relationships derived by bootstrapping. The upper and lower confidence intervals from these curves were used to estimate nutrient fluxes at the calculated discharge rates throughout the monitoring period.

2.4 Results

2.4.1 Hydrology and major ions

Like other Dry Valley glaciers, Joyce Glacier's energy balance is driven primarily by shortwave radiation, resulting in strong diurnal and seasonal fluctuations in the volume of

meltwater produced (Figure 2-2; Hoffman *et al.*, 2008). Supraglacial snow and glacier ice yielded the most dilute samples, with mean total ion concentrations of 180 μeq L^{-1} and 97 μeq L^{-1}, respectively Figure 2-3a). Mean solute concentrations were significantly higher in cryoconite holes (662 μeq L^{-1}), supraglacial streams (596 μeq L^{-1}) and ice-marginal gullies (668 μeq L^{-1}) (ANOVA, $p<0.05$) and continued to increase downstream, including in the ice-marginal pond (1262 μeq L^{-1}) and proglacial environments. Mean solute concentrations increased significantly from the proglacial upstream site (1247 μeq L^{-1}) to the proglacial downstream site (1469 μeq L^{-1}; ANOVA, $p<0.05$), and the concentration of total ions at the proglacial upstream site was negatively correlated with discharge (r_s=-0.64, n=22, $p<0.01$) (Figure 2-4).

2.4.2 Dissolved inorganic nitrogen

DIN in natural waters consists primarily of NO_3^-, NO_2^-, and NH_4^+, all of which were analyzed in this study. While 83% of meltwater samples contained NO_3^- concentrations above the detection limit (0.48 μM), only 64% contained NH_4^+ above the detection limit (0.55 μM), and none contained NO_2^- above the detection limit (0.52 μM). Therefore, the discussion of DIN in this study is limited to NO_3^- and NH_4^+, for which both concentration and/or detection rate varied significantly within and between meltwater environments (Figure 2-3b; Figure 2-5).

In the supraglacial environment, snow contained the highest average concentration of NO_3^- (5.0 μM,) and glacier ice produced the highest detection rate of NH_4^+ (90% of samples). Supraglacial streams and cryoconite holes, which are fed by snow and ice melt, produced a significantly lower detection rate of NH_4^+ than glacier ice (FET, $p<0.05$) and significantly lower NO_3^- concentrations than snow (ANOVA, $p<0.05$). As supraglacial streams were routed through the ice-marginal gullies, mean NO_3^- concentrations increased from 1.87 μM to 3.25 μM (ANOVA, $p<0.05$). The ice-marginal pond waters contained even higher NO_3^- concentrations than were

found in the ice-marginal gully waters (8.61 μM; ANOVA, $p<0.05$), but NH_4^+ was detected in only 50% of samples from these waters. NO_3^- concentrations in the ice-marginal pond were significantly higher than those in potential source waters, including snow, glacier ice, moraine ice, and gully water (ANOVA, $p<0.05$). DIN was depleted and/or diluted in the proglacial stream and lake where the frequency of detection of NH_4^+ and the concentration of NO_3^- decreased from 20% and 1.54 μM at the upstream site to 8% and <0.48 μM at the downstream site, respectively. At the proglacial upstream site, NO_3^- was positively related to discharge ($r_s=0.79$, $n=22$, $p<0.01$; Figure 2-4).

2.4.3 Dissolved inorganic phosphorus

Only 47% of the meltwater samples in this study contained dissolved inorganic phosphorus concentrations (DIP; PO_4^{3-}) above the detection limit (0.24 μM). However, significant variations in both detection rate and concentration were observed along the flow path (Figure 2-5). Low concentrations of rock-derived nutrients, including phosphorus, were found in supraglacial snow and ice (less than 30% of samples contained PO_4^{3-} concentrations above the detection limit). The detection rate of PO_4^{3-} increased significantly from ice to cryoconite holes (FET, $p<0.05$). However, PO_4^{3-} concentrations in cryoconite hole samples were highly variable, with 37% of samples below the detection limit, and others containing the highest concentrations observed among all meltwater samples (i.e. 3.5 μM and 1.6 μM).

All the ice-marginal samples contained PO_4^{3-} concentrations above the detection limit, which is a significantly higher detection rate than for snow (FET, $p=0.02$) and ice (FET, $p=0.002$). Similar to waters from ice-marginal gullies, all samples from the ice-marginal pond contained detectable quantities of PO_4^{3-}, but the average concentration in the pond waters (0.46 μM) was significantly higher than in the gullies (0.34 μM, T Test, $n_1=6$; $n_2=3$, $p<0.01$). All basal ice and

moraine ice samples contained detectable quantities of PO_4^{3-}, with concentrations averaging 1.17 μM and 0.49 μM, respectively. Detection of PO_4^{3-} decreased significantly in the proglacial system, from 100% in the ice-marginal gullies to 25% at the upstream proglacial site (FET, p=0.001), and 0% at the downstream proglacial site (FET, p=0.01).

2.4.4 Dissolved organic matter

Dissolved organic matter (DOM) in the system was assessed by exploring dissolved organic carbon (DOC), nitrogen (DON) and phosphorus (DOP) concentrations and characterizing DOM using spectrofluorescence methods. While all samples contained detectable concentrations of DOC and DON, only 4 samples contained DOP above the detection limit. Although DON comprised most (average of 74%) of the dissolved nitrogen in the meltwater samples, with a mean concentration of 11 μM, no significant differences in DON concentrations were observed between the various meltwater environments (ANOVA, $p>0.05$). Two Principal Components of the fluorescence spectra explained 76.9% and 21.6% of the variance in the dataset, and the remaining components each explained <0.6%. Component 1 had a prominent emission peak at 330 nm, associated with protein-like moieties, and Component 2 had an emission peak at 405 nm, associated with humic-like moieties [*Carstea*, 2012].

Although DOC concentrations in supraglacial snow and ice were not measured in this study, previous work reports DOC concentrations of between ~20 μM and 40 μM in supraglacial snow and ice from the Dry Valleys [*Bagshaw et al.*, 2013; *Barker et al.*, 2013]. Cryoconite hole waters had an average DOC concentration of 125 μM with a standard deviation of 75 μM (n=13). Despite this variability in DOC concentrations, all cryoconite hole DOM samples had similar spectrofluorescence properties. In addition to strong loadings on Components 1 and 2, cryoconite hole samples contained a prominent peak at 298 nm with a fluorophore-like signal (systematic

bell-shaped curve), described by PCA Component 7, suggesting the presence of an additional protein-like moiety [*Carstea*, 2012]. While this component explained only 0.04% of the variability in the total dataset, it had significantly higher loading on cryoconite hole DOM than on DOM from any of the other meltwater environments, including the outflow channels of the cryoconite holes (Figure 2-3h, ANOVA, $p<0.05$). Component 7 was negatively correlated with deuterium excess (r_s=-0.56, n=15, p=0.03) and air temperature (r_s=-0.63, n=10, p=0.05), suggesting that melt-refreeze cycling, evaporation effects and/or weather conditions may affect its abundance.

DOC concentrations decreased by more than 50% between supraglacial streams ($\bar{x}$ = 131 μM) and ice-marginal gullies ($\bar{x}$ = 54 μM) but increased again by a factor of approximately 3.5 in the ice-marginal pond ($\bar{x}$ = 192 μM, the highest mean DOC concentration among all meltwater environments). The ice-marginal pond water also yielded the highest fluorescence of the humic-like Component 2 DOM fraction, and the highest C/N ratio.

The proglacial stream contained some of the lowest DOC concentrations measured and displayed significantly less protein-like Component 1 fluorescence than was found in the supraglacial stream (ANOVA, $p<0.05$), and significantly less humic-like Component 2 fluorescence than the ice-marginal pond (ANOVA, $p<0.05$). In the proglacial stream, DOC concentrations and DOM characteristics remained relatively constant between the upstream and downstream monitoring sites, displaying no significant differences (ANOVA, $p>0.05$), despite the relative abundance of algal mat communities in the littoral zone of the proglacial lake and in stable, slow-flowing sections of the stream. Neither DOC concentrations nor the fluorescence intensity of the DOM components varied significantly with proglacial stream discharge (r_s=0.12, n=22, p=0.58), but DOC concentrations were significantly higher in January 2010 ($\bar{x}$ = 88 μM) than in

December 2008 ($\bar{x}$= 21 μM; T test, n_1 = 6; n_2 = 22, $p<0.05$) and they varied considerably throughout both melt seasons (σ = 47 μM).

2.5 Discussion

2.5.1 Nutrient sources and sinks along the flow path

2.5.1.1 Supraglacial environments

Most water in the Garwood Valley originated from supraglacial snow or ice melt, in which NO_3^- and NH_4^+ concentrations were high (Figure 2-3; Figure 2-5; Figure 2-6). DIN in snow and ice can be derived from atmospheric sources via snowfall or dry deposition. Cryoconite holes and cryolakes functioned as a sink for NH_4^+ and NO_3^- and as a source of PO_4^{3-} and the protein-like DOM Component 7 in this study (Figure 2-3; Figure 2-5; Figure 2-6). They are widely known as active biogeochemical systems [*Bagshaw et al.*, 2007; *Hodson et al.*, 2010b; *Tranter et al.*, 2010] and their nutrient dynamics are important because waters that pass through them comprise a significant portion of supraglacial runoff meltwater [*Fountain et al.*, 2004].

Cryoconite holes and cryolakes facilitate relatively prolonged and extensive rock-water contact, which can add rock-derived nutrients, such as DIP, to the solute-poor meltwaters. Geochemically active biota have been observed in cryoconite holes, which are known to assimilate inorganic nutrients (including DIN and DIP) in the production of organic material [*Hodson et al.*, 2005] and play an important role in defining the biogeochemistry of supraglacial waters and the range of nutrients exported to downstream ecosystems [*Bagshaw et al.*, 2010, 2013, 2016a]. For example, the DIN requirements of primary producers in cryoconite holes in Antarctic blue-ice environments exceed rates of DIN supply from ice melt at the base of the hole, suggesting that DIN is actively recycled within these systems and that they are likely to have an important influence on the nitrogen economy of supraglacial waters [*Hodson et al.*, 2013]. DIN may also be

utilized by microbes as an electron acceptor in energy-producing redox reactions such as denitrification [*Hodson et al.*, 2010b; *Telling et al.*, 2011]. Although nitrogen cycling in cryoconite holes and supraglacial streams can be complex, studies have identified the occurrence of nitrification [*Baron et al.*, 1995; *Hodson et al.*, 2005; *Scott et al.*, 2010], denitrification [*Hodson et al.*, 2010b; *Telling et al.*, 2011], nitrogen assimilation [*Hodson et al.*, 2005] and the production of particulate nitrogen [*Bagshaw et al.*, 2013].

Biological activity in cryoconite holes likely results in long-term net carbon fixation, which may be an important source of DOM for nutrient-poor downstream ecosystems [*Bagshaw et al.*, 2016a] and, potentially, the protein-like DOM (Component 7) observed in this study. The relative abundance of this DOM fraction in cryoconite holes and cryolakes, and its depletion downstream, suggest that this fraction of the DOM pool may be labile and provide a metabolic substrate for downstream ecosystems. Other studies have identified similar autochthonous/microbial/protein-like DOM compounds in cryoconite holes world-wide [*Lawson et al.*, 2013, 2014; *Pautler et al.*, 2013] and uniquely supraglacial fractions of DOM which are likely labile [*Bhatia et al.*, 2010; *Dubnick et al.*, 2010; *Barker et al.*, 2013; *Lawson et al.*, 2014], show non-conservative behaviour, and are depleted in downstream ecosystems [*Barker et al.*, 2006, 2013; *Hood et al.*, 2009; *Scott et al.*, 2010] by biotic or abiotic processes (e.g. photochemical reactions).

2.5.1.2 Ice-marginal environments

Solute-poor meltwaters from the supraglacial environment are routed into sediment-rich ice-marginal gullies, where large increases in NO_3^- occur (Figure 2-3b; Figure 2-6). A large portion of DIN supplied to meltwaters in the ice-marginal system may be sourced from the dissolution of nitrogen-containing salts. Low precipitation rates, humidity, and overland flow allow salts to accumulate in Dry Valley soils, similar to other arid regions where evaporation and sublimation

exceed precipitation [*Bisson et al.*, 2015]. Nitrates of sodium and magnesium, including Darapskite ($Na_3NO_3SO_4H_2O$) and soda niter ($NaNO_3$), are widespread in South Victoria Land [*Claridge and Campbell*, 1968; *Keys and Williams*, 1981], are highly soluble and, if present, could readily contribute NO_3^- to meltwaters. The ice-marginal water chemistries observed here are similar to those observed in ice-marginal ponds elsewhere in the Dry Valleys where the dissolution of atmospheric aerosols (e.g. HNO_3, $(NH_4)_2SO_4$) and nitrate-bearing salts contribute significantly to the solute load [*Healy et al.*, 2006; *Wait et al.*, 2006; *Webster-Brown et al.*, 2010].

Biogeochemical activity in the ice-marginal system may also supply meltwaters with DIN. Active microbial communities, which are likely important in N cycling, have been identified in recently deglaciated ice-marginal soils [*Strauss et al.*, 2012]. Studies of freshly-exposed, ice-marginal soils report that in situ N-cycling is initially dominated by nitrogen mineralization via the decomposition of organic matter (<10 yrs exposed), followed by N-fixation (50 to 70 years exposed) [*Brankatschk et al.*, 2011]. Other studies have identified the presence of nitrification in ice-marginal environments [*Wynn et al.*, 2007; *Hodson et al.*, 2010a; *Ansari et al.*, 2012], and suggest that the amount of NO_3^- derived from nitrification can exceed that derived from atmospheric deposition [*Roberts et al.*, 2010].

There may be similar sources of DIN along the secondary flow path where meltwaters are routed from the apron of calved ice blocks along the terminus and the vertical ice cliffs to the ice-marginal pond. The ice-marginal pond was the most nutrient-rich environment along the flow path and contained the highest concentrations of DIN and DIP. These high concentrations may result from extensive access to nitrogen-containing salt deposits and longer contact with relatively phosphorus-rich glacial till [*Gudding*, 2003] as waters follow spatially and temporally dynamic flow paths in the shallow subsurface between the glacier terminus and the pond. Pond waters may

also acquire DIN and DIP from the melting of basal ice, which is found in nearby ice-cored moraines. Basal ice usually contained NH_4^+ at concentrations at least an order of magnitude higher than found in most other environments, which could be oxidized to NO_3^- by nitrifying bacteria in the hyporheic zone or the soil, as has been reported for other Dry Valley streams [*Mcknight et al.*, 2004] subglacial and ice-marginal sediments [*Wynn et al.*, 2007; *Hodson et al.*, 2010a; *Ansari et al.*, 2012].

Pond water maintained high DIN and DIP concentrations despite the presence of abundant algae that likely function as a sink for inorganic nutrients. Extensive phytoplankton and microbial mat communities dominated by cyanobacteria have been observed in other Dry Valley ice-marginal ponds [*Webster-Brown et al.*, 2010]. The presence of algal communities in the pond may also affect the DOM characteristics of these waters. The ice-marginal pond waters had the highest fluorescence of the humic-like Component 2 DOM fraction and the highest C/N ratio of all meltwater environments sampled (Figure 2-3d,f). Both observations are consistent with the presence of humic substances that fluoresce at long wavelengths and have relatively high C content, and they suggest that the ice-marginal pond may be a source of humic DOM. Although humic DOM is typically produced by terrestrial vascular plants, which are absent from the Garwood Valley, a similar humic-like fluorescent component can be produced in aquatic environments by the microbial degradation of phytoplankton DOM [*Stedmon and Markager*, 2005]. Previous studies suggest that production and consumption of similar humic-like DOM can occur very rapidly, and that degradation can occur by microbial and photochemical processes [*Stedmon and Markager*, 2005].

Although the ice-marginal zone is a potentially important source of nutrients to downstream ecosystems, nutrient transfer from the ice-marginal pond to the proglacial stream

occurs only intermittently. Outflow from the ice-marginal pond was typically active only during the daily flow peak (~12:00-24:00), on days with high solar radiation and/or during seasonal peak melt conditions (~Jan/Feb). The hydrology of the ice-marginal zone therefore plays an important role in the timing of nutrient transport to the proglacial stream.

2.5.1.3 Proglacial environments

DIN and DIP are supplied to meltwaters in the supraglacial and ice-marginal environments and are likely depleted in the proglacial stream. Decreases in DIN and DIP concentrations have been observed in other Dry Valley proglacial streams and have usually been attributed to nutrient uptake by benthic algal communities and mosses [*McKnight et al.*, 1998, 1999; *Mcknight et al.*, 2004]. Microbial processes in the hyporheic zone, including denitrification and dissimilatory NO_3^- reduction to NO_2^- and NH_4^+, are also likely to contribute to DIN losses [*Maurice et al.*, 2002; *Mcknight et al.*, 2004], however these losses are likely minor in comparison to those attributable to benthic algal communities [*Mcknight et al.*, 2004]. Dry Valley streams and lake ecosystems have been identified as among the most nutrient-poor ecosystems on Earth [*Vincent and Vincent*, 1982; *Parker and Simmons*, 1985; *Priscu et al.*, 1989; *Priscu*, 1995; *Dore and Priscu*, 2013] and consequently have a high capacity for nutrient uptake [*Mcknight et al.*, 2004].

2.5.2 Trickle or Treat: hydrologically controlled nutrient dynamics

Distinct biogeochemical environments exist in the supraglacial, ice-marginal and proglacial systems explored in this study (Figure 2-6). Nutrient fluxes from the entire system are therefore likely to be sensitive to the proportions of water that are routed through each individual environment, and their respective residence times. The strong variability in meltwater fluxes and flow routing at daily, seasonal, and inter-annual timescales that is observed in the Dry Valleys led us to hypothesize that there would be a corresponding dynamic in the mix and quantity of nutrients

exported to downstream ecosystems under changing hydrological regimes. To explore this hypothesis, we examined the relationship between discharge and nutrient concentrations and fluxes in the Holland Stream (upstream site) to determine whether nutrient export from the glacial system throughout the melt season occurs as a constant "trickle" or as a series of episodic "treats".

We found differences in the dynamics of nutrient export to downstream environments under changing discharge regimes. The concentrations of most solutes in proglacial stream water are controlled primarily by chemical weathering of the highly permeable, unconsolidated sediments found in the channel margins and hyporheic zone [*Gooseff et al.*, 2004] including carbonate and silicate weathering, and by salt dissolution [*Lyons et al.*, 1998; *Maurice et al.*, 2002; *Fortner et al.*, 2005]. Weathering takes place where source material is supplied directly to the channel by aeolian transport, atmospheric deposition [*Fortner et al.*, 2005, 2013] and/or bed/bank erosion. It is unsurprising then, that the concentrations of these solutes increased in the ice-marginal gullies and proglacial stream where rock-water contact was high (Figure 2-3), and that they increased along both flow paths that fed the proglacial stream. Because the acquisition of these solutes requires prolonged rock-water contact, it is also unsurprising that their concentrations in the proglacial stream decreased with inverse proxies for residence time along both flow paths, including air temperature, incident solar radiation, and discharge (Figure 2-4). Consequently, downstream ecosystems receive relatively high concentrations of rock-derived solutes during low flow conditions and relatively low concentrations during high flow conditions, producing a relatively steady downstream "trickle" of such solutes (Figure 2-7), as has been observed in other Dry Valley streams [*Lyons et al.*, 2003; *Fortner et al.*, 2013].

NO_3^- displayed a different hydrologic dynamic, where its concentration in upstream sections of the proglacial stream generally increased with discharge and the highest concentrations

were observed at relatively high discharges (Figure 2-4). Flux estimates derived from this concentration-discharge relationship suggest that, during high flow conditions, NO_3^- is exported in stronger pulses of DIN rich "treats" than is the case for most solutes (Figure 2-7). While not every high discharge event corresponds with a DIN "treat", particularly late in the melt season (e.g. January 29), a relatively large portion of the seasonal flux of NO_3^- occurs in pulses at times of high discharge.

The DIN sources and sinks identified along both flow paths (Figure 2-6) indicate a number of potential mechanisms that may together facilitate the delivery of episodic pulses of DIN during high discharge events. First, high melt/flow rates may allow more extensive wetting of the ice-marginal zone, where waters can access new stores of reactive geologic nitrogen and accumulated NO_3^- bearing salts. This may be particularly true early in the melt season when sediments are first wetted. Second, the ice-marginal zone along the secondary flow path, where DIN acquisition occurs (Figure 2-6), has relatively large meltwater storage capacity (in ice-marginal ponds and sediments) and only exports meltwater (and therefore DIN) under high melt/flow. Third, the DIN sinks along the flow paths likely consist of ecosystems that consume DIN via processes such as microbial denitrification and nitrogen assimilation. Under high flow conditions, waters containing DIN may travel downstream too rapidly for DIN to be assimilated or converted to N_2 by biota in the upper reaches of the watershed. Therefore, major sources of NO_3^- are likely maximized and major sinks of NO_3^- are likely minimized under conditions of high melt and runoff, allowing DIN to be mobilized and transported downstream as DIN-rich "treats" during pulses of high discharge.

The hydrological dynamics of DOM in the proglacial stream are considerably more complex than those of total ions and NO_3^-, as there is a less consistent relationship between DOC concentrations/DOM composition and either discharge or other indicators of hydrological routing

or runoff rate (e.g. solar radiation, air temperature, or total ion concentrations). DOM cycling in glacier systems is likely complex due to the presence of multiple sources (e.g. kerogen/fossil soil carbon, airborne organic matter, necromass, excretions from plants and other organisms), modes of transformation, and sinks (e.g. consumption, decomposition) that remain poorly understood. The lack of dominant source and sink locations for DOM along the flow path (Figure 2-6) and the complexity of DOM cycling processes likely contribute to the high variability in DOC concentrations and DOM characteristics observed in this study. While neither DOC concentrations nor DOM characteristics appear to be directly influenced by discharge rates, DOC concentrations were significantly higher in January 2010 ($\bar{x}$ = 88 μM) than in December 2008 ($\bar{x}$= 21 μM) and showed considerable variability throughout both melt seasons (σ = 47 μM). Therefore, while DOC may be delivered to downstream ecosystems in episodic pulses ("treats"), these DOC-rich pulses may not occur at times of high discharge as consistently as the NO_3^- "treats". Because DOC concentrations and DOM characteristics in Dry Valley proglacial streams show high variability both within and between catchments (e.g. McKnight *et al.*, 2001; Barker *et al.*, 2006, 2013) hydrologic controls on DOM fluxes in proglacial streams may also be inconsistent.

While we have established general relationships between total solutes and nitrate and proglacial stream discharge, considerable scatter exists (Figure 2-4), likely because watershed hydrology and biogeochemical environments evolve over the melt season. This evolution may involve, for example, changes in the rates of primary production in cryoconite holes due to seasonal variations in light intensity and air temperature [*Bagshaw et al.*, 2016b], changes in the chemistry of ice-marginal pond outflow due to vertical mixing in response to the effects of wind, precipitation, evaporation, and/or temperature [*Wait et al.*, 2006], changes in the availability of nitrate from the dissolution of salts if supplies become depleted as the melt season progresses, and

changes in biological nutrient sources/sinks as microbial, benthic algae, and moss communities develop during the growing season [*McKnight et al.*, 1998, 1999; *Mcknight et al.*, 2004]. Similarly, evolution of the hydrological system may involve flushing of the supraglacial environment during periods of rapid melt, expansion of the hyporheic zone and active layer over the summer, and erosion and sedimentation which can reconfigure supraglacial, ice-marginal, and proglacial drainage systems. The co-evolution of biogeochemical and hydrological systems suggests that the dynamics of nutrient export from these systems may change over time.

