

In-Stream Reactivity of Dissolved Organic Matter and Nutrients in Proglacial Watersheds

Michael Quinn Nassry

Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State
University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
In
Biological Systems Engineering

Durelle T. Scott, Chair
W. Cully Hession
Mary Leigh Wolfe
Kevin J. McGuire
Eran W. Hood

March 27, 2013
Blacksburg, VA

Keywords: Dissolved Organic Matter, In-Stream Metabolism, Landscape Control,
Glacier Meltwater, Climate Change

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ABSTRACT

The unique landscape controls and meltwater contributions associated with glacial landcover along the coast of southeast Alaska were examined to better understand in-stream processing of dissolved organic matter (DOM) and nutrients during downstream transport. Specifically, this study paired glacial streams with nearby non-glacial streams and compared differences in landscape controls to: 1) evaluate the impact of glacial landcover and meltwater contributions on in-stream metabolism and uptake potential of proglacial streams; 2) quantify changes in DOM composition and concentration in glacial runoff during precipitation-driven flushing of a glaciated landscape; and 3) characterize the impact of glacial landcover and meltwater contributions on longitudinal trends in the physical and chemical signature of streamwater through changing watershed landscapes.

Stream metabolism estimates suggested glacial streams receive little DOM from landscape sources and have the potential to function as net autotrophic systems under low flow regimes with unobstructed sunlight. Unlike most watersheds, shallow organic soils and low in-stream respiration rates associated with glacial systems resulted in near equilibrium dissolved CO₂ concentrations, with little flux to the atmosphere. Longitudinal stream analyses concluded low-elevation landscape discharge contributions had little influence on glacial streams compared to non-glacial streams. High specific discharge from

glacial landscapes controlled streamwater chemistry throughout proglacial watersheds suggesting meltwater was delivered from the terminus of coastal glaciers downstream to the Gulf of Alaska (GOA) with little dilution or in-stream processing. Uniform concentrations of DOM and nutrients were found during increased discharge driven by precipitation on the glaciated watershed. This was in contrast to the non-glacial watershed, where streamwater DOM concentrations were largely controlled by connections to DOM-rich landscape sources during storm flows. Results from this study enhance the understanding of in-stream processes and landscape controls in watersheds that deliver freshwater to an ecologically productive marine zone and valuable commercial fishery. Furthermore, this study provides information about watersheds undergoing glacial recession to GOA basin-wide estimates of DOM export and future research initiatives focusing on in-stream DOM processing.

Acknowledgements

I want to thank my family for their support during my academic career. Foremost I want to thank my mother, Donna, for her love and support of my education. I want to thank my uncles Greg and Randy for sparking my interest in an environmental career and teaching me to question authority at a young age.

I want to acknowledge Andrew Vermilyea, whose laboratory, field, and fishing assistance in Juneau was the single most important factor that made this dissertation possible. I'd like to thank the Dolbin family in Blacksburg and State College for feeding me and keeping a roof over my head.

I'd like to acknowledge the National Science Foundation (0838497) for funding this research. I'd like to thank my research committee, especially Cully Hession for his assistance with all things Virginia Tech, Eran Hood for his assistance with all things Alaska, and Kevin McGuire and Mary Leigh Wolfe for their technical contributions and mentoring throughout my graduate program.

I'd like to acknowledge the following BSE staff: Laura Lehman and Amy Egan for instrumentation assistance; Susan Rosebrough, Teresa Cox, Barbara Wills, Ling Li, and Linda Altizer for forcing paperwork through; and, Denton Yoder for technology, coffee, and deer.

I'd like to thank my graduate student colleagues at Virginia Tech for their technical and non-technical assistance: Nate, Luke, and Robert; Matt, Jenae, and Dan; Joe, James, and Javier; and, Chris, Leslie, Jonathan, Andrea, Candice, and Jess. Finally, I'd like to thank everyone in Juneau: Dave D'Amore, Jason Fellman, Jenn Shinn, David Sauer, Nick Korzen, Melissa Woodgate, Keri Bryan, and Steffi Schreiber.

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Chapter 1: Introduction

1.1. Introduction and Research Objectives

The coastal region of the Gulf of Alaska (GOA) is a diverse and productive marine ecosystem that is home to resident and migratory populations of fish, birds, and marine mammals, and supports a valuable recreational and commercial fishery. This aquatic ecosystem receives freshwater, nutrient, and dissolved organic matter (DOM) inputs from meltwater contributions of coastal glaciers during the summer meltseason. These contributions create a favorable environment for the production of microscopic phytoplankton and zooplankton, which compose the base of the food chain and support larger organisms. Changes to the amount, composition, or timing of meltwater contributions delivered to the GOA from the landscape will impact the composition and productivity of the near-shore aquatic ecosystem.

The large volume of glaciers located along the southeast coast of Alaska and the warming air temperatures in this temperate maritime climate have resulted in glacial recession and landscapes transitioning from ice and rock to successional vegetation. Streams in watersheds undergoing glacial recession are receiving discharge from new sources that flow through different landscapes as the glaciers recede. Variations to the pool of DOM and nutrients originating from and being transported through transitioning landscapes will impact the amount and composition of DOM and nutrients delivered to the GOA ecosystem.