Although the negative relationship between solute concentration and discharge (Figure 2-4) is a relatively consistent observation in glacier systems, the strength of this relationship shows spatiotemporal variability between Dry Valley [*Lyons et al.*, 2003; *Fortner et al.*, 2013] and other polar glacier watersheds [*Wadham et al.*, 1998; *Brown*, 2002; *Yde et al.*, 2014]. Even more variability is found among polar glacier systems in the case of DIN concentration vs discharge relationships. While we observed a positive relationship between NO_3^- concentration and discharge in the Holland Stream, these parameters were found to be unrelated at a polythermal glacier in the Swiss Alps [*Tockner et al.*, 2002], and inverse relationships have been observed in nearby Taylor Valley proglacial streams [*Howard-Williams et al.*, 1989; *Fortner et al.*, 2013], a polythermal glacier in Greenland [*Wadham et al.*, 2016] and a temperate alpine glacier in the Canadian Rockies [*Lafrenière and Sharp*, 2005]**.** However, the strengths of these inverse relationships and the degree of scatter show considerable spatiotemporal variability. Proglacial NO_3^- concentration vs discharge relationships in waters draining a polythermal glacier system in Greenland (Leverett Glacier, Wadham *et al.*, 2016) and a cold-based Glacier in the Dry Valleys of Antarctica (Canada Glacier; Fortner *et al.*, 2013) are more similar to each other than those draining two nearby, cold-based glacier systems that have fundamentally similar glacier hydrology,

biogeochemical systems along the flow path, climate and geology (i.e. Joyce Glacier and Canada Glacier). Thus, while there is merit in making broad assumptions about the nutrient dynamics based on macro-scale glaciology and hydrology (e.g. cold-based vs warm-based glacier systems) and upscaling from measurements on one watershed to produce regional nutrient flux estimates [*Bhatia et al.*, 2013b; *Hawkings et al.*, 2016; *Wadham et al.*, 2016] and estimating nutrient fluxes under future climate conditions (e.g. Hawkings *et al.*, 2015), this study suggests that the detail of watershed biogeochemistry and hydrology in defining proglacial nutrient dynamics and spatiotemporal variability in fluxes may be substantial. The influence of nutrient-specific, watershed-specific, and temporal variability on the dynamics of nutrient fluxes from polar glacier systems is not a new theme for studies of the chemistry of glacially-derived meltwater. However, this study also underlines the important influence of dynamic changes in the connectivity of glacier-proglacial biogeochemical systems on nutrient fluxes (Gooseff *et al.*, 2016) and emphasizes the need to develop conceptual models that thoroughly describe the biogeochemical and hydrological components of the systems.

2.6 Conclusions

This study identifies a series of distinct biogeochemical environments in the supraglacial, ice-marginal and proglacial systems of Joyce Glacier in Southern Victoria Land, East Antarctica. While dissolved organic nutrient concentrations (DOC, DON and DOP) were either below our detection limits or showed little variability between these environments, potential sources and sinks for DIN, DIP and specific fractions of organic matter were identified. Specifically, snow, glacier ice, and the ice-marginal zone were important sources of DIN, and cryoconite holes and supraglacial and proglacial streams were sinks for DIN. Cryoconite holes, cryolakes, supraglacial

streams and the ice-marginal environment were sources of DIP, which were likely utilized in the proglacial system.

Seasonal changes in the routing and residence times of meltwaters through the various biogeochemical environments along the flow path yielded nutrient-specific dynamics. The concentration of solutes (total ions) decreased with increasing meltwater discharge and resulted in a relatively constant "trickle" of solutes to downstream ecosystems. In contrast, DIN concentrations increased with discharge, resulting in episodic pulses of DIN-rich "treats" during high discharge events. While DOC concentrations did not correlate with discharge rate, high variability in DOC concentrations may indicate that DOC is also exported downstream as episodic "treats", but that the timing of these "treats" may not coincide with peak discharge conditions as consistently as is the case for DIN. These nutrient-specific dynamics are not always consistent between proglacial streams in watersheds with similar climates, geology, and/or glacial thermal regimes, highlighting the important influence of dynamic changes in the connectivity of glacier-proglacial biogeochemical systems on nutrient fluxes (Gooseff *et al.*, 2016) and emphasizes the need to develop conceptual models that thoroughly describe the biogeochemical and hydrological components of the systems.

2.7 Acknowledgements

This research was supported by Antarctica New Zealand logistics funding for event K064 to S. Fitzsimons and J. Orwin, an NSERC Discovery grant to M. Sharp (155194-2010), an EPSRC grant to J.L. Wadham (EP/D057620/1), the Leverhulme Trust (Phillip Leverhulme Prize to J.L. Wadham, Leverhulme Fellowship to J.L. Wadham), a W. Garfield Weston Award for Northern Research and NSERC CGSD Award to A. Dubnick. We are grateful for Dr C. Butler who contributed to the analytical work.

Table 2-1: Sample descriptions

Environment	Description	# of sites	# of samples (2010 only)
Cryoconite holes / Cryolakes	Representing both open and ice lidded systems near the margin of the Joyce Glacier	7	20
Supraglacial Streams	Representing cryoconite holes/cryolake outflow streams and larger cumulative supraglacial streams	10	22
Gullies	At the glacier margin between the supraglacial and moraine environments	3	7
Pond	At the inflow to the Holland stream	1	5
Upstream	Daily samples immediately downstream of the tributary inflow	1	28
Lake	At the moat on the north shore of the Proglacial Lake	1	5
Downstream	Daily samples from the outflow of the proglacial lake (upstream of Garwood Glacier inflows)	1	26
Snow	Supraglacial and fresh proglacial snow	10	10
Glacier Ice	From ice cliff exposures and the supraglacial environment	16	16
Moraines	Ice cored moraines from within 100 m of the glacier terminus	5	5
Basal Ice	Joyce Glacier basal ice	5	5

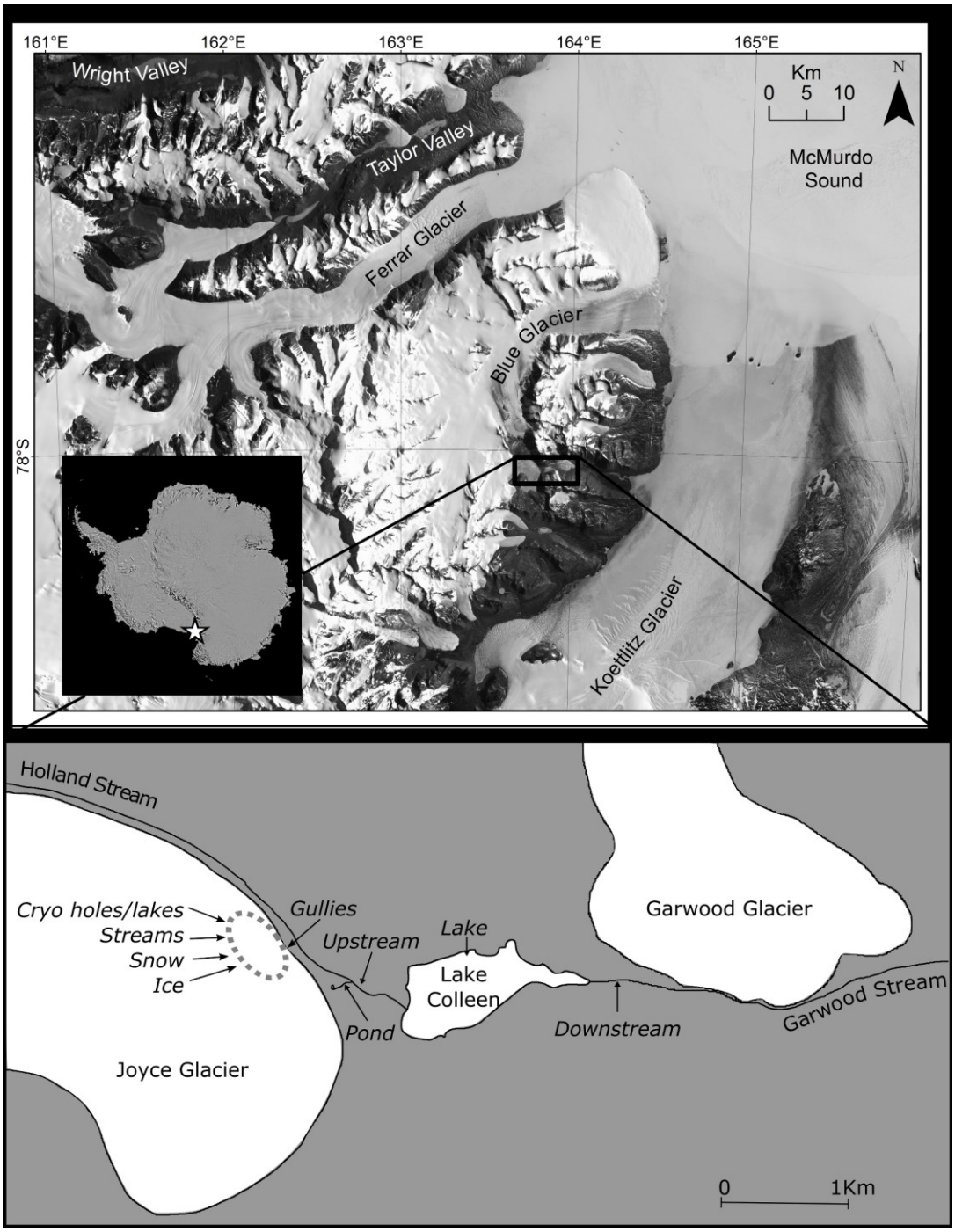

Figure 2-1: Location of the Garwood Valley (top) and study site (bottom) indicating sample locations in italics. Supraglacial samples (cryoconite holes/ cryolakes, streams, snow and ice) were collected within the region indicated by the grey dotted line on the Joyce Glacier.

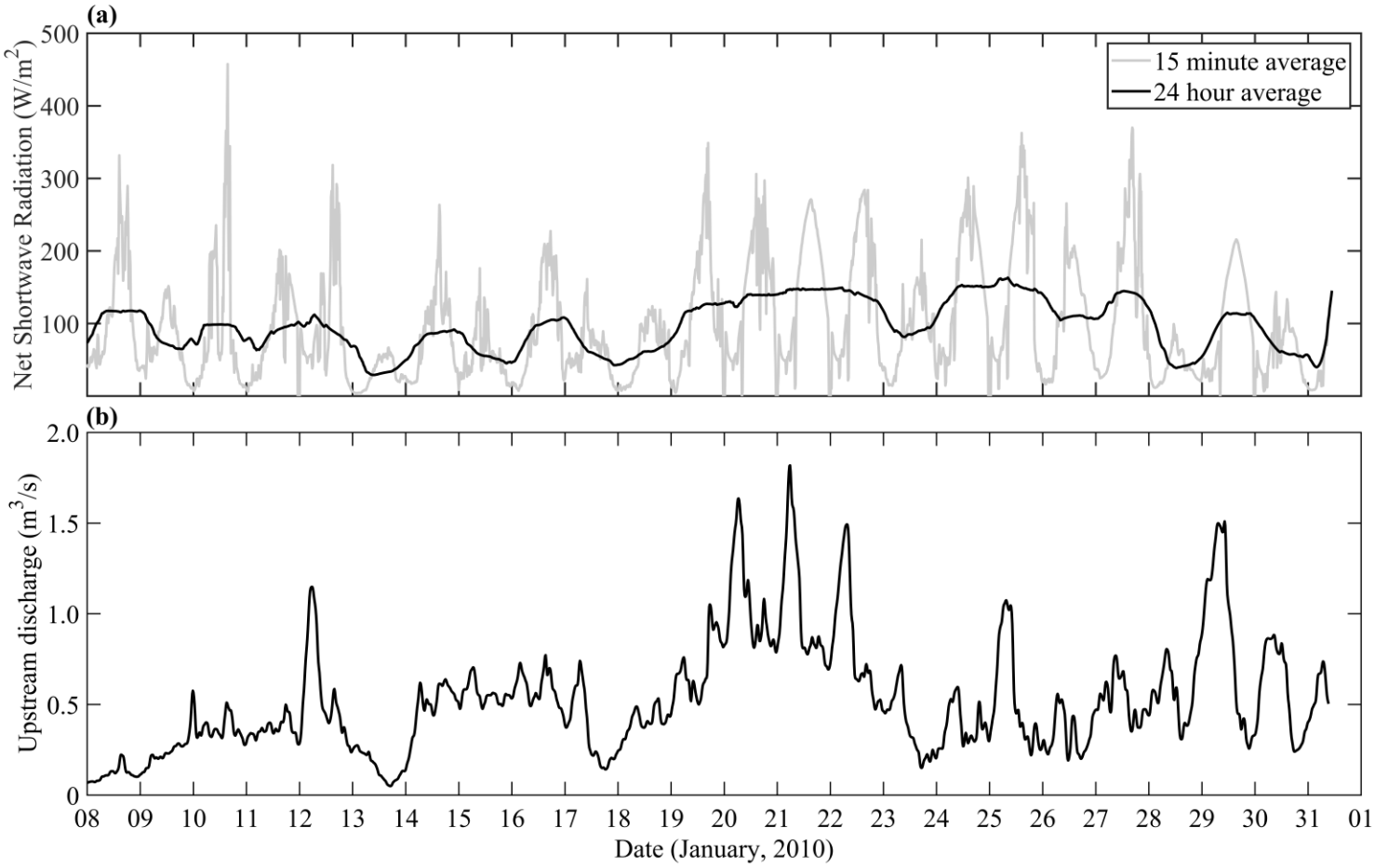

Figure 2-2: (a) Net shortwave radiation on the Joyce Glacier at 15 minute and 24 hour running averages. (b) Discharge rates at the "upstream" (Holland Stream) monitoring site during the study period.

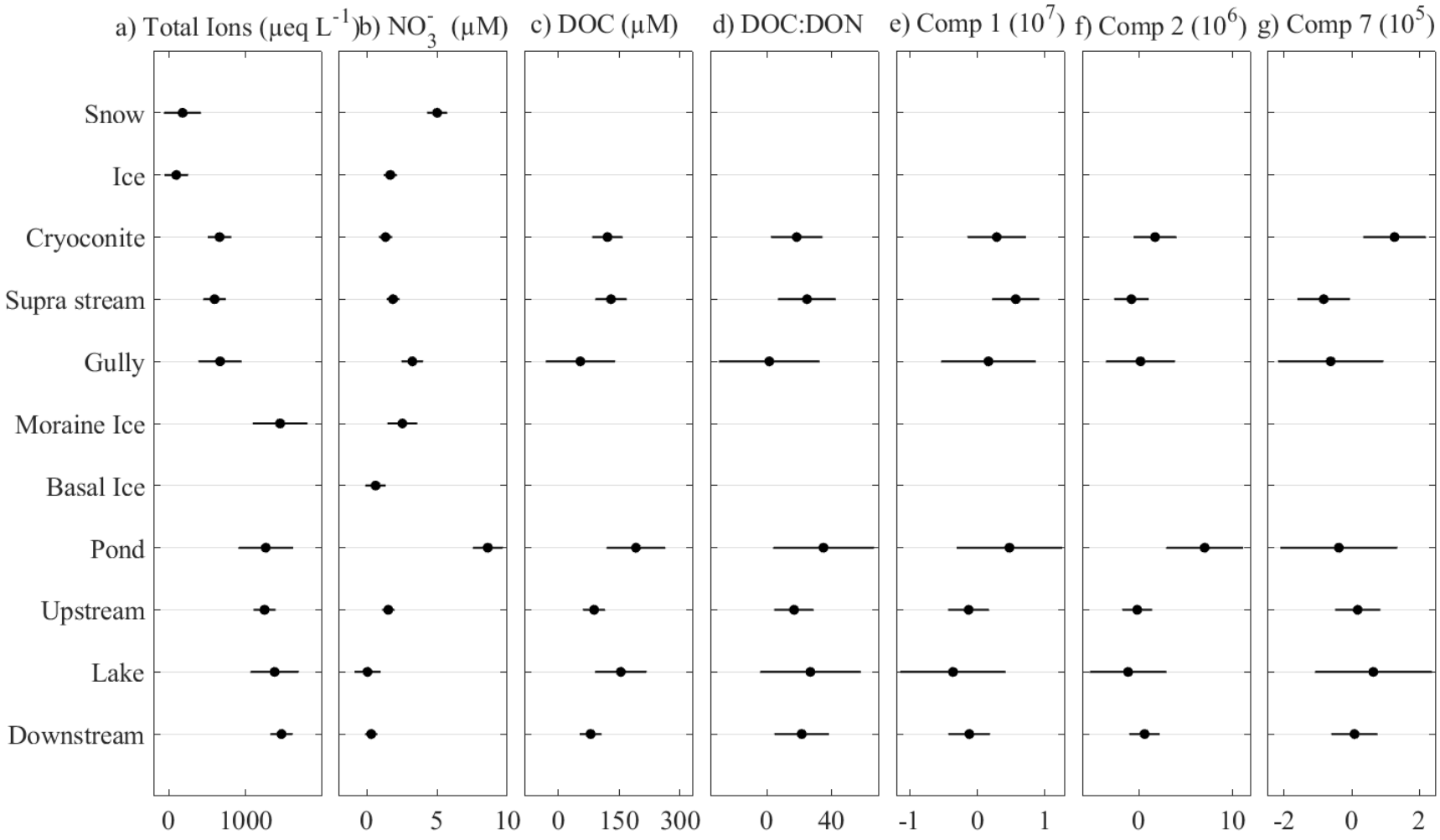

Figure 2-3: ANOVA with Tukey's range test for various biogeochemical parameters along the flow path. Circles represent the mean and lines indicated the 95% confidence intervals

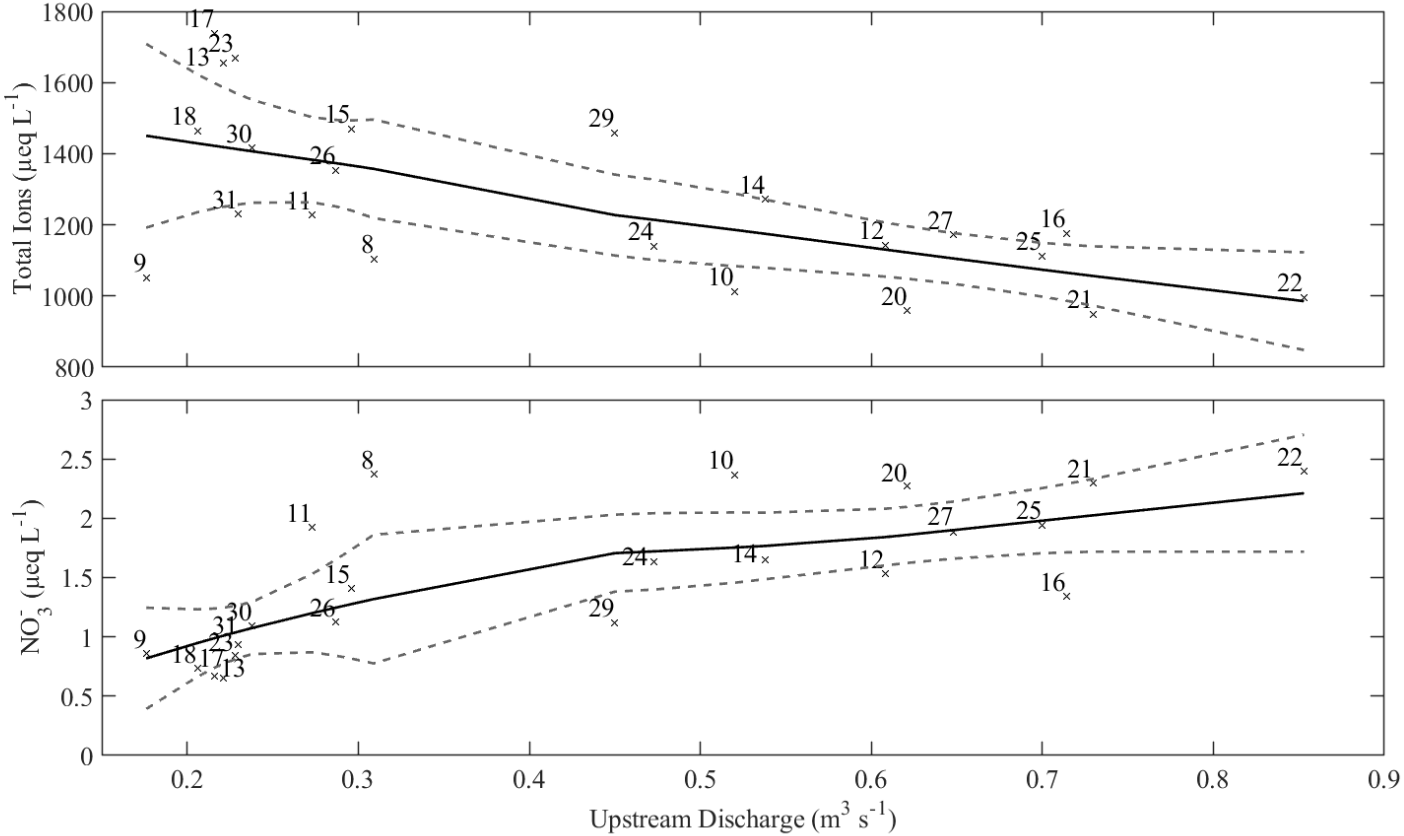

Figure 2-4: Concentration and fluxes of total ions (top) and nitrate (bottom) in the Holland Stream (Upstream Site). x represent the concentrations measured in samples vs the discharge in the stream at the time of sampling and the number corresponds to the day of month for each data point. The black solid line represents the concentration-discharge relationship determined via LOWESS smoothing, and the dashed grey line indicates the confidence intervals (calculated as ± two times the standard deviation of 1000 LOWESS curves derived by bootstrapping).

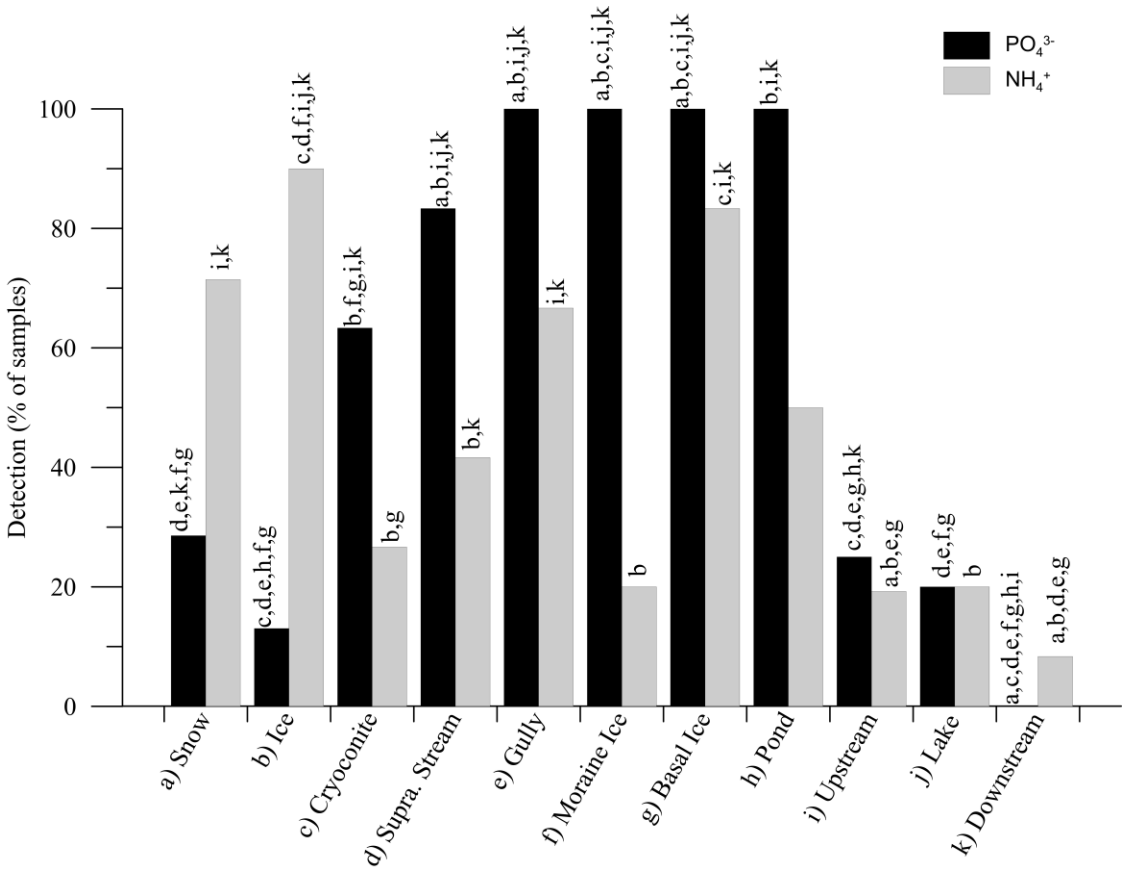

Figure 2-5: Percentage of samples above the PO_4^{3-} and NH_4^+ detection limits. Letters above each bar indicate significant differences with other environments. Significance was determined using Fisher's exact test (FET) and $p<0.05$.

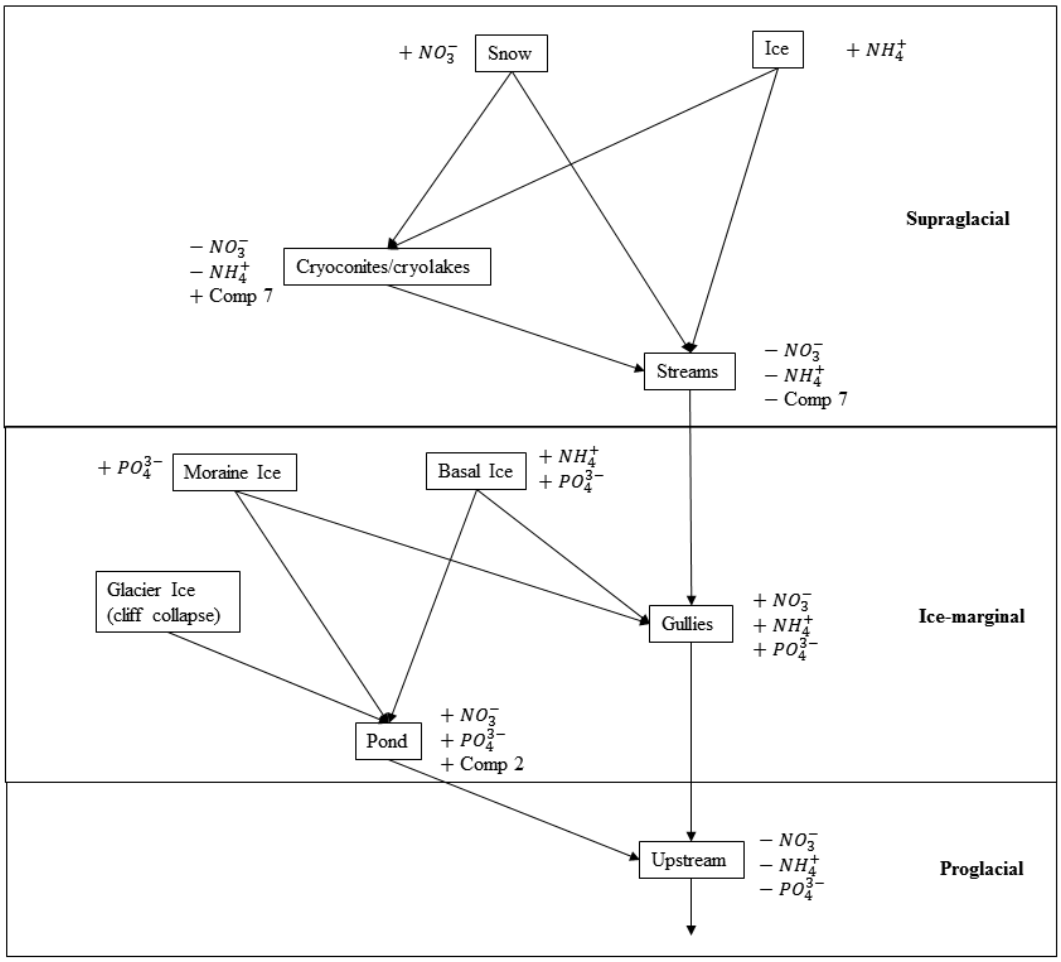

Figure 2-6: Summary of the sources and sinks for organic and inorganic nutrients in the supraglacial, ice-marginal and proglacial environments. Arrows indicate flow paths, "+" indicate sources, "-" indicate sinks.

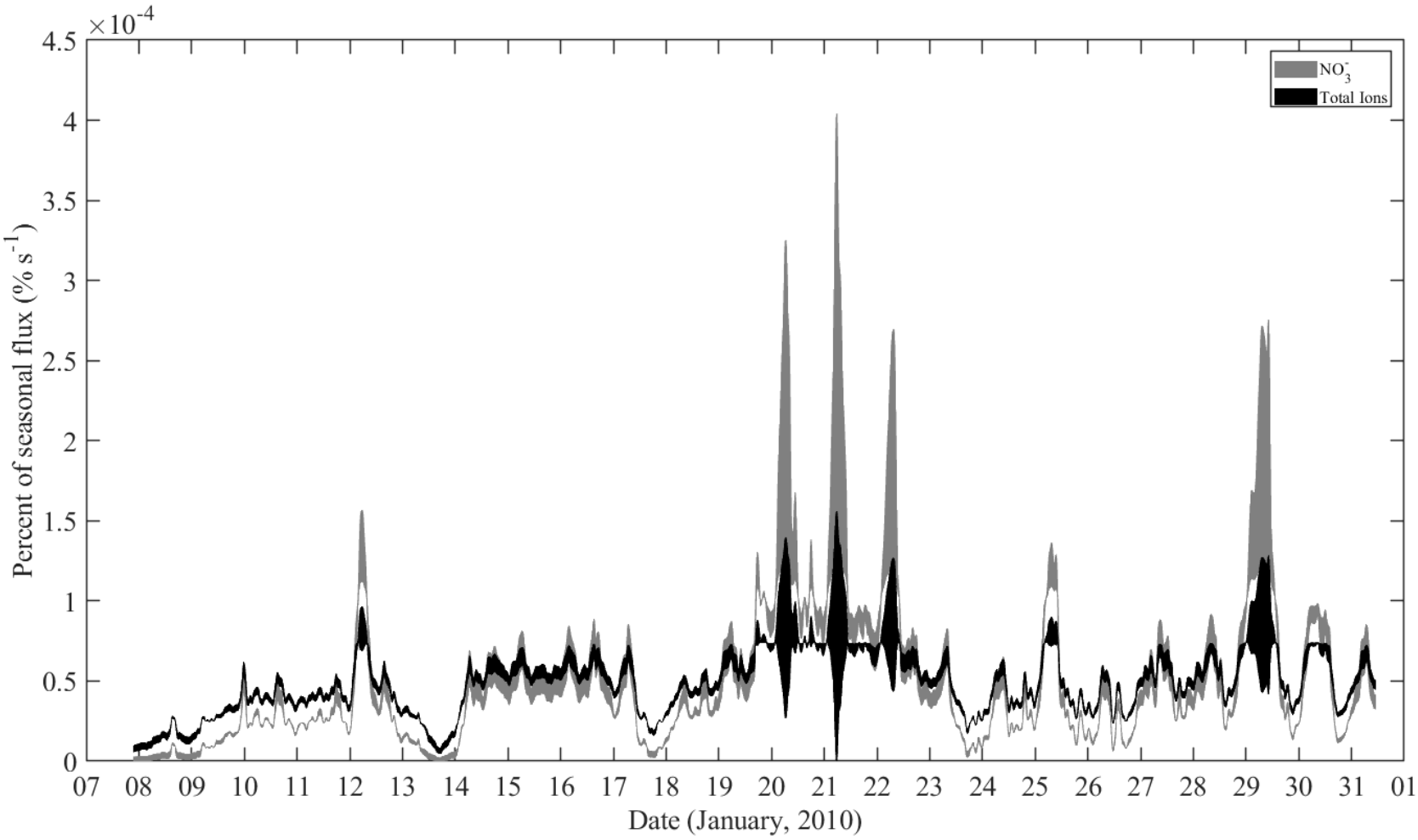

Figure 2-7: Estimated total ion and NO_3^- fluxes in the Holland Stream (Upstream site) over the study period. Ranges were calculated using the upper and lower confidence intervals presented in Figure 2-4.

Chapter 3: Hydrological controls on glacially exported microbial assemblages

3.1 Abstract

The Greenland Ice Sheet (GrIS) exports approximately 400 km^3 of freshwater annually to downstream freshwater and marine ecosystems. These meltwaters originate in a wide range of well-defined habitats that can be associated with very different physical environments within the ice sheet, ranging from oxygenated surface environments that are exposed to light and supplied with nutrients from atmospheric/aeolian sources to subglacial environments that are permanently dark, isolated from the atmosphere, and potentially anoxic. Hydrological conditions in the latter likely favour prolonged rock-water contact. The seasonally-evolving hydrological system that drains meltwaters from the GrIS connects these distinct microbial habitats and exports the microbes contained within them to downstream ecosystems. The microbial assemblages exported in glacier meltwater may have an impact on downstream ecosystem function and development. We explored how the seasonal development of a glacial drainage system influences the character of microbial assemblages exported from the GrIS by monitoring the seasonal changes in hydrology, water chemistry and microbial assemblage composition of meltwaters draining from a glacier in Southwest Greenland. We found that the microbial assemblages exported in meltwaters varied in response to glacier hydrological flow path characteristics. Whether or not meltwaters passed through the subglacial environment was the first-order control on the composition of the microbial assemblages exported from the glacier, while water source (i.e. supraglacial or extraglacial) and subglacial residence time were second-order controls. Glacier hydrology therefore plays a fundamental role in determining the microbial exports from glaciated watersheds.

3.2 Introduction

Once thought to be devoid of active microbial life, glacier systems are now known to harbour productive and diverse microbial assemblages [*Anesio and Laybourn-Parry*, 2012; *Boetius et al.*, 2014] that can be exported to downstream ecosystems in meltwater. The microbial exports from glacier systems can influence downstream ecosystem processes [e.g. *Battin et al.*, 2004], biodiversity [*Wilhelm et al.*, 2013], and the biogeochemistry [*Logue et al.*, 2004; *Battin et al.*, 2009; *Singer et al.*, 2012] and microbial ecology of fjord surface waters [*Gutiérrez et al.*, 2014; *Cameron et al.*, 2016]. The microbial characteristics of glacier runoff is of importance since downstream ecosystems support particularly high rates of primary productivity [*Rysgaard et al.*, 2012], contain genetically isolated populations [*Sköld et al.*, 2003], function as refugia for cold-water species [*Węsławski et al.*, 2011], and are important feeding grounds and critical habitats for a number of marine mammals and seabirds [*Kuletz et al.*, 2003; *Mathews and Pendleton*, 2006; *Arimitsu et al.*, 2012].

Some of the best documented microbial glacier habitats are those that are present on the glacier surface in wet snow, cryoconite holes, supraglacial lakes and streams (supraglacial environment) [*Hodson et al.*, 2008], and at the glacier bed in the pore waters of saturated till, water-filled cavities, and large subglacial channels and lakes (subglacial environment) [*Tranter et al.*, 2005; *Christner et al.*, 2014]. These habitats vary widely in terms of physical conditions, including the presence/absence of light energy and meltwater, the type/quantity of sediment available, allochthonous input of nutrients and microbes, redox conditions, temperature, seasonality, and meltwater residence times. These physical differences can give rise to site-specific microbial assemblages and biogeochemical processes. The most notable difference in microbial assemblages is the presence of photosynthetic species in the supraglacial environment [*Anesio et al.*, 2009;

Hodson et al., 2010b] and chemosynthetic organisms in the permanently dark, sediment-rich subglacial environment [*Boyd et al.*, 2014; *Christner et al.*, 2014]. However, even within the subglacial environment, microbial assemblages consist of both locally distinct [*Bhatia et al.*, 2006; *Lanoil et al.*, 2009] and globally distributed species [*Foght et al.*, 2004; *Tranter et al.*, 2005; *Bhatia et al.*, 2006; *Lanoil et al.*, 2009].

The hydrological networks that exports the ~400 km^3 of meltwater from the GrIS to coastal environments each year [*Tedesco et al.*, 2013] evolve over the course of a melt season and dictates the proportion of water that is exported from microbial habitats within the supraglacial and subglacial systems, and the meltwater residence times in each. Most surface meltwater on the GrIS is derived from snow and ice melt on the glacier surface (supraglacial environment), where it may be routed through snow and firn, cryoconite holes, and/or supraglacial or ice-marginal lakes and streams. In these environments, microbial cells and nutrients are largely supplied by atmospheric/aeolian sources, and organisms are exposed to light. While some regions of the GrIS are cold-based, and supraglacial meltwater drains directly into the proglacial system, polythermal outlet glaciers draining the GrIS are believed to have similar hydrology to that of smaller, temperate and polythermal alpine glaciers [*Bartholomew et al.*, 2011; *Bhatia et al.*, 2011; *Chandler et al.*, 2013]. In these systems, the accumulation of summer meltwaters on the glacier surface can induce the hydrologically-driven propagation of fractures and initiate connections between the surface and bed of the glacier via crevasses and moulins [*Boon and Sharp*, 2003], and drive the seasonal development of subglacial drainage.

The subglacial drainage system of polythermal glaciers drainage the GrIS, can include permanent elements as well as elements that form, grow, and change structure over the course of a melt season and then collapse over winter. There are two endmembers of subglacial drainage

system structure, “distributed” and “channelized” networks [*Fountain et al.*, 1998, and references therein]. “Distributed” or multi-thread drainage networks dominate the subglacial environment in the winter and early in the melt season, when runoff is largely derived from basal melt (from geothermal or frictional heat), groundwater, and/or water stored at the bed in a preceding summer. Such networks typically lack large, well-defined channels and water passes through them relatively slowly following inefficient pathways where it is under high pressure (Fountain et al., 1998). These pathways include water films, till porewaters, and poorly inter-connected, water-filled cavities.

Large channels develop and form a more efficient “channelized” drainage system as the flux of supraglacial meltwater delivered to the glacier bed increases during the melt season. These systems receive meltwaters from both the supraglacial environment and regions of the bed with distributed drainage, and promote rapid transit to the terminus [*Chandler et al.*, 2013]. Efficient hydrological connectivity with the glacier surface allows channelized drainage systems to experience weather-related or diurnal discharge-related fluctuations in water pressure, which can result in reversals of the pressure gradient between the channelized and distributed drainage systems and bi-directional exchanges of water between the two systems [*Hubbard et al.*, 1995].

We hypothesized that seasonal changes in both hydrological routing and water sources would yield strong intra-seasonal differences in the makeup of microbial assemblages exported from the GrIS to downstream ecosystems in meltwaters. Here, we examine how the seasonal evolution of meltwater sources and subglacial drainage system properties affects the character of the microbial assemblages exported in runoff from a sector of the Greenland Ice Sheet (GrIS). We monitored meltwater discharge, hydrochemistry, and the composition of the microbial assemblages contained in waters exiting the GrIS throughout a single melt season. We found a

significant change in the microbial assemblage composition exported in meltwaters as they were routed through the subglacial system. In addition, microbial assemblages in the proglacial stream became more similar to those in ice sheet surface waters as a more efficient, channelized subglacial drainage system developed, and as high channel discharges and water pressures restricted export of waters and microbes from the distributed component of the subglacial drainage system.

3.3 Methods

3.3.1 Field site

Kiattuut Sermiat (KS; Figure 3-1) is a 36 km^2 glacier in southern Greenland that terminates on land approximately 9 km from Tunulliarfik Fjord [*Hawkings et al.*, 2016]. The glacier is located in a mountainous region with a bedrock geology dominated by crystalline granite and diorite, pyroxene-biotite monzonite, and basaltic intrusions [*Henriksen et al.*, 2009]. The surrounding landscape contains podzolic soils [*Jones*, 2010] which support a vegetation cover of lichens, shrubs, sedges, and herbs. KS has an active subglacial drainage system fed by runoff from both the glacier surface and surrounding hills. It currently terminates in a small proglacial lake (0.5 km^2).

3.3.2 Sample collection and processing

Fieldwork was completed at KS from May 1 to August 9, 2013 and, in summary, included 1) continuous hydrometric monitoring (water level and electrical conductivity, EC) on the proglacial stream, 2) daily biogeochemical (major ions, nutrients, pH and EC) and suspended sediment sampling on the proglacial stream, 3) microbial (~bi-weekly) sampling of the proglacial stream, and 4) microbial and biogeochemical spot-sampling of waters from cryoconite holes and both supraglacial and extraglacial (draining non-glaciated upland areas) streams (Figure 3-1).

A continuous discharge record was generated for the KS proglacial stream using multiple water level loggers (two HOBO® Onset water level loggers and two Druck wired pressure transducers), installed in the upper 3 km of the river. Water level data at 10 minute intervals were converted to discharge estimates using a rating curve generated from 51 instantaneous discharge measurements derived from rhodamine dye-dilution experiments as described by Bartholomew et al. [2011] and Hawkings et al. [*Hawkings et al.*, 2016]. Temperature-compensated electrical conductivity **(**EC) records were collected using Campbell Scientific sensors with 10 minute resolution. pH was measured continuously using an ISFET (ion-selective field-effect transistor) Honeywell Durafet® pH sensor, calibrated monthly using low ionic strength pH 4.01 and pH 6.96 Reagecon buffers. The pH and EC of discrete samples were measured using a Beckman Coulter ϕ 470 series handheld meter with the pH sensor calibrated daily using NIST-certified Fisherbrand™ pH 7 and 10 buffers.

Proglacial meltwater samples were collected daily using a three-times sample-rinsed 1 L HDPE bottle (Nalgene®). This water was used for analyses of suspended sediment concentration, dissolved organic carbon (DOC), dissolved phosphorus species (dissolved inorganic phosphorus (DIP) and dissolved organic phosphorus (DOP)), dissolved nitrogen (NO_3^-, NH_4^+ and dissolved organic nitrogen (DON)), and major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, and F^-). Additional samples were collected from the supraglacial and extraglacial environments throughout the melt season. Separate collection bottles were used for each sample site. For suspended sediment concentration, a known water volume was filtered through a pre-weighed 47 mm 0.45 um Whatman® cellulose nitrate filter paper using a polyethersulfone filtration unit (Nalgene®). Papers were later oven dried overnight and re-weighed. Samples for analysis of $\delta^{18}O$, $\delta^{2}H$, and DOC were filtered through a 0.7 μm sample-rinsed syringe filter (Whatman® GD/X filter with

GF/F membrane), and collected into either a dry 1.5 ml Chromacol™ glass vial (isotopes), or a pre-combusted and three-times sample-rinsed 30 ml borosilicate glass vial (DOC). Samples for DIP, DOP, NH_4^+ and NO_3^- were filtered through 0.45 µm syringe filters (Whatman® GD/XP polyethersulfone) into three-times sampled-rinsed 30 mL HDPE bottles (Nalgene®) and stored frozen near -20ºC until analysis [*Hawkings et al.*, 2016]. Similarly, major ion samples were filtered through 0.45 µm syringe filters (Whatman® GD/XP polyethersulfone) into three-times sample-rinsed plastic 30 ml HDPE Nalgene® bottles, but were refrigerated until analysis.

Samples for microbial analyses were collected in sterile Nasco Whirl-Pak™ sample bags and filtered within 2 hours through a three-times sample- rinsed glass filtration kit and a Pall Supor® 47mm diameter, 0.2 µm pore size, sterile filter paper. The filter paper was retrieved using acid-washed and rinsed forceps and placed into an autoclave-sterilized Eppendorf tube with 1 ml RNALater (Qiagen). Samples were frozen immediately and stored at -20ºC until analysis.

3.3.3 Chemical indices

Differences in the geochemical histories of waters emerging from the glacier were detected using four simple chemical indices:

Equation 3-1
$$D:M = \frac{(Ca^{2+}+Mg^{2+})}{(Na^{+}+K^{+})}$$

*Where concentrations are in µeq L^{-1}

Equation 3-2
$$SMF = \frac{SO_4^{2-}}{(SO_4^{2-}+HCO_3^{-})}$$

*Where concentrations are in µeq L^{-1}

Equation 3-3
$$\rho CO_2 = \log_{10}[HCO_3^-] - pH + K_H + K_1$$

*Where concentrations are mol, K_H is $10^{-1.12}$ mol L^{-1} amt $^{-1}$ and $K_1 = 10^{-6.6}$ mol L^{-1} amt $^{-1}$

(i) the ratio of divalent to monovalent cations (D:M; Equation 3-1), which is a proxy for the relative contributions of silicate and carbonate weathering to the total solute load. Na^+ and K^+ are assumed to be derived primarily from silicate weathering, and Ca^{2+} and Mg^{2+} primarily from carbonate weathering [*Tranter et al.*, 2002; *Wadham et al.*, 2010]. Silicate weathering has relatively slow reaction kinetics and is thought to occur primarily in the distributed drainage system, while carbonate weathering, which has relatively rapid reaction kinetics, dominates the solute load of waters that pass rapidly through the channelized system [*Tranter et al.*, 2002]. As a result, waters from distributed drainage networks typically yield low divalent to monovalent cation ratios while those from channelized drainage systems typically yield high divalent to monovalent cation ratios [*Wadham et al.*, 2010].

(ii) the sulphate mass fraction of the total anion load (SMF; Equation 3-2), provides a measure of the fraction of HCO_3^- that is derived from sulphide oxidation coupled with carbonate dissolution. As meltwaters from distributed drainage networks have more prolonged access to freshly comminuted reactive sulphide minerals than waters from channelized systems they typically have higher SMF values than those from channelized drainage networks [*Wadham et al.*, 1998, 2004; *Tranter et al.*, 2002]. Sulphide oxidation coupled with carbonate dissolution (Equation 3-1) results in SMF = 0.5. Carbonation reactions (where aqueous CO_2 provides the proton source Equation 3-2) dominate weathering in channelized systems where meltwater residence times are short and result in SMF < 0.5. Sulphide oxidation coupled with silicate weathering and/or precipitation of carbonate (Equation 3-3) yields SMF > 0.5.