Previous research efforts have documented the effects of glacial recession on the quantity and quality of DOM delivered to streams, but little is known about the in-stream processing of DOM prior to reaching the GOA. Glacial meltwater contributions

alter both the physical and chemical characteristics of streams, which can impact microbial communities that process DOM and nutrients. Furthermore, landscape controls such as riparian shading, soil composition, and vegetation type also influence the in-stream processing of DOM and nutrients in glaciated watersheds. Understanding in-stream changes to the DOM pool delivered to the GOA is critical to understanding the impact of glacial recession on the ecologically and economically valuable marine ecosystem of southeast Alaska.

The overall goal of this study was to characterize the effect of glacial landcover and meltwater contributions on the in-stream processing of DOM and nutrients during downstream transport from high-elevation headwaters to the GOA. Glacial streams were compared with nearby non-glacial streams to achieve the following specific research objectives:

1. Evaluate the impact of glacial landcover and meltwater contributions on the in-stream metabolism potential of proglacial streams;
2. Characterize the impact of glacial landcover and meltwater contributions on longitudinal trends in the physical and chemical signature of streamwater; and
3. Quantify changes in DOM composition and concentration in glacial runoff and total event flux of DOM and nutrients during precipitation-driven flushing of a glaciated landscape.

The results of this research will provide insight into glacier landcover and meltwater contribution controls on in-stream processes regulating DOM and nutrient dynamics, and eventual delivery to the GOA. This information will enhance the understanding of processes that influence the health of an ecologically productive marine zone and valuable commercial fishery.

1.2. Literature Review

1.2.1 Background

Glacial recession and thinning along the southeastern coast of Alaska has resulted in changes in the export of freshwater, nutrients, and dissolved organic matter (DOM) from coastal watersheds to the Gulf of Alaska (GOA) (Hood and Scott, 2008). Since the mid-1950's, melting Alaskan glaciers contributed more freshwater to coastal marine zones than any other group of glaciers in the world and the rate of glacial thinning in southeastern Alaska is increasing (Arendt et al., 2002). An estimated 78% of freshwater contributions to the GOA, including glacial meltwater, originate from small drainages along the coast (Neal et al., 2010), where streams start in the coastal mountains and quickly descend along short flow paths to the GOA. These freshwater contributions to the GOA can result in seasonal stratification of near-shore marine waters (Etherington et al., 2007). Along the southeast coast of Alaska, this stratification is a critical component in creating a biologically active ecosystem by producing conditions ideal for abundant chlorophyll a (Etherington et al., 2007). The productivity of the aquatic food web and health of the marine ecosystem in the GOA is of critical concern because it is both an ecologically important resource (Baker et al., 1992) and supports a commercial fishery that produces over 4 billion pounds of fish and shellfish each year (AKRDC, 2009).

1.2.2. Climate

The mean annual air temperature in southeast Alaska, near Juneau, is 5°C at sea level and ranges from a January average temperature of -3.8°C to a July average of

13.4°C (NOAA, 2013). Since 1951, warmer air temperatures in southeast Alaska during the winter and spring have led to both increased total precipitation and decreased snowfall (Hartmann and Wendler, 2005). Mean annual precipitation is 1480 mm, with the wettest month (October) averaging 211 mm and the driest month (April) averaging 75 mm (NOAA, 20013). Rainfall in this region is frequently associated with coastal storms that release moisture when they encounter high elevation mountain ranges near the coast. Stream discharge usually peaks in late summer or early fall when contributions from glacial meltwater and permanent snowfields combine with rainfall associated with coastal storms from the GOA (Hood and Berner, 2009).

Juneau is surrounded by the Tongass National Forest and the coastal landscape is characterized by Sitka spruce forests, forested wetlands, muskegs, exposed bedrock, and glacial landcover in small, steep watersheds. The larger GOA drainage basin is 18% (75,640 km²) glacier ice with a total area of 420,230 km² (Neal et al., 2010). Thin soils and successional vegetation dominate much of the high elevation landscape, particularly recently deglaciated areas. High-elevation, non-glaciated areas are snow covered much of the year, and make snowmelt contributions to both glacial and non-glacial streams in the spring and summer melt seasons.

1.2.3. Dissolved Organic Matter

One of the most complex and ecologically important materials rivers transport from the landscape to marine systems is dissolved organic matter (DOM), the portion of the organic matter pool that can pass through a defined filter size ranging from 0.2 – 0.45µm (Tranvik and Wachenfeldt, 2009) to 0.7µm (Aitkenhead-Perterson et al., 2003). Contributions to the DOM pool in aquatic systems are influenced by both the

surrounding landscape (D'Amore et al., 2010) and in-stream conditions. DOM in aquatic systems, including streams, lakes, and marine environments, can be divided into two main groups based on source: (1) allochthonous and (2) autochthonous. Allochthonous DOM describes components of the DOM pool from external sources (e.g. terrestrial DOM), and autochthonous components originate in the aquatic system (e.g. biofilm, aquatic vegetation). Each group can be further divided into sub-components based on composition (e.g. protein, humic), mass (e.g. low molecular weight (LMW), high molecular weight (HMW)), or ecological properties (e.g. bioavailable, recalcitrant) (Findlay and Sinsabaugh, 2003), and then related to landscape source or ecosystem function. For example, the aromatic molecules related to lignin components in plant material are more readily degraded by photochemical reactions than DOM comprised of amino acids, which are more readily degraded through biological oxidation (Benner and Kaiser, 2011).