(iii) the partial pressure of CO_2 with which the waters appear to be in equilibrium (ρCO_2 ; Equation 3-3) provides a measure of the degree to which waters appear to be in equilibrium with atmospheric CO_2 and indicates the balance between CO_2 diffusion into/out of solution and the rate

of CO_2 drawdown via chemical weathering processes [*Raiswell*, 1984; *Raiswell and Thomas*, 1984]. Waters in equilibrium with atmospheric CO_2 have a ρCO_2 of $10^{-3.5}$ atm. Higher ρCO_2 values are possible if the rate of proton supply exceeds the rate of consumption, for example if there is an additional source of H^+ beyond the dissolution of atmospheric CO_2 in water (e.g. from oxidation of organic carbon or sulphide minerals). In contrast, lower ρCO_2 values occur when rates of CO_2 consumption by chemical weathering processes exceed rates of CO_2 diffusion into solution [*Sharp*, 1991]. Differences in proton supply and consumption between distributed and channelized systems tend to suggest that high ρCO_2 waters are characteristic of distributed systems, while low ρCO_2 waters are associated with channelized systems.

(iv) the EC of meltwaters is a proxy for the solute concentration in meltwaters. EC tends to be higher in distributed drainage networks, where prolonged contact between water and highly reactive minerals yields higher solute concentrations, and lower in dilute supraglacial and channelized subglacial systems where the duration of rock-water contact is limited.

3.3.4 Analytical procedures

Major cation (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anion (Cl^-, NO_3^-, SO_4^{2-}) concentrations were measured using a Thermo Scientific™ Dionex™ capillary ICS-5000 fitted with simultaneous anion and cation columns, with HCO_3^- estimated as the charge deficit [*Hawkings et al.*, 2015].DOC and TN were measured via high-temperature combustion (680ºC) using a Shimadzu TOC-V_{CSN}/TNM-1 analyzer. DIP and DOP were measured using a LaChat QuickChem® 8500 series 2 flow injection analyzer as in Hawkings *et al*. [*Hawkings et al.*, 2016] with DOP determined after acid persulfate digestion. NH_4^+ was also measured using a LaChat QuickChem® 8500 series 2 flow injection analyzer, as described by Wadham *et al.* [*Wadham et al.*, 2016]. Oxygen and

hydrogen isotopes were measured using a Los Gatos Research liquid-water isotope analyzer following the procedure described by Lis et al. [*Lis et al.*, 2008].

DNA extraction from preserved filters was performed using a FastDNA® SPIN KIT following the manufacturer's protocol. DNA was extracted from duplicate filter papers collected from each sampling site, and combined prior to library preparation. Library construction included a two-step PCR protocol designed to prepare amplicons for IonTorrent Personal Genome Machine sequencing. In the first step, the V3 variable region was targeted using a 341 forward primer (5' -CCTACGGGAGGCAGCAG- 3') carrying a universal GLENN tag (5' -CAGTCGGGCGTCATCA- 3'; developed by Travis Glenn, http://www.gvsu.edu/dna/universal-primer-tag-6.htm), and a 518 reverse primer (5' -ATTACCGCGGCTGCTGG- 3') carrying a trP1 adapter (5' -CCTCTCTATGGGCAGTCGGTGAT- 3'). Barcodes to allow multiplexing of samples were added in the second step, which used the matching GLENN universal tag carrying a barcoded forward primer and the matching trP1 adapter as the reverse primer. PCR conditions were as follows: 95°C for 4 minutes, followed by 10 cycles of 95°C for 15 seconds, 65°C for 30 seconds, and 72°C for 30 seconds; the next 20 cycles included 95°C for 15 seconds, 55°C for 30 seconds, and 72°C for 30 seconds; finally, the last elongation step was performed at 72°C for 10 minutes. Subsamples were mixed in equal concentrations and purified using UltraClean GelSpin DNA Extraction Kit. Samples were amplified in triplicate in the first step, combined, and amplified in triplicate and combined in the second step to control for PCR biases. Negative control blanks were extracted and processed along with the samples and no PCR product or sequences were obtained from these blanks. The subsequent sequencing protocol was performed using Ion Torrent technology with the Ion PGM™ Sequencing 200 Kit v2 with the Ion 316 Chip v2.

3.3.5 DNA sequence processing and statistical analyses

Raw sequences were processed using the Mothur 454 SOP (v. 1.33.3; http://www.mothur.org/wiki/454_SOP; [*Schloss et al.*, 2009, 2011]). Briefly, sequences were initially subject to quality control parameters that discarded those sequences (i) below a quality score of 25; (ii) shorter than 100 bp; (iii) containing primer and barcode mismatches; (iv) containing homopolymers longer than 8 bp. Alignment of sequences was performed using the SILVA reference database. Sequences were then pre-clustered for further noise reduction as recommended [*Pruesse et al.*, 2007; *Huse et al.*, 2010; *Schloss*, 2010; *Schloss et al.*, 2011]. Chimeras were removed using the UCHIME implementation within Mothur [*Edgar et al.*, 2011; *Schloss et al.*, 2011]. Operational Taxonomic Units (OTUs) were assigned using a 97% sequence similarity definition with the average-neighbor clustering algorithm. OTUs were then classified to the highest taxonomic resolution possible (i.e. phylum, class, family, and/or genus level) using the Ribosomal Database Project classifier (train set 9) with a 60% confidence threshold (RDP; http://rdp.cme.msu.edu/). Those sequences corresponding to chloroplast, mitochondria, Eukarya, or unknown were removed; furthermore, those OTUs represented by only a single sequence were removed.

Processed sequences were subsampled to lower than the smallest library size to allow identical sequencing depth for each sample before further alpha and beta diversity analyses [*Gihring et al.*, 2012]. For the complete dataset (supraglacial, extraglacial and proglacial samples), each sequence dataset was subsampled to 1000 sequences, while for the sample group including only the proglacial samples, each sequence dataset was subsampled 2500 sequences.

Taxon (OTU) richness was measured in Mothur using observed richness and estimated richness with Chao1 non-parametric richness estimator; overall diversity was estimated using

inverse Simpson's index (1/D) as well as the Shannon diversity index (H), which are non-parametric diversity estimators that consider both species richness and species evenness [*Shannon*, 1947; *Simpson*, 1949; *Chao*, 1984; *Chao and Shen*, 2003].

Beta diversity was examined using PC-ORD (version 6; McCune & Grace, 2002) where changes in bacterial assemblage composition were visualized using nonmetric multidimensional scaling (NMS) ordination using 100 runs of real data. To determine if axes created were significantly better than would be obtained by chance, a Monte Carlo test of 100 runs on randomized data was also performed. Based on three distinct hydrological periods, we grouped samples in the NMS ordination into "Early Season", "Transition Period", and "Late Season" groups and determined whether there were significant changes in assemblage composition between these groups using the multi-response permutation procedure (MRPP; McCune & Grace, 2002). Three statistical values are obtained in MRPP analysis: the test statistic (T) describing separation between groups, where greater separation is implied as values become more negative; within-group agreement (A), which is a chance-corrected value where A=0 when within-group heterogeneity equals that expected by chance, A<1 when within-group heterogeneity is greater than expected by chance, A=1 (max value) when all samples within a group are identical; MRPP also produces a p value for overall and multiple comparisons [*McCune et al.*, 2002].

The relationship between physical/chemical variables and changes in bacterial assemblage composition were determined in PC-ORD using Mantel tests; Mantel tests were conducted using independent runs for each environmental parameter. To determine specific changes in biogeochemical or microbial parameters, we used ANOVA with Tukey's post hoc HSD for multiple comparisons.

3.4 Results

3.4.1 Hydrology/hydrochemistry

Three distinct hydrological periods were defined on the basis of major shifts in the discharge, electrical conductivity, suspended sediment content, and chemical composition of the proglacial stream waters at KS. We use these shifts to define three distinct runoff periods that we refer to as the Early Season, Transition Period, and Late Season (Figure 3-2). Although there is some variability in the exact dates on which distinct shifts in each parameter occur, the shifts are present in all records and, in each case, are synchronous to within a 2-day period (Figure 3-2).

The Early Season (prior to June 6) was characterized by low proglacial discharge (<10 m^3s^{-1}) with little diurnal variability, even though daytime high air temperatures were above 0ºC and there was a strong diurnal air temperature signal. The chemistry of these waters was distinct from that of waters leaving the glacier in subsequent periods. It is characterised by the lowest average ratio of divalent to monovalent cations (5.91) and the highest mean values of SMF (0.16), ρCO_2 ($10^{-3.90}$ atm), and EC (49.6 µS cm^{-1}; ANOVA, $p<0.05$), indicating long transit times. Only during this period did suspended sediment concentrations increase consistently over time (from ~0.04 g L^{-1} to ~ 0.22 g L^{-1}).

The Transition Period lasted from June 7 to ~June 26. Its onset was marked by a "spring event" [*Mair et al.*, 2004], including a distinct peak in discharge (43 m^3 s^{-1}) and suspended sediment concentration (0.22 g L^{-1}) (Figure 3-2). Waters draining from the glacier during this interval showed a consistent increase in the ratio of divalent to monovalent cations (5.59 to 6.81), and consistent decrease in ρCO_2 ($10^{-4.36}$ to $10^{-5.20}$ atm), SMF (0.18 to 0.08) and EC (39.7 to 24.6 µS cm^{-1}) (Figure 3-2), indicating that meltwater residence times decreased as the flux of dilute supraglacial meltwaters increased.

The Late Season extended from ~June 26 to the end of sampling in early August. Discharge reached a seasonal peak in mid-July (64 $m^3 s^{-1}$) in response to the high daytime temperatures (Figure 3-2) and then receded (to 25 $m^3 s^{-1}$ in mid-August). Throughout this period, clear diurnal variations in discharge were superimposed upon longer-term trends. Suspended sediment concentrations generally decreased over time, from 0.15 g L^{-1} to 0.09 g L^{-1}, as in the Transition Period. Late Season waters had chemical signatures distinctly different from highest average ratio of divalent to monovalent cations (7.32), and the lowest average values for ρCO_2 ($10^{-5.23}$ atm), SMF (0.078) and EC (22.2 μS cm^{-1}) (ANOVA, $p<0.05$), indicating a strong influence of surface waters and short subglacial residence times.

3.4.2 Microbiology

To estimate coverage of diversity, Good's coverage indicated high coverage within all samples collected, with the lowest sample having 84% coverage (data not shown). However, we propose some caution with respect to these results as both rarefaction analysis and the relatively high number of Chao1 estimated OTUs compared to observed OTUs imply increased sampling may lead to discovery of new OTUs and increased diversity.

Microbial assemblages in the proglacial stream waters were significantly different from those in waters sampled from the extra-glacial and supra-glacial environments throughout the melt season (Figure 3-3a, T= -12.96; A= 0.15; $p<0.001$). The composition of the microbial assemblage in the proglacial stream waters was remarkably stable throughout the melt season (Figure 3-3a). For example, the variability in microbial assemblage composition among the 21 proglacial stream samples collected over a 10-week period is approximately the same as that found among the assemblages from the 4 extraglacial stream samples that were collected over a 4-week period (Figure 3-3a). This stability in proglacial stream microbial assemblage composition occurred

despite large inferred changes in subglacial residence times, flow paths, and water sources over the melt season. These hydrological changes include a more than 100-fold increase in discharge, a 9-fold increase in suspended sediment concentration, a decrease in electrical conductivity from ~50 μS cm^{-1} to 20 μS cm^{-1}, an increase in the divalent to monovalent cation ratio from ~6 to 8, a drop in the SMF from ~0.15 to 0.07 and a drop in the partial pressure of CO_2 (ρCO_2) from ~10-4 atm to 10-5 atm (Figure 3-2).

Although microbial assemblage composition in the proglacial stream was generally stable throughout the melt season, it is possible to recognize three statistically significant clusters of microbial assemblages corresponding to the Early Season, Transition Period, and Late Season hydrological periods (MRPP; T= -10.59; A= 0.21; $p<0.001$, Figure 3-3b). The changes in microbial assemblage composition between the three periods appear to involve a shift from a "subglacial" assemblage to one more similar to assemblages from the extraglacial and supraglacial samples. The meltwater microbial assemblage composition shifted towards that of the extraglacial environment during a short period from June 6 – June 16 (the beginning of the Transition Period; Figure 3-3b, Axis 2). Another, more dramatic, shift occurred between June 16 and June 29 when the proglacial stream assemblage composition became more characteristic of the supraglacial environment (Figure 3-3b, Axis 1). These compositional shifts were associated with changes in discharge, pH, major ion content and composition (total IN, SO_4^{2-}, NO_3^-, Na^+, Mg^{2+}, K^+, HCO_3^-, F^-, Cl^-, Ca^{2+}), and $\delta^{18}O$ (Mantel tests; $p<0.001$; Figure 3-3b). There were no significant correlations with other parameters such as deuterium excess (indicative of melt-freeze processes), or the concentrations of suspended sediment, DON, DOC, DIP, or DOP. However, the occurrence of seven of the ten most dominant classified OTUs found in the proglacial waters (*Acetobacteraceae*, *Flavobacteriaceae*, *Comamonadaceae, Rhizobiaceae,* and unclassified

families belonging to the phylum *Proteobacteria*, *Actinobacteria,* and the order *Sphingobacteriales*) were significantly ($p<0.05$) and positively correlated with suspended sediment concentration.

3.5 Discussion

3.5.1 Hydrological regime

Early Season meltwaters displayed a chemical signature characteristic of both relatively long rock-water contact (e.g. silicate weathering) and weathering processes that involve reactive sediments (e.g. sulphides and carbonates). This suggests the existence of a relatively inefficient subglacial drainage system, with water sources that might include basal ice melt (from geothermal or frictional heating), supraglacial snowmelt from the current season that was routed slowly through the subglacial system, and/or meltwater from the end of the previous melt season that was retained in the subglacial environment over winter.

High runoff volumes and diurnal hydrograph signatures suggest that channelized drainage was established by the onset of the Transition Period (~June 7). The seasonal peak in suspended sediment concentration in the proglacial stream coincides with the first major peak in discharge of the melt season (Figure 3-2), suggesting that this was likely a period of high basal water pressure, reduced basal drag, increased basal motion by sliding and/or sediment deformation, and reorganization of the subglacial drainage system [*Mair et al.*, 2004; *Swift et al.*, 2005]. The water chemistry suggests a growing contribution from dilute supraglacial waters that passed rapidly through an increasingly efficient subglacial drainage system during this period. However, the stream water chemistry does show a continuing but diminishing contribution to the solute load from slow reactions and reactive minerals (such as sulphide oxidation coupled to carbonate and

silicate dissolution), suggesting drainage from areas of the bed with an inefficient distributed meltwater drainage system.

The chemical signature of Late Season waters, which began to emerge on ~June 24 and continued to do so until the end of the sampling period, suggest an increasing proportion of water draining through an efficient, channelized subglacial drainage network. These waters are likely sourced predominantly from supraglacial snow and ice melt and are routed relatively quickly and efficiently across the largely snow-free lower elevations of the glacier surface. During transit through the channelized subglacial drainage network, these relatively dilute meltwaters are involved in chemical weathering reactions, such as the carbonation of carbonates, which have relatively quick reaction kinetics and occur in the absence of proton supply from sulphide oxidation. However, there is also evidence for continued drainage from distributed elements of the subglacial drainage system throughout the Late Season. This is particularly obvious at times when surface melt inputs to the channelized drainage system were exceptionally low (e.g. between June 24 and July 5). Persistent drainage from regions of the bed with distributed drainage systems, even during seasonal peak discharge conditions, has been described previously [*Tranter et al.*, 2005] and observed elsewhere on the GrIS [*Bhatia et al.*, 2011; *Hawkings et al.*, 2016].

The Early Season, Transition Period, and Late Season subglacial drainage regimes reported here imply strong intra-seasonal variability in the sources of water and solute exported from the glacier, and in subglacial water residence times and the rock-water contact that occurs during passage through the glacier. These hydrological characteristics are typical of many warm-based and polythermal glacier systems, and are consistent with observations elsewhere on the GrIS [*Bartholomew et al.*, 2010, 2011; *Bhatia et al.*, 2011; *Chandler et al.*, 2013].

3.5.2 First-order control on exported microbial assemblages: subglacial drainage

The proglacial stream at KS had microbial assemblages that differed significantly from those found in supraglacial and extraglacial source waters, suggesting that the passage of water through the subglacial environment was a first-order control on the microbial assemblages exported from the glacier. The microbial assemblages in proglacial stream waters remain distinct from source waters (i.e. extraglacial and supraglacial), even during periods of high discharge in the late season when meltwaters were routed relatively quickly through the subglacial system. Therefore, changes in the microbial assemblages contained in meltwaters as they were routed from the supraglacial system through the subglacial system must have also occurred relatively rapidly. Changes in the microbial assemblages contained in meltwater in the subglacial environment likely resulted from the mixing of surface-derived waters with subglacial delayed-flow waters that were routed slowly through distributed drainage networks. The microbial contributions from delayed-flow waters are likely to contain both distinct microbial assemblages and high microbial abundances [*Sharp et al.*, 1999; *Foght et al.*, 2004].

Areas of the glacier bed away from major channels provide microbial habitats that are permanently dark and cold, relatively isolated from the atmosphere, and which allow prolonged rock-water contact. These environments support psychrotolerant or psychrophilic organisms that acquire nutrients and energy from reactions involving minerals or organic compounds derived from both underlying and entrained debris and bedrock [*Sharp et al.*, 1999; *Bottrell and Tranter*, 2002; *Foght et al.*, 2004; *Wadham et al.*, 2008, 2012], which is different from those found in surface environments where light and oxygen are more abundant. Remote areas of the bed may tend towards anoxia because oxidation of sulphides and organic matter can consume the oxygen available in these relatively closed systems [*Wadham et al.*, 2012]. As a result subglacial

environments host microbial species capable of nitrate, iron, or sulphate reduction and methanogenesis [*Skidmore et al.*, 2000; *Boyd et al.*, 2010; *Yde et al.*, 2010; *Stibal et al.*, 2012a; *Wadham et al.*, 2012; *Telling et al.*, 2015].

Entrainment of distinctive microbes that reside in both sediments and water within the subglacial system may change the composition of the microbial assemblage in emergent meltwaters. While glacier ice, snow, cryoconite hole waters, and supraglacial stream water typically contain bacterial cell concentrations on the order of 10^4 cells ml^{-1} [*Säwström et al.*, 2002; *Foreman et al.*, 2007; *Anesio et al.*, 2010], basal ice and subglacial water can contain cell concentrations 1-2 orders of magnitude higher [*Karl et al.*, 1999; *Sheridan et al.*, 2003; *Gaidos et al.*, 2004; *Skidmore et al.*, 2005]. More than 0.03 g L^{-1} sediment was acquired by meltwaters in the subglacial environment at KS and subglacial microbial concentrations are positively correlated with sediment concentrations in basal ice and meltwater [*Sharp et al.*, 1999] and are orders of magnitude higher in subglacial sediment than in basal ice [*Sharp et al.*, 1999; *Foght et al.*, 2004; *Tung et al.*, 2006]. At other sites, the GrIS subglacial environment hosts between 10^5 cells g^{-1} sediment [*Lawson*, 2012] and up to the equivalent of 10^{11} cells g^{-1} dry weight silt [*Tung et al.*, 2006]. Thus, entrainment of even small concentrations of subglacial water and/or sediment likely strongly influences the composition of the proglacial stream microbial assemblage.

3.5.3 Second-order control on exported microbial assemblages: source water and subglacial residence time

Despite the remarkably consistent microbial assemblage composition of proglacial stream waters at KS, there is still significant seasonal variability ($p<0.001$; Figure 3-3b). Although this variability is relatively small compared to the changes that occur as supraglacial or extraglacial

waters are routed through the subglacial system, it does suggest a second-order control on the nature of the microbial assemblages exported from KS.

Two independent lines of evidence suggest that seasonal variability in microbial exports from KS is a response to changes in the sources, flow routing and subglacial residence time of emerging meltwaters. First, changes in microbial assemblage composition were significantly correlated with changes in pH, discharge rate, $\delta^{18}O$, EC, and major ion composition (Figure 3-3b), which are proxies for water sources and/or subglacial residence time. Second, the microbial assemblage found in Early Season proglacial stream waters was most distinct from the assemblages found in supraglacial and extraglacial waters, and it become more similar to that of extraglacial waters during the Transition Period, and to supraglacial waters during the Late Season (Figure 3-3a). These shifts are consistent with inferred changes in the relative contributions to runoff of the different water sources over the melt season. Early Season proglacial stream waters likely spent a prolonged period at the glacier bed, where viable microbial populations that are distinct from those found in supraglacial and extraglacial environments are known to exist [*Sharp et al.*, 1999; *Foght et al.*, 2004; *Skidmore et al.*, 2005; *Lanoil et al.*, 2009; *Yde et al.*, 2010]. The shift in microbial assemblage composition during the Transition Period, towards one characteristic of extraglacial waters, coincides approximately with the timing of the spring freshet, when extraglacial snowmelt inputs to the subglacial system likely peaked. The subsequent shift in microbial assemblage composition towards that typical of supraglacial waters during the Late Season coincides approximately with the timing of peak supraglacial meltwater production.

3.6 Conclusions

We used next-generation sequencing of bacterial small subunit rRNA genes to explore the microbial assemblage compositions recovered from a glacial drainage system in southwest

Greenland. Drainage through the subglacial environment significantly altered the microbial assemblages exported in meltwater. Changes in assemblage composition occurred relatively rapidly relative to the subglacial residence times (i.e. significant changes occurred even during those parts of the season with the shortest subglacial residence times) and were consistent in nature (i.e. they resulted in relatively stable microbial assemblages in the proglacial stream). These results contribute to mounting evidence that suggests the presence of an active, endogenous microbial assemblage in the subglacial environment [*Skidmore and Sharp*, 1999; *Foght et al.*, 2004; *Skidmore et al.*, 2005; *Lanoil et al.*, 2009; *Stibal et al.*, 2012a; *Wadham et al.*, 2012]. They also confirm that the subglacial environment is a strong and stable source of distinct microbial assemblages to waters that pass through it [*Cameron et al.*, 2016].

While passage (or not) through the subglacial drainage system is the first-order control on the composition of proglacial stream microbial assemblages, changes in water source and subglacial residence time have second-order effects. These explain small but significant shifts in the composition of microbial assemblages in the proglacial stream over a melt season and highlight the potential influence of water from supraglacial and extraglacial environments on the microbiology of proglacial and downstream environments. Although this study only examined the microbial assemblages exported during a single melt season from one glacier and may not represent the full range of spatial and temporal conditions on the GrIS, it does suggest a strong connection may exists between the microbial assemblages contained in proglacial stream and the hydrological regime of the glacial system.

3.7 Acknowledgements

This research was supported by an NSERC Discovery grant to M. Sharp (05234-2015), a NERC grant (NE/I008845/1) and Leverhulme research fellowship to J. Wadham, and an NSTP

grant, C/BAR grant, W. Garfield Weston Award for Northern Research, and a NSERC CGSD Award to A. Dubnick. We thank the entire field team at KS and the staff in LOWTEX laboratories at the University of Bristol. Data from this paper can be made available upon request to the corresponding author.

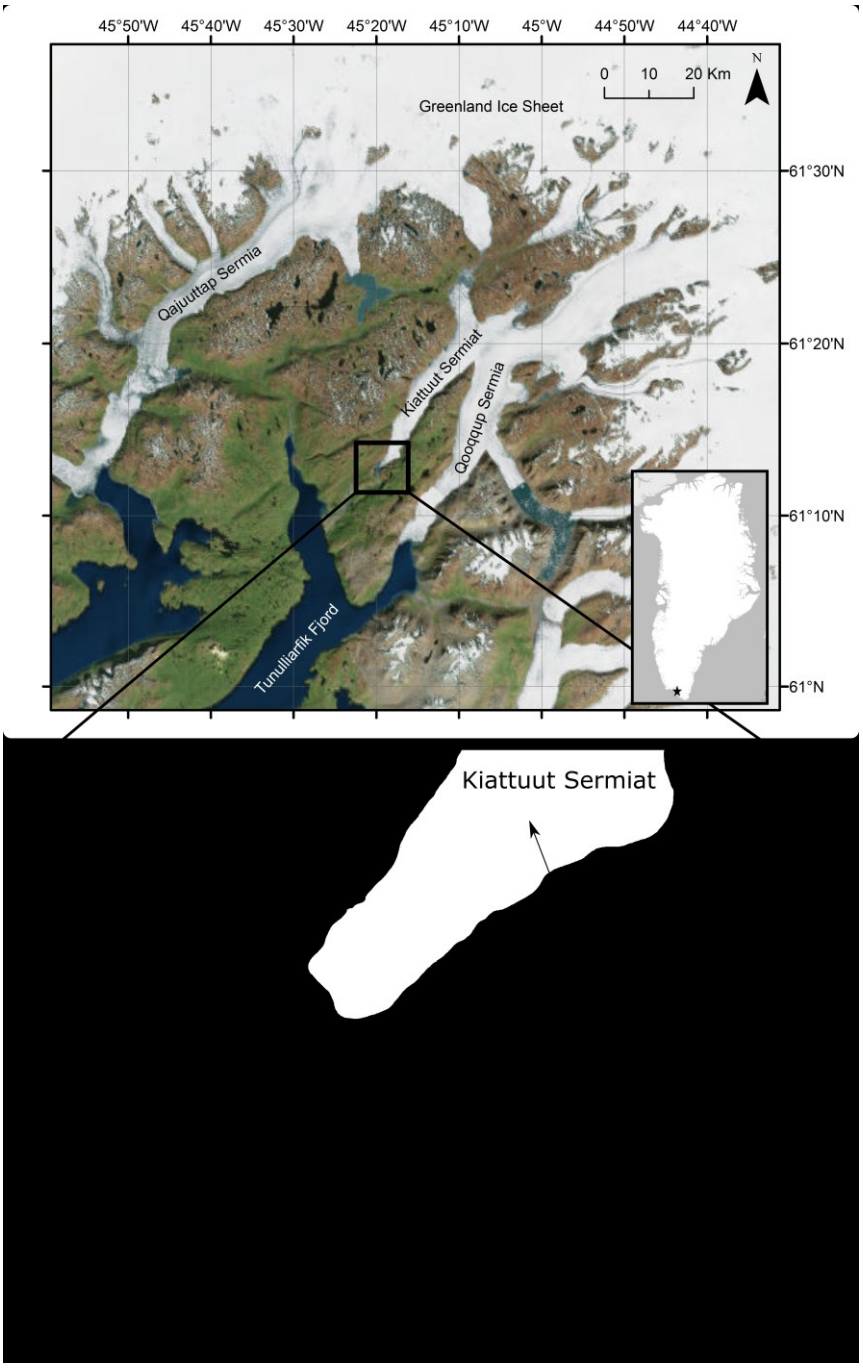

Figure 3-1: Study site including Kiattuut Sermiat (white), its proglacial lake/stream (dark grey) and extraglacial streams (black), and sample locations (italics).

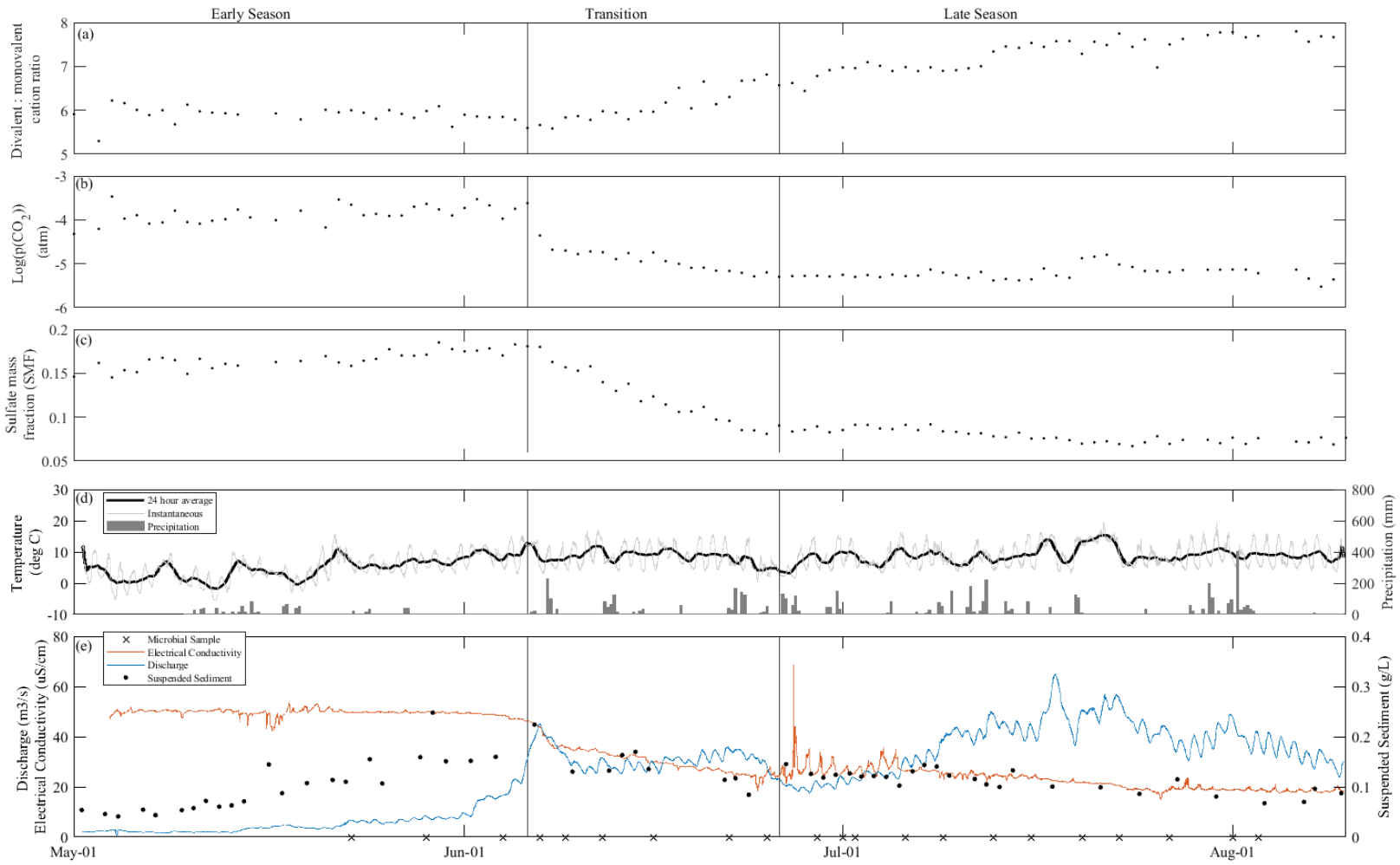

Figure 3-2: (a) Divalent (Mg^{2+}+Ca^{2+}) to monovalent (K^{+}+Na^{+}) cation ratios, (b) partial pressure of CO_2 with which the water appears to be in equilibrium (c) Sulfate mass fraction (SMF), (d) air temperature and precipitation (from Cappelen [2015]) and, (e) discharge, electrical conductivity, suspended sediment and microbial sampling dates of proglacial stream waters. Vertical lines distinguish the "Early Season", "Transition", and "Late Season" hydrological phases.

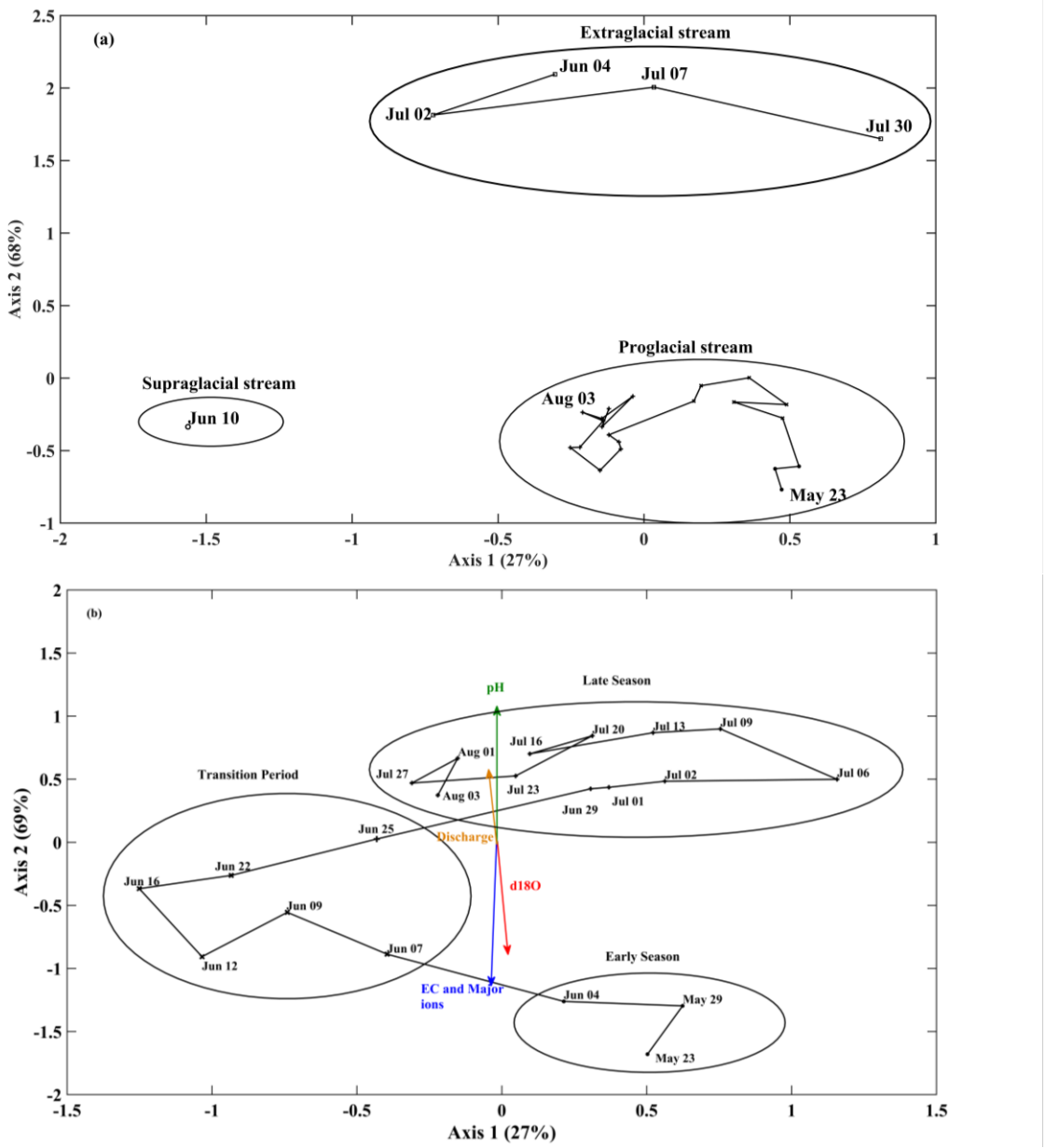

Figure 3-3: Microbial assemblage composition determined by Nonmetric Multidimensional Scaling (NMS) ordination of Bray-Curtis distance measure using 16S rRNA gene sequencing (stress=0.06). Values in parentheses next to axis labels indicate the percent of variance in the distance matrix explained by each axis. Multiresponse Permutation Procedure (MRPP) reveals significant differences between a) proglacial, supraglacial and extraglacial microbial assemblages (1000 subsamples) and b) Early Season, Transition Period, and Late Season proglacial stream microbial assemblages (2500 subsamples). Colored arrows represent significant correlations with physical parameters using Mantel tests ($P<0.001$).

Chapter 4: The effects of basal thermal regime on the biogeochemistry of subglacial systems

4.1 Abstract

Ice formed in the subglacial environment can contain some of the highest concentrations of solutes, nutrients and microbes found in glacier systems. Upon glacial melt, these biogeochemical materials can be exported to downstream freshwater and marine ecosystems and glacier forefields. Basal thermal regime might play an important role in controlling variability in subglacial biogeochemistry by influencing the extent to which glaciers mobilize material from the underlying substrate and the extent and type of biogeochemical activity that can occur *in situ*. To explore the biogeochemical variability in subglacial systems, we characterized the solutes, nutrients, and microbes found in the basal regions of polythermal glaciers (which host relatively 'warm' subglacial environments) and a cold-based glacier (which host relatively 'cold' subglacial environments) and compare them to material from their parent glacier ice. We also characterized the solutes, nutrients and microbes contained in meltwater that survived the winter as liquid beneath a polythermal glacier to evaluate the subglacial biogeochemical processes that can occur in the presence of liquid water. Compared to its parent glacier ice, we find basal ice from polythermal glaciers to be consistently enriched in major ions, dissolved organic matter (including a specific fraction of humic-like fluorescent material), and microbes, and occasionally enriched in dissolved phosphorus, reduced nitrogen (NH_4^+) and a second component of humic-like fluorescent dissolved material. However, over-wintered subglacial meltwater showed evidence of *in situ* biogeochemical activity that depleted its reservoir of potentially labile dissolved nutrients, including dissolved inorganic

phosphorus and nitrogen and dissolved organic matter. These waters also contained a unique microbial assemblage, of which at least a portion is closely related to psychrophilic or oligotrophic microbes. In contrast, the biogeochemistry of basal ice from cold-based glacier systems remained remarkably similar to that of its parent glacier ice. Although the 'cold' basal ice samples explored show some evidence that they may have acquired inorganic and organic nutrients from the subglacial substrate, the substrate did not appear to contribute significant amounts of solutes or microbes to the basal ice. Findings from this study suggest that basal thermal regime and the presence of subglacial water can play important roles in controlling the subglacial biogeochemistry and the mix of solutes, nutrients, and microbes that are acquired from substrates beneath glaciers or produced within subglacial environments.

4.2 Introduction

Subglacial environments can host a diverse range of physical and biogeochemical conditions. Basal ice forms at or near the bed of glaciers as ice deforms and/or slides over the underlying substrate, erodes bedrock and/or subglacial sediments and entrains these materials. In relatively fast-flowing temperate and polythermal glaciers, geothermal and frictional heat sources can warm ice near the bed; in some areas, to the pressure-melting point. Relatively warm ice temperatures and melt-freeze processes near the bed can increase subglacial erosion and ice deformation, and promote chemical weathering reactions with both the underlying bedrock and unconsolidated sediments. In slow-flowing cold based glaciers, ice is frozen to the bed, and the cold temperatures limit erosion, ice deformation and chemical weathering processes. Subglacial processes in glaciers with relatively 'warm' or relatively 'cold' basal temperatures can produce sequences of basal ice that are chemically and/or physically distinct from the parent glacier ice,

which has a largely meteoric origin through snowfall [*Knight*, 1997; *Hubbard et al.*, 2009]. Basal ice typically acquires solutes (often dominated by Ca^{2+}, Mg^{2+}, HCO_3^- and SO_4^{2-}), via reactions involving carbonate and sulphide minerals, which are trace components in most types of bedrock [*Holland*, 1978]. It may also incorporate nutrients (e.g. phosphorus, silica, potassium) and microbes from the underlying substrate [*Sharp et al.*, 1999; *Montross et al.*, 2014]. Basal ice and subglacial water may also host microbes that mediate redox reactions [*Sharp et al.,* 1999] and play an active role in bedrock weathering [*Tranter et al.*, 2002], producing and/or consuming ecologically important nutrients such as sediment-bound phosphorus [*Hodson et al.*, 2005; *Hodson*, 2007], iron [*Statham et al.*, 2008; *Bhatia et al.*, 2013a; *Wadham et al.*, 2013], sulphate [*Bottrell and Tranter*, 2002; *Wadham et al.*, 2004], silica [*Hodson et al.*, 2000; *Tranter et al.*, 2002], nitrogen [*Boyd et al.*, 2011], and organic carbon [*Barker et al.*, 2006; *Wadham et al.*, 2012; *Bhatia et al.*, 2013b].

A large portion of the sediment, solutes, nutrients and microbes that are contained in glacier systems are initially mobilized by subglacial processes and stored within basal ice and subglacial water [e.g. *Raiswell*, 1984; *Sharp et al.*, 1999; *Barker et al.*, 2010; *Hawkings et al.*, 2016]. As such, elements of subglacial environments can play a fundamental role in defining the biogeochemistry of meltwater discharge from glaciers and ice caps. In temperate and polythermal glaciers, water can be produced and stored in remote areas of the bed (in pools, lakes and streams, in the pore volume of subglacial sediments, and in fractured bedrock) before it eventually drains into downstream environments. Meltwater flow through subglacial drainage networks can dramatically alter the geochemical [*Tranter et al.*, 2002], nutrient [*Hawkings et al.*, 2014; *Wadham et al.*, 2016] and microbial composition [*Dubnick et al.*, 2017a] of supraglacially-derived meltwater during its transit to downstream proglacial environments. During glacial retreat, melting of basal ice can also

release the sediment, solutes, nutrients and microbes it contains to glacier forefields. Subglacial microbes released from melting basal ice are initial colonizers of forefield soils and contribute to the nutrient dynamics in these terrestrial environments [*Mindl et al.*, 2007; *Sattin et al.*, 2010; *Kazemi et al.*, 2016]. Glacial deposits form the basis of the soils from which postglacial landscapes evolve [*Kastovská et al.*, 2005], making their biogeochemical attributes of importance to these changing ecosystems.

Despite the relatively high concentrations of solutes, nutrients and microbes found in subglacial systems, and their potential impact on downstream ecosystems and forefield composition, our understanding of subglacial biogeochemical processes and products, and their spatio-temporal variability, remains limited. We expect basal thermal regime to play an important role in defining the physical and biogeochemical environment of basal ice and subglacial water. Basal thermal regime can influence the extent to which glaciers mobilize material from the underlying substrate, and the extent and types of biogeochemical activity that can occur *in situ*. Thus, to explore the spatio-temporal variability in the biogeochemistry of subglacial systems, we have characterized the solutes, nutrients, and microbes found in the basal regions of glaciers inferred to have different basal thermal regimes. Fast-flowing glaciers typically have warmer basal temperatures than slow-flowing glaciers since warm ice deforms more easily than cold ice and subglacial water promotes basal sliding [*Iken*, 1981; *Iken and Bindschadler*, 1986]. We therefore sampled basal ice from three fast-flowing, polythermal outlet glaciers (Sverdrup Glacier, Belcher Glacier, and East 7 Glacier) that drain from the Devon Ice Cap (DIC, Devon Island, Nunavut, Canada). These samples represent basal ice that likely formed and persisted under relatively warm conditions. Additionally, we collected liquid water that was stored over-winter in a subglacial channel beneath Sverdrup Glacier. We also collected basal ice that likely formed and persisted

under relatively cold conditions from the slow-flowing Western Margin of the DIC. We compared the biogeochemistry of these basal ice samples to that of the likely source ice (overlying glacier ice of meteoric origin, or subglacial channel ice formed by refreezing of subglacial meltwater) to evaluate how basal thermal regime affects the biogeochemical materials that glaciers mobilize from the substrate or produce/cycle within subglacial environments.

4.3 Methods

4.3.1 Study Site

The Devon Ice Cap (DIC) covers an area of approximately 14,400 km^2 [*Burgess and Sharp*, 2004] and has had a relatively consistent negative mass balance since 2005 [*Sharp et al.*, 2011]. Its recent decrease in surface area [*Burgess and Sharp*, 2004] and ice thickness [*Mortimer et al.*, 2018] is coincident with increases in regional summer air and glacier surface temperatures [*Mortimer et al.*, 2016]. We studied three fast-flowing outlet glaciers (Sverdrup Glacier, Belcher Glacier, and East 7 Glacier) and the slow-flowing Western Margin of the ice cap (Figure 4-1). Although the surface velocities along the fast-flowing glaciers can be variable, all three have surface velocities that exceed 20 m a^{-1} and a component of this flow is attributed to basal motion [*Burgess et al.*, 2005; *Van Wychen et al.*, 2017] (Figure 4-1). The presence of basal motion implies that geothermal and frictional heat sustain basal ice temperatures at or near the pressure-melting point in a considerable portion of their beds [*Burgess et al.*, 2005; *Cuffey and Paterson*, 2010]. These findings are consistent with field observations of large subglacial meltwater channels draining the margins of both Sverdrup Glacier and Belcher Glacier. Air temperatures in these subglacial channels, at distances of 500-1000 m from the glacier margin, were relatively warm (near or slightly below 0ºC) in May, prior to the melt season. We have therefore assumed that the

basal ice in these systems likely formed and persisted under relatively warm conditions and is referred to hereafter as 'warm' basal ice.

The slow-flowing Western Margin of the ice cap is not constrained laterally by bedrock topography and surface velocities are generally <10 m a^{-1} [*Burgess et al.*, 2005]. Ice motion in this region is believed occurs exclusively by internal deformation and ice is frozen to the bed [*Burgess et al.*, 2005]. Therefore, unlike the 'warm' basal ice that formed and persisted at the beds of fast-flowing glaciers, we assume that the basal ice at the Western Margin formed and persisted under relatively cold conditions, so we refer to this ice as 'cold' basal ice.

While the three fast-flowing, polythermal glaciers explored in this study, located up to ~100 km apart, are underlain by metasedimentary rocks and gneiss, the Western Margin is largely underlain by sandstone, dolomite and limestone bedrock [*Harrison et al.*, 2016] (Figure 4-1). Ice marginal – subglacial channels were observed beneath both the Sverdrup Glacier and Belcher Glaciers and a slushy subglacial meltwater pond (with no ice cover) was present in multiple years at approximately 750 m into the subglacial channel beneath the Sverdrup Glacier. The subglacial channel water was observed prior to the onset of the melt season and temperatures at this remote location of the bed were likely relatively stable throughout the winter. We therefore assume that most of this water originated as late-season subglacial runoff that remained ponded in the subglacial channel over-winter. Channel ice, found in colder areas nearer the channel entrance, likely also originated as late-season runoff but did not remain liquid over winter, probably because of cold air drainage into the channel.

4.3.2 Field sampling

We sampled 'warm' basal ice, from the three fast-flowing glaciers, and 'cold' basal ice from the Western Margin of the ice cap, as well as their parent meteoric glacier ice (Figure 4-1).

We used visual observations to identify basal ice near the glacier bed as an ice facies with high debris and low air bubble contents, distinctive ice and debris structures, and ice crystallography [*Knight*, 1997]. While glacier ice of meteoric origin is typically white bubbly ice that is horizontally stratified, basal ice can have a much higher debris content and an anisotropic structure with features such as discontinuous layers, lenses and pods of varying size [*Hubbard and Sharp*, 1989]. Basal ice samples were collected from marginal ice cliff faces, ice rubble at the base of cliff faces, and the walls of subglacial meltwater channels. Meteoric glacier ice was sampled from cliff faces or from rubble at the bases of cliff faces.

We also sampled subglacial channel water from a slushy subglacial meltwater pond (with no ice cover) located at approximately 750 m into the subglacial channel beneath the Sverdrup Glacier. We consider its parent material to be late-season meltwater draining this subglacial channel. Although we did not sample late-season meltwater in this channel, we collected 'channel ice' as a proxy. Channel ice was found in colder areas nearer the channel entrance and thus represents runoff that froze *in situ* at the end of the melt-season, thereby preserving the general biogeochemical characteristics of late-season runoff.

All ice samples were collected using sterile (furnaced at 500ºC for 8 hrs) carbide chisels that were ethanol-bathed and flame-sterilized in the field before each use. One chisel was used for debris-poor samples and another was used for debris-rich samples. At least 10 cm of material was removed from exposed surfaces in the field before samples were collected. Samples were stored in 5L Whirl-pak bags (Nasco, Fort Atkinson, USA) and kept frozen (~ -20ºC) until analysis. The subglacial channel water sample was collected by scooping with separate Whirl-pak bags in different areas of the subglacial pond system that were separated by >1m. The subglacial channel water samples were kept frozen (~-20ºC) until analysed.

4.3.3 Sample Processing

Prior to analysis, samples were removed from the freezer and melted at 4ºC in Whirl-pak bags. For each sample, a sterile syringe (60 ml) with a 0.45 µm cellulose acetate luer-lok filter was used to fill two 15 ml centrifuge tubes for analyses of soluble reactive phosphorus (SRP), NO_3^- +NO_2, and NH_4^+. One 120 ml Nalgene® bottle was also filled (with no headspace) for major ion analyses. This sample was stored at 4ºC for approximately 2 weeks until analysis. A 0.7 µm GF/F luer-lok filter was used to fill two 45 ml universal glass vials and a piece of foil was placed beneath the cap for closure. These samples were frozen immediately until analysis for dissolved organic carbon (DOC) quantification and dissolved organic matter (DOM) characterization. For sediment concentration measurements, 50 ml of unfiltered sample was measured using a 60 ml syringe, put in a (pre-weighed) 50 ml polystyrene hexagonal weigh dish (Cole-Palmer), and placed in a drying oven at 50 ºC. A glass filter tower and 0.2 µm Pall Supor® polysulfone 47 mm sterile filter papers were used to filter samples for 16S rRNA gene sequencing. Filter papers were collected in duplicate and stored in sterile petri dishes at -80ºC until further processing.

All filtration equipment was rinsed 3 times with sample, and a minimum of 5 ml of sample was passed through each filter paper before the sample was filtered for analysis. Glassware was acid-washed (10% HCl for >48 hrs), and both glassware and foil were combusted (450ºC for 8 hrs) prior to use. All storage bottles, lids, and foil caps were rinsed 3 times with filtrate before a sample was collected for analysis.

4.3.4 Analytical Methods

Nutrient concentrations (SRP/TDP/NH_4^+/NO_3^-+NO_2^-/TDN/SiO_2): Determinations of soluble reactive phosphorus (SRP) and total dissolved phosphorus (TDP), ammonium (NH_4^+), nitrate (NO_3^-) + nitrite (NO_2^-), total dissolved nitrogen (TDN) and reactive silica (SiO_2) were made with

a Lachat QuickChem QC 8500 FIA Automated Ion Analyzer (Lachat Instruments, Loveland, CO, USA) using methods outlined by Rice *et al.* [2012] and O'Dell [1993] for NO_3^- + NO_2^-. Detection limits were TDP = 1.8 ppb, SRP = 0.9 ppb, NH_4^+ = 3 ppb, NO_3^- + NO_2^- = 2 ppb, TDN = 7 ppb, and SiO_2 = 0.02 ppm.

DOC concentrations: dissolved organic carbon was quantified using a Shimadzu TOC-5000A Total Organic Carbon Analyzer (Shimadzu, Japan) equipped with a high-sensitivity platinum catalyst using US EPA method # 415.1. Detection limit for DOC was 0.2 mg L^{-1}.

DOM characteristics*:* Although isolating and defining the compositional characteristics of DOM often requires large sample volumes and can be analytically expensive, fluorescence spectroscopy provides a relatively rapid, simple and inexpensive technique for characterizing DOM in dilute concentrations with small sample volumes. Fluorescence spectroscopy and three-dimensional Excitation Emission Matrices (EEMs) can broadly characterize DOM into humic-like and protein-like fractions and correlate specific fluorescent signatures with signatures previously identified and explored in the literature. DOM fluorescence was measured in ratio mode (S/R) using an Agilent G1321B fluorescence detector (Agilent Technologies, Santa Clara, USA) and methods outlined by Cuss and Gueguen [2015]. Prior to each run, the system was rinsed 3 times with deionized water and 3 times with sample that was brought to room temperature. Excitation-emission matrices (EEMs) were produced by measuring the fluorescence intensity every 1 nm at excitation wavelengths 220-450 nm and every 5 nm at emission wavelengths 280-545 nm. EEMs of deionized water were produced at the start of each day for data processing (see below).

Major Ions (Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}): Anions were quantified using a Dionex DX-600 Ion Chromatograph (Dionex, USA) and methods outlined by US EPA method # 300.1. Cations were measured using Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES; Thermo

Scientific iCAP 6300, Cambridge, UK) and US EPA method #200.7. Detection limits were Cl^- = 0.85 µeq L^{-1}, SO_4^{2-} = 0.83 µeq L^{-1}, Na^+=0.87 µeq L^{-1}, K^+=0.26 µeq L^{-1}, Mg^{2+}=0.82 µeq L^{-1}, and Ca^{2+}= 0.5 µeq L^{-1}.

Sediment concentration: 50 ml of unfiltered sample was placed in a pre-weighed 50 ml dish and dried at 50 ºC. The dish was then reweighed and the sediment in 50 ml was calculated as the change in mass from before to after the sample was added/dried.

16S rRNA gene sequencing: DNA was extracted from filter papers using a PowerSoil ® DNA Isolation kit following the manufacturer's protocol, but with several modifications to maximize the efficiency of the extraction, including: 1) at Step 14, solution C4 was added for a total of 4 ml instead of 1,200µl and vortexing was for 20 seconds instead of 5 seconds, 2) prior to step 15, the samples were incubated for 30 minutes, and 3) at step 20, the DNA was eluted in 50µl of solution C6 instead of 100µl. Polymerase chain reaction (PCR) was performed using a Veriti 96 well thermal cycler (Applied Biosystems) and 0.25 µM primers targeting the V3 region, including Primer 341F (5′-CCTACGGGAGGCAGCAG-3′) and Primer 518R (5′-GTATTACCGCGGCTGCTGG-3′). The procedure for a 25 µL reaction included 1x Q5 Reaction buffer (New England BioLabs Inc.), 100 µM dNTP mixture (Invitrogen/ThermoFisher), 1.25 U/µl Q5 High-Fidelity DNA Taq polymerase (0.25 µL per reaction; New England Biolabs Inc), 17.5 µL Nuclease-free H_2O (Integrated DNA Technologies) and 2 µL of the 1:2 and 1:10 diluted template DNA in Nuclease-free H_2O. PCR conditions were as follows: 94°C for 3 min, followed by 10 cycles of 94°C for 30 s, 65-55 °C for 40 s, 72°C for 1 min, followed by 20 cycles of 94ºC for 30s, 55ºC for 40s, 72ºC for 1 min; 53ºC for 40s, with a final elongation step for 10 min at 72ºC, with a holding temperature at 4ºC. PCR amplicons were quantified in a 1.0% agarose gel (GelRed) and equal quantities of amplicon from replicate samples were pooled. The pooled 16S rRNA

amplicons were purified using Wizard SV Gel and PCR Clean-Up Systems (Promega). Illumina libraries were denatured and diluted according to Illumina guidelines (Document no 15039740 v01). An 8 pM library (containing 7% PhiX) was sequenced using a MiSeq (Illumina Inc, San Diego, USA) with 2 x 250 cycle MiSeq Reagent Kit v2 (Illumina Canada Inc) at the Department of Biology, University of Waterloo.

4.3.5 Data Processing and Statistical Analyses

Geochemistry and inorganic nutrients: The concentration of HCO_3^- (μeq L^{-1}) was calculated as the charge deficit between the sum of cations (μeq L^{-1}) and the sum of anions (μeq L^{-1}). To summarize the geochemical composition of the solute load in each sample, we (i) calculated the fractional contribution of each major ion to the total solute load by dividing the concentration of each major ion (μeq L^{-1}) by either the sum of cations or the sum of the anions in the respective sample, (ii) normalized the fractional contributions of each ion species by their respective mean and variance [*Iwamori et al.*, 2017] and (iii) conducted a Principal Components Analysis (PCA) in Matlab R2018a using these data. To summarize the nutrient composition of each sample and evaluate the concentration of TDP and TDN relative to the solute load, the concentrations of TDP (μg P L^{-1}) and TDN (μg N L^{-1}) were divided by the solute concentration (μeq L^{-1}) of the corresponding sample. To evaluate the significance of dependency between geochemical/nutrient variables, Spearman rank correlations were used.

DOM Characterization*:* Parallel Factor Analysis (PARAFAC) is a statistical technique commonly applied to EEMs to decompose complex spectral signatures into discrete components. Although the modeled components cannot be identified as specific organic compounds, they can be compared to fractions of fluorescent DOM that have previously been described in the literature. To complete PARAFAC, we used the drEEM toolbox and methods developed by *Murphy et al*.

[2013] in Matlab R2018a. Corrections were applied for instrument spectral bias and for inner filter effects, and Raman scatter was normalized to daily Raman scans, as described by *Murphy et al.* [2013]. The scatter region for each EEM was excised and smoothed and EEMs were normalized to unit variance. The PARAFAC was completed using non-negativity constraints and the EEM normalization was reversed after modeling. Although split-half analysis is typically used to validate PARAFAC models, it does not validate models that are produced from datasets that are small relative to the intra-sample variance [*Stedmon and Bro*, 2008]. Since the samples in this dataset were few (<50) and came from diverse environments with highly variable fluorescence, split-half analysis did not successfully validate our PARAFAC model. The modeled components were, however, identified using the OpenFluor database [*Murphy et al.*, 2014] and comparisons with previous literature. To summarize the DOM composition of each sample, the fluorescent intensity of each component was normalized to its mean and variance across the dataset and a PCA was completed.

Microbial Assemblage: Paired-end reads were assembled using PANDAseq [*Masella et al.*, 2012] and analyzed using Quantitative Insights Into Microbial Ecology (QIIME, [*Caporaso et al.*, 2010]), managed by the automated exploration of microbial diversity v. 1.5 (AXIOME, [*Lynch et al.*, 2013]). Sequences were clustered with UPARSE [*Edgar*, 2013] and compressed into unique taxa with 97% similarity, and classified by The Ribosomal Database Project (RDP) [*Wang et al.*, 2007] with a confidence threshold of 0.8. Rarefaction analysis was used to sub-sample the processed dataset to lower than the smallest library for subsequent analyses. The microbial assemblages in each sample were summarized by completing non-metric multidimensional scaling (NMDS) in R with the Vegan toolbox. Unlike PCA, NMDS is particularly well suited for sequencing datasets that often have many zeros. The NMDS code used in this study calculates

NMDS using multiple random starting configurations until a similar minimum stress solution is resolved twice. Multiple linear regressions were used to fit environmental vectors onto the NMDS (also using the Vegan toolbox in R). The environmental variables included the major ion concentrations and percent composition, nutrient concentrations or fluorescent index, and sample location (calculated as the distance from the most northerly glacier).

Channel water concentration effects: The subglacial meltwater pond was slushy at the time of sampling and the channel roof and walls were covered in hoar frost. The pond therefore likely experienced extensive cryo-concentration and evapo-concentration over the winter. We assumed that the Cl^- content of each sample behaves conservatively in solution and that the un-concentrated Cl^- content of the channel water was equivalent to that of its parent material. We consider its parent material to be late-season meltwater draining this subglacial channel. Although we did not sample late-season meltwater in this channel, we collected 'channel ice' as a proxy. Channel ice was found in colder areas nearer the channel entrance and thus represents runoff that froze *in situ* at the end of the melt-season, thereby preserving the general biogeochemical characteristics of late-season meltwater. Therefore, to correct for the effects of concentration and evaluate the biogeochemical composition of this water relative to other samples in the dataset, we standardized the concentration of each major ion and nutrient species in the subglacial channel water sample as follows:

Equation 4-1
$$*X = X_{meas} \times \frac{Cl^-_{CI}}{Cl^-_{CW}}$$

Where $*X$ is the corrected concentration of species X in subglacial channel water, X_{meas} is the measured concentration of species X in subglacial channel water, Cl^-_{CI} is the measured concentration of Cl^- (µeq/L) in subglacial channel ice and Cl^-_{CW} is the measured concentration of Cl^- (µeq/L) in subglacial channel water.

4.4 Results

4.4.1 Major Ion Chemistry

'Warm' basal ice had different solute compositions than its parent glacier ice (Figure 4-2), suggesting that distinct solute sources exist in relatively 'warm' subglacial systems. Glacier ice had relatively low solute concentrations ($\bar{x}$ = 15.6 μeq L^{-1}) that were dominated by atmospherically-derived solutes, including Cl^-, SO_4^{2-}, and Na^+ (Table 4-1). 'Warm' basal ice samples contained significantly higher concentrations of solutes ($\bar{x}$ = 241 μeq L^{-1}), including common rock-derived solutes such as K^+, Ca^{2+}, Mg^{2+}, and HCO_3^-, than did glacier ice (T-test, $p<0.05$) (Table 4-2; Figure 4-3). The concentration of Cl^- in subglacial channel water was 16 times higher than the concentration of Cl^- in corresponding channel ice, indicating extensive cryo-concentration and/or evapo-concentration. After correcting the solute concentrations in subglacial channel water for the effects of cryo-concentration and evapo-concentration (Equation 4-1), subglacial channel water had solute concentrations similar to those in glacier ice (Figure 4-3). However, the solute composition was similar to that of 'warm' basal ice (Figure 4-2). Cold basal ice samples had relatively low solute concentrations ($\bar{x}$ = 22 μeq L^{-1}) that, like its parent glacier ice, were dominated by Cl^-, SO_4^{2-}, and Na^+ **(**Table 4-1).

4.4.2 Nutrients (N and P)

There were no significant differences in the mean concentrations of dissolved inorganic nitrogen (NH_4^+, NO_3^-) or phosphorus (TDN, SRP and TDP) species between 'warm' basal ice and glacier ice (T-Test, $p>0.05$), but the inter-sample variability in concentrations of NH_4^+, SRP and TDP in 'warm' basal ice was significantly higher (F-Test, $p<0.05$; Table 4-2, Figure 4-3). Therefore, the sources (and potentially also sinks) of these inorganic nutrients may be spatially heterogeneous in relatively 'warm' subglacial systems. Subglacial channel water had among the

lowest concentrations of NH_4^+, SRP, TDP in the dataset, suggesting *in situ* processes function as a sink for some inorganic nutrient species. Cold basal ice samples had significantly higher concentrations of NH_4^+, TDN, SRP, TDP than samples of parent glacier ice (T-test, $p<0.05$; Table 4-2), suggesting the presence of a subglacial source for these nutrients.

4.4.3 Dissolved Organic Matter

A 5 component PARAFAC model was produced that explained 98.6% of the variability in the spectrofluorescence dataset. PARAFAC Component 1 (C1) (Table 4-3) was not similar (>90% certainty) to any previously modeled fluorphores that are available in the online repository of published fluorescence data (OpenFluor [*Murphy et al.*, 2014]). However, this component's fluorescence peak is close (within 5 nm) to that of 'Peak B' [*Coble*, 1996], which is considered tyrosine-like fluorescence [*Kowalczuk et al.*, 2003] (Table 4-3) and may originate from the degradation of terrestrially-derived humic-like DOM [*Mopper and Schultz*, 1993; *Coble et al.*, 1998; *Stedmon and Markager*, 2005; *Coble*, 2007] and microbial exudates [*Smith et al.*, 2017]. Component 2 (C2) (Table 4-3) is similar (>95% certainty) to three modeled components available in OpenFluor and is referred to as tryptophan-like fluorescence [*Coble et al.*, 1998; *Lakowicz*, 1999] and has been associated with the autochthonous production of DOM in various environments [*Mopper and Schultz*, 1993; *Coble*, 1996; *Yamashita and Tanoue*, 2003; *Fellman et al.*, 2008]. Component 3 (C3) (Table 4-3) is similar (>95% certainty) to a component found in 9 previous studies [*Murphy et al.*, 2014], and is referred to as humic-like or fulvic acid-like fluorescence that is derived from higher plants, can be of terrestrial origin, and/or is a product of microbial degradation of organic matter [*Cory and McKnight*, 2005; *Osburn et al.*, 2016]. Component 4 (C4) (Table 4-3) is less similar to any previously modeled components (90%-95% certainty), but is similar to humic-like DOM and highly processed terrestrial DOM of low

bioavailability [*Lapierre and Del Giorgio*, 2014]. Lastly, Component 5 (C5) (Table 4-3) is similar (>95% certainty) to 12 other modeled components in the OpenFluor database and is the mostly widely modeled component resolved in this study. C5 has been associated with humic-like fluorescence derived from marine [*Coble*, 1996] and/or terrestrial [*Stedmon et al.*, 2003] environments, but it has also been linked to microbial reprocessing of organic matter [*Stedmon and Markager*, 2005].

DOC concentrations in 'warm' basal ice ($\bar{x}$ = 0.4 ppm) were significantly (T-test, $p<0.05$) higher than those in glacier ice ($\bar{x}$ = 0.2 ppm) (Table 4-1; Table 4-2), suggesting basal ice acquires DOC in relatively 'warm' subglacial environments. DOC concentrations in 'warm' basal ice were positively correlated with the tyrosine-like C1 fluorescence (r_s =0.61, p=0.01, n=9). 'Warm' basal ice also contained significantly more humic-like C3 fluorescence (T-test, $p<0.05$), and significantly more variable humic-like C3 and C5 fluorescence (*F*-test, $p<0.05$) than its parent glacier ice (Table 4-3). Thus, a relatively consistent fraction of the DOC derived from these subglacial systems was probably in the form of proteinaceous and humic organic matter. Subglacial channel water had lower *DOC concentrations and lower fluorescence intensity for components *C2-*C5 than any other sample in this dataset, indicating biogeochemical processes in subglacial channel water may function as a sink for DOM.

Cold basal ice contained significantly higher DOC concentrations ($\bar{x}$ = 0.4 ppm) than did glacier ice ($\bar{x}$ = 0.2 ppm) (T-test, $p<0.05$; Table 4-1; Table 4-2) suggesting that ice can acquire DOC in 'cold' basal environments. 'Cold' basal ice also contained significantly higher and more variable fluorescence of humic-like DOM component C3 and C5 (T-test and F-Test, $p<0.05$; Table 4-2) and had significantly more variable fluorescence of protein-like DOM component C2 (*F*-test, $p<0.05$) (Table 4-2; Table 4-3). Since C3 and C5 humic-like DOM is typically associated with

terrestrial soils and vegetation [*Stedmon et al.*, 2003; *Cory and McKnight*, 2005; *Osburn et al.*, 2016], this DOM may have been acquired during past glacial advances over soils and sediments.

4.4.4 Microbial Assemblages

'Warm' basal ice and glacier ice microbial assemblages were two distinct sample groups (Figure 4-2). 76% of the operational taxonomical units (OTUs) observed in 'warm' basal ice were absent in its parent glacier ice (Figure 4-4), suggesting a large portion of the microbial assemblage in 'warm' basal ice was sourced from the subglacial environment. Microbial assemblages in 'warm' basal ice were also highly variable as less than half a percent of the OTUs found in 'warm' basal ice were present in all 'warm' basal ice samples. Geographic location influenced the structure of microbial assemblages in 'warm' basal ice since 'warm' basal ice samples from a given glacier had more OTUs in common with other basal ice samples from the same glacier (42% of their OTUs and 26% of their assemblages) than they did with basal ice samples from other 'warm' based glaciers (32% of their OTUs and 15% of their assemblages) (T-test, $p<0.001$). Furthermore, although there were no significant correlations between the major ion concentrations, major ion composition, nutrient concentrations or fluorescence index and the microbial assemblage structure of 'warm' basal ice samples using multiple linear regressions, sample location significantly correlated with the structure of microbial assemblages in 'warm' basal ice samples ($p=0.01$).

Subglacial channel water contained a microbial assemblage that was distinct from the assemblages found in potential water sources, including 'warm' basal ice, glacier ice and subglacial channel ice (Figure 4-2), suggesting that the microbial assemblage of these waters probably changed *in situ* over the winter. The most abundant OTU in the subglacial channel water (comprising 42% of the assemblage) was identified in the family Comamonadaceae and genus

Paucibacter. The other most dominant OTUs included an actinobacterium ACK-M1 (comprising 6% of the assemblage), a Comamonadaceae in the genus *Polaromonas* (comprising 4% of the assemblage), a Gemmataceae (comprising 4% of the assemblage) and *Flavobacterium succinicans* (comprising 4% of the assemblage).

The microbial assemblages in 'cold' basal ice were broadly similar to those in glacier ice (Figure 4-2). Cold basal ice shared most (73%) OTUs with glacier ice (Figure 4-4). Of the shared OTUs between 'cold' basal ice and glacier ice, many (37%) were absent from 'warm' basal ice samples. Thus, the microbial assemblages in 'cold' basal ice remained remarkably similar to those in its parent material, despite potential interaction with the substrate.

4.5 Discussion

4.5.1 The biogeochemistry of 'warm' basal ice

Glacier ice that flows towards the bed of glaciers (i.e. the parent material of basal ice) originates as snow in the accumulation zone of glaciers/ice caps. This ice is of meteoric origin and receives chemical and biological inputs primarily from the atmosphere, experiences consistently sub-freezing temperatures and is likely to host limited *in situ* biogeochemical activity. Geothermal and frictional heat sources in warm sections of polythermal glaciers can cause glacier ice to melt and potentially refreeze. The interaction between ice/water and the substrate can mobilize and incorporate sediment, solutes, microbes, and nutrients from the underlying substrate into the base of the glacier during the formation of 'warm' basal ice. Relatively warm temperatures at and near the glacier bed may also promote biogeochemical activity by increasing the abundance of water, the metabolic rates of micro-organisms, and rates of chemical weathering. Thus, 'warm' basal ice can generate very different biogeochemical environments than those found in overlying

glacier ice and can have some of the highest concentrations of solutes, nutrients and microbes found in glacier systems [e.g. *Raiswell*, 1984; *Sharp et al.*, 1999; *Barker et al.*, 2010].

The basal ice layers of the polythermal glaciers explored in this study were consistently enriched in solutes, including SiO_2, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, and HCO_3^-, compared to their parent glacier ice (Table 4-1; Table 4-2; Figure 4-3). These solutes were likely derived from weathering of reactive minerals such as carbonates (e.g. dolomite and calcite), sulphides (e.g. pyrite) and aluminosilicates (e.g. feldspars) [*Tranter et al.*, 1996], which are commonly present in trace amounts in bedrock [*Holland*, 1978]. Furthermore, the presence of water during the formation of 'warm' basal ice, and in veins along ice crystal boundaries, would support reactions involving acid hydrolysis, which are usually the most important weathering processes in subglacial environments [*Raiswell*, 1984].

'Warm' basal ice was also consistently enriched in DOM, containing on average ~ 0.3 ppm DOC. Unlike the DOM in glacier ice, 'warm' basal ice consistently contained humic-like C3 material and occasionally contained humic-like C5 material (Table 4-2). Previous studies have associated both C3 and C5 fluorescence with microbial processing of organic matter [*Cory and McKnight*, 2005; *Stedmon and Markager*, 2005; *Osburn et al.*, 2016], suggesting the occurrence of heterotrophic microbial activity in subglacial environments, extraglacial soils and sediments that were subsequently overridden and entrained by glaciers, or in supraglacial or ice marginal material that drained into the subglacial system. Although basal ice in polythermal glaciers was not consistently enriched in protein-like DOM relative to glacier ice, DOC concentrations in 'warm' basal ice were positively correlated with the tyrosine-like C1 fluorescence (r_s = 0.61, p=0.02, n=9) suggesting that a relatively consistent fraction of the DOC derived from these subglacial systems was proteinaceous in character. The production of tyrosine-like fluorescence

has been widely linked to the degradation of terrestrially-derived humic-like DOM [*Mopper and Schultz*, 1993; *Coble et al.*, 1998; *Stedmon and Markager*, 2005; *Coble*, 2007] and microbial exudates [*Smith et al.*, 2017]. Since tyrosine-like fluorophores are considered to be highly biodegradable [*Yamashita and Tanoue*, 2003], it is likely that tyrosine-like fluorescence was produced *in situ* within the subglacial environment from the degradation of allochthonous organic matter and/or the production of autochthonous organic matter. This is consistent with other studies that suggest subglacial environments contain both allochthonous organic matter (i.e. from bedrock/paleosols/overridden soils and vegetation) and autochthonous organic matter that may be produced *in situ* from microbial metabolism [*Hodson et al.*, 2005; *Wadham et al.*, 2016].

Although the 'warm' basal ice samples explored in this study were not enriched in nitrate, they were occasionally enriched in reduced nitrogen (NH_4^+) and dissolved phosphorus (SRP and TDP) (Table 4-2), suggesting that the sources (and potentially also sinks) of these inorganic nutrients in the subglacial system were spatially heterogeneous. Phosphorus in rocks is almost exclusively found in apatite mineral groups [*Taylor and McClennan*, 1985], and concentrations of P in shield rocks and volcaniclastics can be spatially heterogeneous [*Porder and Ramachandran*, 2013]. Similarly, the nitrogen content of bulk granite can vary by over two orders of magnitude [*Holloway and Dahlgren*, 2002], and other rock types in the Canadian Shield contain highly variable nitrogen concentrations [*Honma and Schwarcz*, 1979; *Honma*, 1996]. Although nitrogen can occur as recalcitrant organic matter in rocks, it commonly occurs as NH_4^+ in silicate minerals. Subglacial microbial communities may also function as a source of NH_4^+. Catabolic processes and the degradation of organic matter by subglacial microbes may release NH_4^+. Excess NH_4^+ would be particularly prevalent during the degradation of nitrogen-rich organic matter, such as the protein-like DOM that was observed in basal ice (described by PARAFAC C1 and C2). In

subglacial environments where organic matter contains insufficient nitrogen to meet the requirements for anabolic metabolism, specific organisms may fix nitrogen *in situ.* Genes indicative of nitrogen fixation (nitrogenase iron protein (*nifH*) gene) have been found in subglacial microbial communities [*Boyd et al.*, 2011]. However, despite the presence of *nifH* genes [*Boyd et al.*, 2011] and observations of N_2 fixation on glacier surfaces [*Telling et al.*, 2011] N_2 fixation has yet to be detected in subglacial environments.

Although sample location did not affect the major ion chemistry, nutrient, or organic matter composition of basal ice, it was an important and dominant influence on the composition of the microbial assemblages in 'warm' basal ice. We also observed that microbial assemblages in basal ice samples from the same glacier were more similar to each other than were assemblages in basal ice from different glaciers. Inter-glacier differences in basal microbial assemblages were therefore resolved over relatively small distances (less than 100 km), and between glaciers with similar basal thermal regimes and underlying substrates (Figure 4-1). Geographic location has been previously identified as an important determinant of microbial assemblages across various spatial scales, from meters [*Lear et al.*, 2014] to global [*Fuhrman et al.*, 2008] scales and within other polar environments including Antarctic and Arctic terrestrial and aquatic habitats [*Yergeau et al.*, 2007; *Comte et al.*, 2016]. Compared to most other terrestrial and aquatic habitats, basal ice environments are particularly isolated from each other, so microbial dispersal between systems is probably very limited. Furthermore, although residence times of 'warm' basal ice within a system is difficult to estimate, it may be sufficiently long to allow stochastic processes, such as random extinction, chance colonization, drift, and priority effects [*Vellend and Agrawal*, 2010; *Chase and Myers*, 2011], to play particularly important roles in shaping the structure of microbial assemblages in basal ice. In contrast, basal processes within a system, including ice deformation and melt-

freeze effects, would provide some degree of intra-glacial mixing of microbial assemblages and may explain the higher degree of similarity between assemblage in basal ice from the same system.

The subglacial environments explored in this study yielded a very small portion of 'ubiquitous' OTUs. Less than 1% of the OTUs found in the 'warm' basal ice samples were present in all 'warm' basal ice samples. The abundances of these 'ubiquitous' subglacial organisms were, however, highly variable between samples, ranging between a minimum of <0.01% of the assemblage, to a maximum of 2-40% of the assemblages, suggesting that the distributions of either the source(s) of these microbes and/or their *in situ* activity (i.e. reproduction) are spatially heterogeneous. Thus, even though there is evidence for globally-distributed microbial species that are capable of survival across the range of extreme subglacial environments [*Skidmore et al.*, 2005; *Bhatia et al.*, 2006; *Lanoil et al.*, 2009], these species appear to be few and their local abundance may be highly dependent on site-specific conditions.

4.5.2 Biogeochemical processes in subglacial water

In polythermal glaciers, geothermal and frictional heat sources can produce enough heat to warm areas of the bed to the point where melting occurs, and where liquid water can be stored at the bed. Since 'warm' basal temperatures and liquid water promote biogeochemical cycling, these areas are likely to be hotspots for microbial activity and nutrient cycling. However, due to the inaccessible nature of subglacial water systems, few studies have cleanly-accessed subglacial water *in situ* to explore its biogeochemistry. The subglacial channel water sample collected in this study from the base of the polythermal Sverdrup Glacier probably originated as late-summer runoff that drained into the subglacial system around the time of freeze-up and remained ponded in the subglacial channel over-winter. Water from areas of the bed with basal ice melt and/or distributed subglacial drainage may also have drained into the pool over winter. During its ~8 months of

storage beneath the glacier, this pool of water would have experienced relatively stable environmental conditions including continuous darkness, stable temperatures near or slightly below 0ºC, abundant oxygenated headspace, and increasing solute concentrations because of cryo-concentration and/or evapo-concentration. Although biogeochemical conditions in subglacial meltwater drainage systems are likely variable, the unique subglacial water sample collected in this study nonetheless provides some initial insights into the potential characteristics of *in situ* subglacial water and the biogeochemical processes that can occur where water is stored at the bed over-winter.

Although the major ion composition of the channel water was like that of basal ice and subglacial channel ice (Figure 4-2), it differed from its likely water sources (basal ice, glacier ice and subglacial channel ice) in terms of its DOM characteristics, inorganic nutrient content, and microbial assemblage structure (Figure 4-2; Figure 4-3). Part of the microbial assemblage observed in this sample is closely related to psychrophilic or oligotrophic bacteria. The microbial assemblage was dominated by an unidentified species in the family Comamonadaceae and genus *Paucibacter* (comprising 42% of the assemblage). The genus *Paucibacter* includes gram-negative, rod-shaped, non-spore forming, motile bacteria found in oligotrophic fresh water (*Paucibacter oligotrophus*) [*Pheng et al.*, 2017]. The other most dominant OTUs included an actinobacterium ACK-M1 (comprising 6% of the assemblage), a Comamonadaceae in the genus *Polaromonas* (comprising 4% of the assemblage), a Gemmataceae (comprising 4% of the assemblage) and *Flavobacterium succinicans* (comprising 4% of the assemblage). Comamonadaceae, *Polaromonas* and *Flavobacterium succinicans* have been widely observed in polar environments including subglacial water and basal ice [*Skidmore et al.*, 2000; *Sheridan et al.*, 2003; *Marteinsson et al.*, 2013; *Dubnick et al.*, 2017a; *Kayani et al.*, 2018] and glacier forefields [*Bradley et al.*, 2016;

Kazemi et al., 2016; *Kim et al.*, 2017] in Arctic, Antarctic and alpine systems. Some *Flavobacterium* are thought to function as heterotrophs in glacial habitats [*Margesin et al.*, 2002; *Mikucki and Priscu*, 2007] and a species of *Flavobacterium* (*glaciei*) was isolated from the China No 1 glacier and identified as a obligate aerobic psychrophile [*Zhang et al.*, 2006]. *Polaromonas* are abundant and ubiquitous in glacier systems and although different strains of *Polaromonas* can have almost identical 16S rRNA genes, they can display very different metabolic traits in different glaciers [*Gawor et al.*, 2016]. Local chemical and physical conditions and/or interactions with other microbiota may play an important role in shaping the metabolic traits of these organisms [*Gawor et al.*, 2016]. The presence of specific OTUs that are closely related to species that inhabit similar environments supports the notion that at least some members of the microbial assemblage observed in these subglacial waters may have adaptations that allow them to function in glacial habitats.

Even without correcting for the effects of concentration in the subglacial channel waters, these waters had distinct biogeochemical characteristics, including the lowest concentrations of presumably labile nutrients observed in this study. For example, the subglacial water sample contained the lowest measured levels of tryptophan-like (C2) and humic-like (C4) fluorescence, and amongst the lowest levels of NH_4^+, SRP, TDP and tyrosine-like (C1) fluorescence. After correcting nutrient concentrations for the effects of cryo-concentration and evapo-concentration (Equation 4-1), this sample had the lowest * NH_4^+, *DOC and *C2, *C3 and *C4 and *C5 DOM fluorescence in the dataset (Figure 4-3; Table 4-1). These solutes are presumably some of the most labile and biogeochemically important nutrients explored in this study. Tryptophan and tyrosine are associated with the autochthonous production of DOM in various environments [*Mopper and Schultz*, 1993; *Coble*, 1996; *Yamashita and Tanoue*, 2003; *Fellman et al.*, 2008] and are widely

considered to be among the most labile fluorescing components of DOM [*Wu et al.*, 2003; *Saadi et al.*, 2006; *Fellman et al.*, 2008]. SRP in particular, is considered to be a preferred and universal source of phosphorus to microbes [*Björkman and Karl*, 1994]. Fixed nitrogen (NH_4^+, NO_3^- and TDN) can be assimilated by microbes to relieve fixed N limitation, as has been previously observed in subglacial environments [*Boyd et al.*, 2011]. NO_3^- can also serve as an electron acceptor for microbially-mediated redox reactions in subglacial systems [*Yde et al.*, 2010].

The relatively low concentrations of specific biologically-important nutrients, coincident with a distinct, and potentially psychrophilic/oligotrophic, microbial assemblage, suggest the presence of *in situ* microbial activity and biogeochemical cycling in the subglacial pool. Heterotrophic and chemoautotrophic microbial activity can deplete reservoirs of labile solutes in subglacial water, as has been demonstrated from laboratory incubations of subglacial sediments and water [*Stibal et al.*, 2012b; *Montross et al.*, 2014]. The processes that occurred *in situ* in the subglacial channel water occurred at rates that resulted in significant changes to the biogeochemistry of the water over the course of ~8 months. Thus, although the subglacial environment of polythermal glaciers can be a source of solutes, nutrients and microbes, distinct microbial assemblages can develop in isolated subglacial water bodies and may cycle nutrients *in situ.*

4.5.3 The biogeochemistry of 'cold' basal ice

The subglacial conditions in cold-based glaciers that are frozen to the bed differ considerably from those in polythermal glaciers where meltwater is present in some areas of the bed, and where basal temperatures are generally warmer. The modes of formation of 'cold' basal ice can vary between glaciers and are generally poorly understood. Thus, interpretations of the environments in, and processes by, which such ice is formed are often ambiguous. Our

understanding of the biogeochemistry of these facies is consequently even more limited. The classic model for the formation of basal ice in cold-based glaciers is described by the 'apron entrainment model' that invokes the production of basal ice by the overriding of apron material (snow, ice blocks, refrozen melt water and debris) along an advancing margin [*Shaw*, 1977]. This model does not involve a role for meltwater and consequently implies limited opportunities for biogeochemical alterations to occur. The absence of coarse-grained debris and blocks of white bubbly ice in Western Margin basal ice facies examined here suggests that the apron entrainment model may not describe its mode of formation. Case studies have demonstrated that basal ice in cold-based systems can also be produced by subglacial processes such as the deformation and entrainment of subglacial permafrost [*Fitzsimons et al.*, 2008], the overriding of ice marginal lakes [*Lorrain et al.*, 1999], and from refreezing of water produced in warm thermal zones and/or high pressure zones at the glacier bed that then flows into cold thermal zones and/or low pressure zones where it refreezes [*Wettlaufer et al.*, 1996; *Knight*, 1997] and can entrain debris [*Gilpin*, 1979; *Walder*, 1986]. The dark, largely bubble-free character of Western Margin basal ice suggests that melt-freeze effects may have been involved in the formation of these facies.

The 'cold' basal ice at the Western Margin shows some evidence that it interacted with the substrate and acquired specific 'subglacial' biogeochemical characteristics, as was the case in polythermal glaciers. The 'cold' basal ice explored here contained sediment and, in comparison to glacier ice, had relatively high concentrations of TDP, TDN (particularly NH_4^+) and DOC, and high/variable proportions of humic-like fluorescence (C3 and C5) (Table 4-2; Figure 4-3). The substrate surrounding the Western Margin sample sites is composed largely of Cambrian and Ordovician sandstone, dolomite, limestone and conglomerate [*Harrison et al.*, 2016], which likely contain higher phosphorus concentrations than do the metasedimentary rocks [*Porder and*

Ramachandran, 2013] that underly the polythermal glaciers in this study. The sedimentary rocks around the Western Margin also support relatively well-developed soils and vegetation, which are common sources of the humic DOM and humic-like C3 and C5 fluorescence [*Stedmon et al.*, 2003; *Cory and McKnight*, 2005; *Osburn et al.*, 2016]. The 'cold' basal ice could have acquired these 'subglacial' biogeochemical characteristics during past glacial advances and/or if meltwater interacted with the substrate during the formation of the basal ice.

Although the 'cold' basal ice along the Western Margin may have acquired some inorganic and organic nutrients from the underlying substrate, there is little evidence to suggest that it acquired other major ions or microbes from the subglacial environment. The relatively low mean solute concentration (22 ueq/L) of the 'cold' basal ice was dominated by atmospherically-derived solutes (Cl^-, SO_4^{2-}, and Na^+), rather than by solutes likely to be derived from the local sandstone, dolomite, limestone and conglomerate rocks (Ca^{2+}, Mg^{2+}, HCO_3^-). Furthermore, the microbial assemblages in the 'cold' basal ice were very similar to those in the parent glacier ice, sharing most (i.e. 73%) OTUs, of which many (37%) were unique to glacier ice and absent from other 'warm' basal ice samples.

Unlike the 'warm' basal ice and channel water, which consistently acquired biogeochemical characteristics from the underlying substrate and probably hosted *in situ* microbial activity, the 'cold' basal ice explored in this study remained remarkably similar to its parent material of meteoric origin. However, the mechanism that facilitated the acquisition or *in situ* production/decomposition of specific inorganic and organic nutrients in 'cold' basal ice, but not of other major ions or microbes, remains unknown. It is not clear whether the biogeochemical differences between the 'cold' basal ice and the 'warm' basal ice reflect (i) differences in the characteristics of the underlying/surrounding substrates, (ii) specific glaciological/hydrological

processes that occurred during the formation of the 'cold' basal ice, or (iii) biogeochemical processes that occur *in situ* within 'cold' basal ice. Further research is clearly required to define how the 'cold' basal ice at the Western Margin of the DIC was formed, and to identify those biogeochemical processes that do occur in subglacial environments where liquid water is limited.

4.6 Conclusions

We investigated the biogeochemical properties of 'warm' basal ice from three polythermal glaciers that drain a region of the Devon Ice Cap that is underlain by metasedimentary rocks and gneiss. We found samples of basal ice from their subglacial environments to be consistently enriched in solutes (i.e. SiO_2, SO_4^{2-}, K^+, Ca^{2+}, Mg^{2+}, and HCO_3^-), dissolved organic matter (including a specific fraction of humic-like fluorescent DOM (C3)), and microbes compared to their parent glacier ice. Although these basal ice samples were not enriched in nitrate, they were occasionally enriched in dissolved phosphorus (SRP and TDP), reduced nitrogen (NH_4^+) and a second component of humic-like fluorescent DOM (C5), compared to glacier ice. The sources and/or sinks of these nutrients can therefore be spatially heterogeneous in the relatively warm subglacial systems of polythermal glaciers. Large fractions of the solutes, microbes, and nutrients derived from these subglacial systems were probably acquired directly from the underlying substrate. However, *in situ* microbial activity likely also influences the biogeochemical characteristics of these systems, particularly where meltwater is present. Waters that persisted over winter (~8 months) in a subglacial meltwater channel, showed evidence of *in situ* biogeochemical activity that significantly altered aspects of their biogeochemistry. Relative to their probable water sources (i.e. basal ice, glacier ice, and/or re-frozen late-season subglacial channel water), these subglacial waters had a depleted reservoir of potentially labile dissolved nutrients (i.e. DIP, DIN and DOM), and a unique microbial assemblage of which at least a portion is closely related to

known psychrophilic/oligotrophic microbes. These findings suggest that microbial activity in subglacial water can deplete reservoirs of labile solutes at rates that result in significant changes to the biogeochemistry of the water over the course of a single winter season. Thus, the subglacial environments of polythermal glaciers can be sources of solutes, nutrients and microbes and can host active biogeochemical environments in which distinct microbial assemblages develop, and nutrients are cycled *in situ.*

Unlike the biogeochemistry of the basal ice produced in relatively warm subglacial systems, and water that resides in relatively warm subglacial systems, basal ice produced in cold-based systems remained remarkably similar to that of its parent glacier ice. Although the 'cold' basal ice samples analyzed in this study may have acquired some inorganic and organic nutrients from the subglacial substrate, the substrate did not appear to contribute significant solutes or microbes to the basal ice. It remains unknown whether the biogeochemical differences between 'cold' basal ice and 'warm' basal ice reflect (i) differences in the characteristics of the underlying/surrounding substrate, (ii) specific glaciological/hydrological processes that occurred during the formation of the 'cold' basal ice, or (iii) biogeochemical processes that occur *in situ* in 'cold' basal ice. Further research is required to define how the 'cold' basal ice at the Western Margin of the DIC developed, and to better characterize the biogeochemical processes that occur in subglacial environments where liquid water is limited. Nevertheless, findings from this study suggest that basal temperature and the presence of subglacial water play an important role in controlling subglacial biogeochemistry and the suite of solutes, nutrients, and microbes that glaciers mobilize from the substrate or produced within subglacial systems.

4.7 Acknowledgements

This research was supported by an NSERC Discovery grant to M. Sharp (05234-2015), Polar Continental Shelf Program (PCSP) field support (604-16 and 620-17) and an NSTP grant, C/BAR grant, the W. Garfield Weston Award for Northern Research, and a NSERC CGSD Award to A. Dubnick. We thank the staff at the BASL Laboratory for chemical analyses, Chad Cuss at the SWAMP Laboratory for assistance with DOM/PARAFAC analyses, the Neufeld lab at the University of Waterloo for DNA sequencing and past field crews on the Devon Ice Cap for accumulating such a valuable wealth knowledge about the ice cap.

Table 4-1: Mean and standard deviation of measures of major ions, inorganic nutrients and DOM components in basal ice, glacier ice, subglacial channel ice and subglacial channel water.

	Units	Detection limit	Mean					Standard Deviation		
			Glacier ice	'Warm' Basal ice	'Cold' Basal ice	Channel Ice	Channel Water*	Glacier ice	'Warm' Basal ice	'Cold' Basal ice
Ionic strength	(μeq/L)	N/A	16	241	22	29	22	7	265	10
SiO_2	(ppm)	0.02	0.04	0.24	0.04	0.02	0.02	0.0	0.3	0.00
Cl^-	(μeq/L)	0.85	2.9	9.1	5.2	1.4	1.4	1.1	16.5	2.3
SO_4^{2-}	(μeq/L)	0.83	3.6	19.6	4.3	4.2	2.7	3.1	25.8	3.7
Na^+	(μeq/L)	0.87	3	46	4	2	2	2	101	2
K^+	(μeq/L)	0.26	0.34	9.04	0.50	0.77	0.66	0.24	7.60	0.45
Ca^{2+}	(μeq/L)	0.50	2.31	43.29	2.50	8.48	6.18	1.36	52.96	2.39
Mg^{2+}	(μeq/L)	0.82	1.4	22.3	3.0	3.3	2.4	0.8	18.3	2.6
HCO_3^-	(μeq/L)	0.87	1	92	0	9	7	5	104	8
TDP	(P μg/L)	0.2	25	24	90	8	3	9	17	110
NH_4^+	(N μg/L)	3	11.9	9.1	6.0	13.0	11.1	6.0	10.7	3.7
NO_2^-+ NO_3^-	(N μg/L)	2	45	44	134	28	15	16	25	138
TDN	(N μg/L)	7	1.0	11.9	3.2	0.9	0.1	0.3	32.6	2.8
SRP	(P μg/L)	0.9	1.8	13.7	3.8	1.8	0.1	0.1	35.5	3.0
DOC	(ppm)	1.8	0.15	0.49	0.40	0.10	0.02	0.06	0.59	0.25
DOM C1	(FI)	N/A	3.24	3.72	3.22	5.85	0.02	2.94	3.71	2.24
DOM C2	(FI)	N/A	5.27	6.40	3.28	3.41	0.03	4.27	4.41	1.25
DOM C3	(FI)	N/A	1.63	6.44	21.22	2.97	0.27	1.46	6.48	28.47
DOM C4	(FI)	N/A	2.96	4.69	2.74	4.68	0.04	2.39	3.49	0.94
DOM C5	(FI)	N/A	1.95	4.78	6.77	2.65	0.19	2.25	5.48	5.29

* the concentration of each dissolved species in channel water was corrected for concentration effects (Equation 4-1)

Table 4-2: Statistical tests between 'warm' basal ice and 'cold' basal and their parent material (glacier ice). P-values that represent significant differences ($p<0.05$) are red.

	'Warm' basal ice vs glacier ice		'Cold' basal ice vs glacier ice	
	T-test p-value	**F-test p-value**	**T-test p-value**	**F-test p-value**
Ionic strength	0.00	0.00	0.17	0.30
SiO_2	0.01	0.00	0.75	0.00
Cl^-	0.17	0.00	0.02	0.06
SO_4^{2-}	0.33	0.17	0.68	0.59
Na^+	0.01	0.37	0.56	0.88
K^+	0.00	0.00	0.81	0.39
Ca^{2+}	0.00	0.00	0.85	0.14
Mg^{2+}	0.00	0.00	0.09	0.00
HCO_3^-	0.00	0.00	0.85	0.17
NH_4^+	0.86	0.04	0.03	0.04
$NO_2^- + NO_3^-$	0.00	0.00	0.06	0.36
TDN	0.96	0.17	0.03	0.11
SRP	0.27	0.26	0.00	0.03
TDP	0.08	0.00	0.03	0.00
DOC	0.12	0.61	0.00	0.68
DOM C1	0.76	0.50	0.99	0.63
DOM C2	0.58	0.91	0.33	0.03
DOM C3	0.04	0.00	0.00	0.00
DOM C4	0.22	0.28	0.85	0.09
DOM C5	0.15	0.02	0.03	0.03

Table 4-3: Excitation and emission maxima for the 5 component PARAFAC model, including the identification of each component

	Ex (nm)	**Em (nm)**	**Description**	**# of OpenFlour matches (>95% certainty)**
C1	276	300	**Protein (tyrosine)-like fluorescence** that can be microbial in origin [*Coble*, 1996; *Kowalczuk et al.*, 2003; *Stedmon and Markager*, 2005]	0
C2	230 (286)	325	**Protein (tryptophan)-like fluorescence** [*Coble et al.*, 1998; *Lakowicz*, 1999] that has been liked to microbial activity [*Elliott et al.*, 2006]	3
C3	232 (336)	460	**Humic (fulvic acid)- like fluorescence** derived from higher plants (terrestrial) and/or organic matter with a certain degree of microbial processing [*Cory and McKnight*, 2005; *Osburn et al.*, 2016]	10
C4	298 (231)	410	**Humic-like fluorescence** that can be highly processed terrestrial DOM with low biolability [*Lapierre and Del Giorgio*, 2014]	0 (4*)
C5	237 (317)	395	**Humic-like fluorescence** from marine [*Coble*, 1996] and terrestrial [*Stedmon et al.*, 2003] environments and can be affiliated with microbial reprocessing of organic matter [*Stedmon and Markager*, 2005]	12

* 90-95% certainty

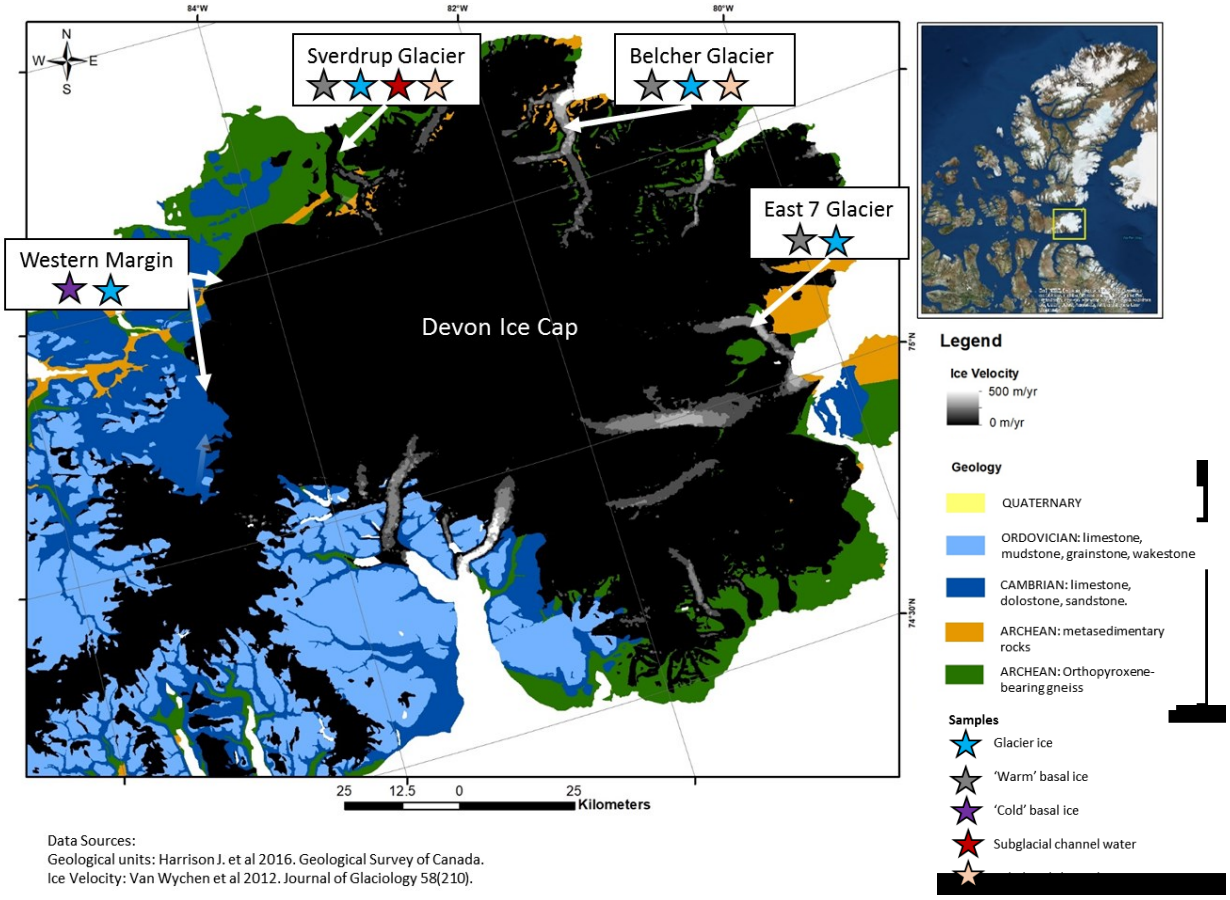

Figure 4-1 Study Site indicating the geology of the surrounding substrate [*Harrison et al.*, 2016] and flow velocity of the Devon Ice Cap [*Van Wychen et al.*, 2012]. Samples were collected from 3 polythermal glaciers with relatively fast flowing ice that are surrounded by Archean bedrock, and two locations along the relatively slow flowing cold-based section of the Western Margin

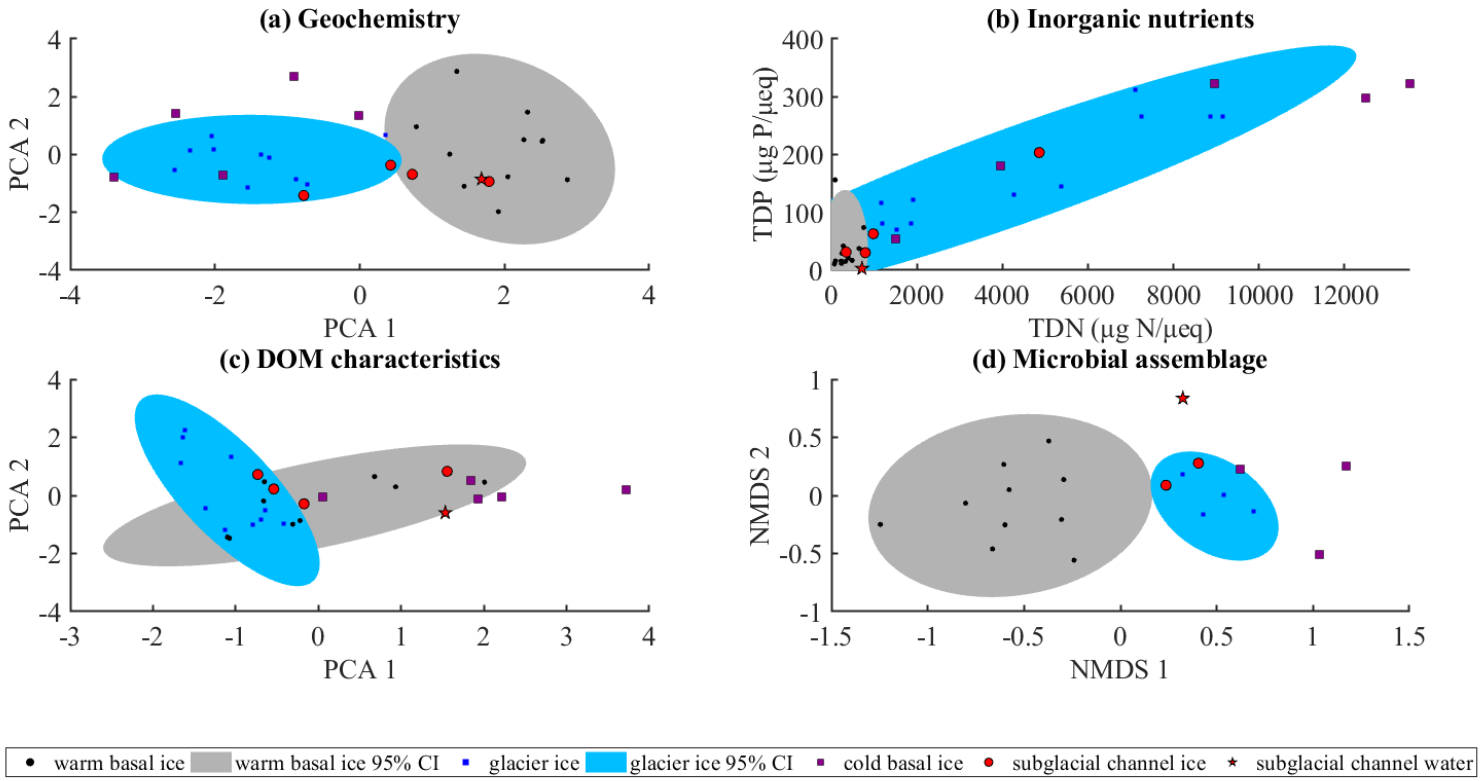

Figure 4-2: Summary of a) major ion composition, produced by PCA using the contribution of each major ion to the solute load, with each major ion normalized to its mean and variance b) inorganic nutrients relative to the solute load (TDP (µg P/µeq) and TDN (µg N/µeq)) (c) character of dissolved organic matter determined by principle component analysis using the relative contributions of the 5 modeled fluorescent components, with each component normalized to its mean and variance and d) microbial assemblage structure determined by nonmetric multidimensional scaling (NMDS) of Bray-Curtis distance measure using 16S rRNA gene sequencing (stress =0.16).

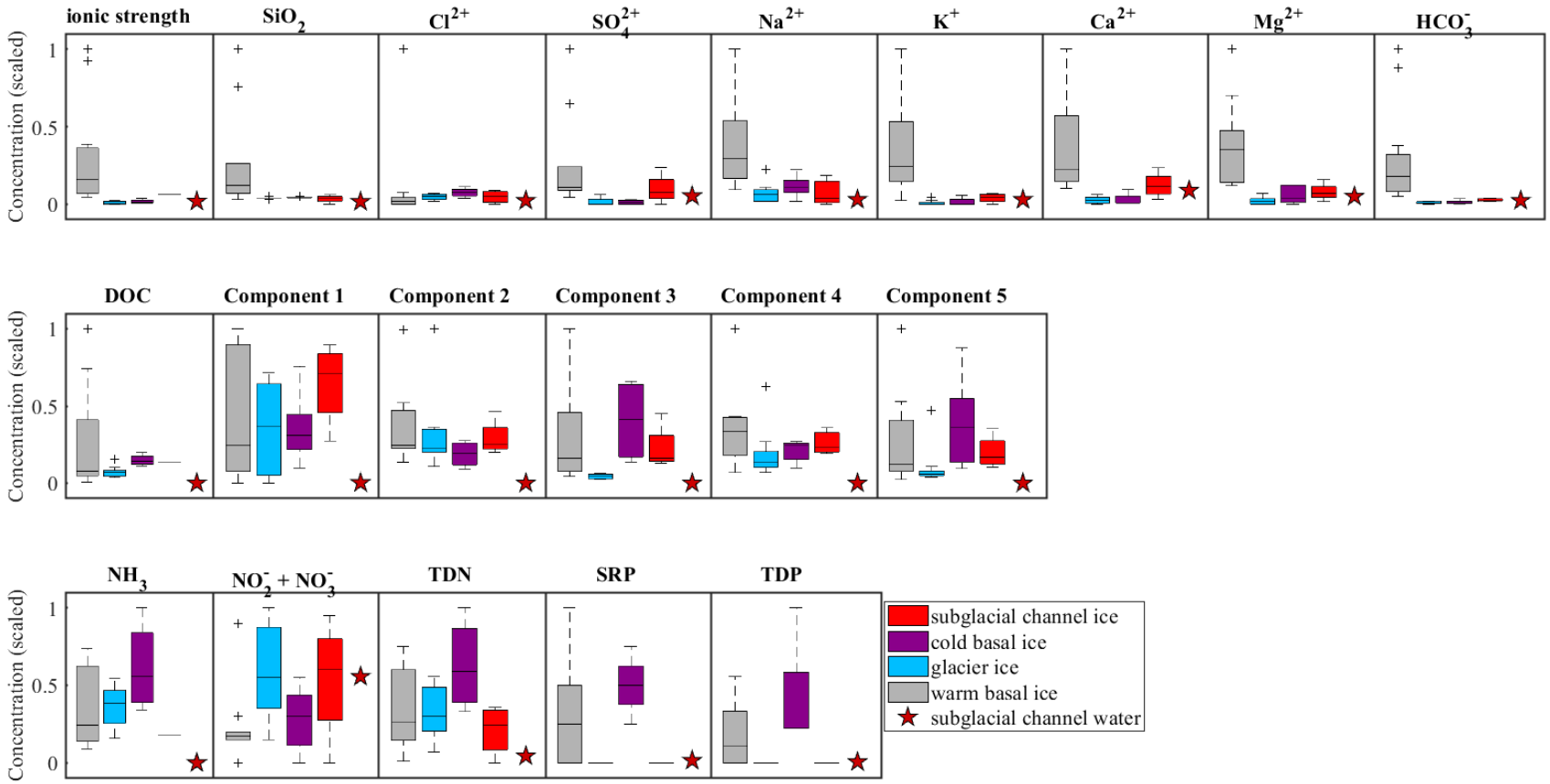

Figure 4-3: Relative abundance and range in concentrations of major ions (top), organic nutrients (middle) and inorganic nutrients (bottom) in basal ice, glacier ice, subglacial channel ice, and subglacial channel water. Data were scaled to the interval 0-1 and boxplots indicate the median, 25th and 75th percentiles, whiskers indicate the most extreme datapoints not considered outliers and outliers are indicated with a '+' symbol.

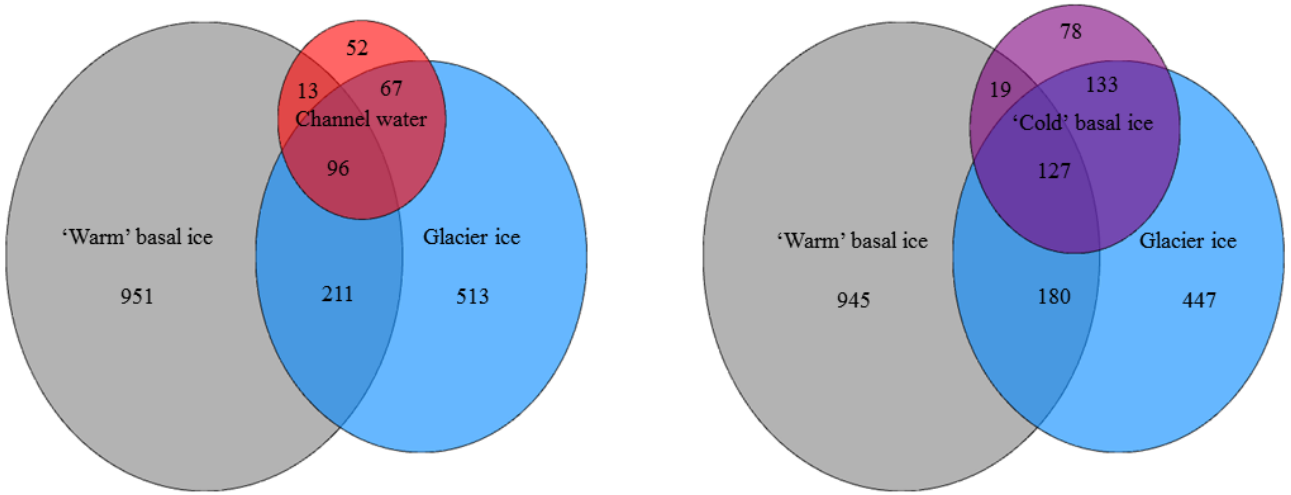

Figure 4-4: Venn Diagrams showing overlap in membership between the microbial assemblages observed in 'warm' basal ice, glacier ice, channel water and 'cold' basal ice samples. Numbers represent the number of operational taxonomic units (OTUs) that are unique to each environment or shared between environments.

Chapter 5: Conclusions

Glacier systems host distinct biogeochemical environments on the glacier surface (supraglacial system), inside the glacier (englacial system) and near the glacier bed (subglacial system). Sub-environments in the supraglacial system, including wet and dry snow, firn and bare glacier ice, cryoconite holes, and lakes and streams, are typically exposed to the atmosphere and light for at least part of the year and experience seasonal fluctuations in temperature. However, the physical conditions of these sub-environments can differ substantially in terms of the quantity of water that is available, and the type and quantity of sediment, nutrients and microbes they contain. In contrast, sub-environments within the subglacial system (including thin films of water, linked cavity systems, large meltwater channels, permeable subglacial sediments, basal ice, and vein water found along ice and sediment grain boundaries) are permanently dark, are characterised by relatively stable temperatures, and can contain abundant sediment. However, physical conditions in the subglacial environment can vary spatially and temporally, largely in response to variability in the availability and distribution of water, the type and reactivity of sediment, and redox conditions. The different physical and thermal/hydrological conditions that exist within glacier systems result in locally-distinct mixtures of allochthonously-derived and autochthonously produced nutrients and microbes, and physical and chemical products of rock weathering. Meltwater flow rates, flow paths, and residence times can vary over time and both within and between glacier systems and can yield varying degrees of connectivity and exchange between different biogeochemical environments. The hydrology of glaciers can therefore play an important role in controlling both the mixture of water sources that contribute to glacier runoff, and the range of nutrients and microbes that are exported from glaciers.

The objectives of this research were to (1) investigate the variability in microbial assemblages and nutrient species/concentrations that exists within and between the various biogeochemical environments that are found in polar glacier systems and (2) evaluate how glacier hydrology influences the development and export of microbes and nutrients from these systems. The results of this research lead to a refinement in our understanding of the biogeochemical characteristics of supraglacial, englacial and subglacial ice and meltwater environments, and of the roles of authochthonous and allochthonous processes in defining these biogeochemical characteristics. In addition, this research highlights the important influence of glacier hydrology on nutrient and microbe export from these systems. Specifically, the studies completed in this thesis show that:

- Definable sources and sinks for specific fractions of dissolved organic matter (DOM), dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) can exist along combined supraglacial-ice marginal-proglacial meltwater flow pathways (Chapter 1) and within relatively warm subglacial environments (Chapter 4).
- Basal thermal regime plays an important role in controlling the subglacial biogeochemistry and the mix of solutes, nutrients, and microbes that are acquired from substrate beneath glaciers or produced within subglacial environments. We found basal ice produced in relatively cold subglacial environments contain solutes and microbial assemblages that are remarkably similar to those in its parent glacier ice. In contrast, we found basal ice produced in relatively warm environments to be consistently enriched in major ions, dissolved organic matter (including humic material), and microbes, and occasionally enriched in dissolved phosphorus and reduced nitrogen (NH_4^+) (Chapter 4). The subglacial

system of relatively warm-based polar glaciers can also consistently change both the solute composition and microbial assemblages of meltwaters that drain though them (Chapter 3).

- Subglacial water that is stored over-winter in subglacial channels (with residence times of ~8 months) probably sustains *in situ* microbial activity that can deplete the reservoirs of labile dissolved nutrients (i.e. DIP, DIN and specific fractions of DOM) and develop distinct microbial assemblage structures (Chapter 4).
- The nutrients (Chapter 1) and microbes (Chapter 2) exported in glacial meltwaters can vary with the sources, flow routing, and residence times of meltwaters draining via the glacier-proglacial flow path. As a result, biogeochemical exports can 1) differ between glaciers with different biogeochemical sub-environments and/or hydrological systems, 2) change over the course of the melt season as the hydrological system within a glacier evolves, and 3) show different seasonal patterns for specific microbiological and nutrient parameters. For example:
    - In a cold-based glacier system in the Dry Valleys of Antarctica, nitrate concentrations increased with discharge, resulting in the export of episodic pulses of DIN-rich waters from the system. The sources and sinks of major ions along the same flow path were very different, and an inverse relationship was observed between major ion concentrations and discharge, resulting in a relatively constant 'trickle' of these solutes to downstream ecosystems. These dynamics differ from those in glacier systems that have different sources and sinks of nutrients and solutes, and/or different meltwater drainage system structures and flow routing (Chapter 1).

- In a glacier system with connected supraglacial and subglacial drainage elements, and an active subglacial drainage network that evolves spatially and structurally over the course of a melt season, the microbial assemblages exported from the system depended on whether the waters originated in the supraglacial or extraglacial environment, and on how long they spent in the subglacial system before draining from the glacier (Chapter 2).

The results from this thesis indicate that sources and sinks can be distinct for specific microbiological and nutrient parameters. It also indicates that the spatial and temporal variability of watershed characteristics have an important influence on the biogeochemical conditions that exist on, within and beneath glaciers and on the biogeochemical properties of the meltwater that they exported to downstream environments. These concepts are not new to studies of the chemistry and microbial ecology of glacier ice and meltwater; however, there are still few conceptual models that provide an integrated and detailed interpretation of the biogeochemical and hydrological characteristics of glacier systems. Furthermore, studies of glacier biogeochemistry over the past decade have frequently made broad generalizations about the nutrient and microbial characteristics and dynamics based on macro-scale glaciology and hydrology (e.g. temperate vs polar glacier systems) and upscale from measurements on one watershed to produce regional nutrient flux estimates [*Bhatia et al.*, 2013a; *Cameron et al.*, 2016; *Hawkings et al.*, 2016; *Wadham et al.*, 2016] or extrapolate observed relationships to estimate nutrient fluxes from glaciers under future climate conditions [*Hawkings et al.*, 2015]. Although there is merit in making these extrapolations, the studies completed in this thesis suggest that spatiotemporal variability in the biogeochemical characteristics of glacier ice and the meltwater derived from it may currently be underappreciated. This thesis also highlights the overwhelming need for future research to investigate and define the

dominant controls on the biogeochemistry of glacier ice and meltwater so that we can develop a more comprehensive and coherent understanding of the biogeochemistry all glacier systems and their meltwater exports. Only with such an understanding will it become possible to model these environments and their biogeochemical outputs, how they have changed in the past, and how they are likely to change in the future.

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