The source of OM in glacial systems is not well understood, but many studies have suggested meltwater contains the DOM composition signature from a microbial source (Lafreniere and Sharp, 2004; Skidmore et al., 2000) and glacial systems are home to microbial communities in the basal ice and along the ice / rock interface (Sharp et al., 1999; Skidmore et al., 2000). Other possible sources of organic matter in glacial systems are remnants of forest covered under an advancing mountain glacier (Bardgett, 2007) or aerosol deposits from fossil fuel burning (Stubbins et al., 2012). Stream water DOM from microbial sources (e.g. degradation of cells) is generally more bioavailable than DOM additions from terrestrial sources with higher aromatic content (McKnight et al., 2001). Part of the discrepancy in DOM bioavailability is associated with flow paths

through the soil, where biological removal of labile DOM fractions from terrestrial sources results in less bioavailable DOM reaching the stream channel (Findlay and Sinsabaugh, 2003). As DOM moves through the landscape, there is preferential uptake of non-aromatic components of the DOM pool. Watersheds with large contributing areas of DOM-rich land cover, such as wetlands and bogs, including the southeast Alaska coast, are likely to see stream DOM signatures linked to wetland DOM composition (Fellman et al., 2009b).

The composition of meltwater and meltwater-dominated streams is different from streams draining landscapes characterized by forests and wetlands (Hood and Berner, 2009; Fellman et al., 2010). DOM, specifically dissolved organic carbon (DOC), concentrations in proglacial streams are lower than nearby streams draining non-glacial watersheds (Barker et al., 2006; Hood and Berner, 2009), and DOC concentrations have an inverse relationship with watershed glacier coverage in southeast Alaska (Hood et al., 2009). Previous studies on glacial outflows in southeast Alaska measured DOC levels below 33 $\mu\text{mol/L}$ (Stubbins et al., 2012), on glacial streams in the Canadian Rockies below 59 $\mu\text{mol/L}$ (Lafreniere and Sharp, 2004), and from sub and supraglacial streams in British Columbia of 39 $\mu\text{mol/L}$ (Barker et al., 2006). These values are well below documented DOC concentrations in non-glacial streams across a wide range of climates and landscapes including a forested stream in southeast Alaska (183 $\mu\text{mol/L}$) (Hood et al., 2009), a mixed forest/wetland stream in Canada (341 $\mu\text{mol/L}$) (Hinton et al., 1997), and in a forested catchment in New York (405 $\mu\text{mol/L}$) (Inamdar et al., 2009).

1.2.4. Nutrients

Nutrient concentrations and form in streamwater are important to both primary producers and heterotrophic organisms and can influence in-stream processes and water quality. Stream nutrient concentrations can exhibit seasonal trends because of biological processes influencing retention in the landscape or changes in the generation or mobilization of sources (Mulholland, 2004; Goodale et al., 2009). Nitrate concentration in non-glacial streams can peak during the summer months either because of increased rates of nitrification associated with higher soil temperatures (Stark, 1996) or a combination of lower stream discharge associated with a constant source of nitrate in the stream. Despite seasonal trends in non-glacial catchments, normalized NO_3^- concentrations are frequently found to have an inverse relation to stream discharge (Goodale et al., 2009). In southeast Alaska, Hood and Berner [2009] found that glacial coverage was inversely proportional to both organic and inorganic nitrogen concentrations in coastal streams.

Riparian areas in these deglaciated landscapes are often colonized by successional vegetation including nitrogen-fixing alders. Alders have been associated with increased organic and inorganic nitrogen concentrations in streamwater and even nitrogen saturation in riparian forest in the Pacific Northwest (Compton et al., 2003). Evidence also points to nitrogen controls in the glacier ice system. Cycling in cryonite holes on the glacier surface and in the basal ice at the ice/rock interface can transform nitrogen deposited on the glacier surface in rain and snow (Hodson et al., 2005).

Unlike the inverse relationship between stream nitrogen concentrations and watershed glacier coverage, concentrations of soluble reactive phosphorus (SRP)

increase with increasing glacier coverage (Hood and Scott, 2008; Hood and Berner, 2009). Increased phosphorus yields have been associated with erosive forces acting on bedrock at the glacier-rock interface, with high concentrations observed at points of discharge at the glacier terminus and then decreasing downstream (Williams et al., 2001). In addition to higher SRP values in the water column, glacial systems are also associated with increased phosphorous export bound to fine glacial sediment (Hodson et al., 2004). Fine sediments in glacial streams retain SRP through mostly abiotic sorption reactions, while streams with coarse sediments retain more SRP through biotic uptake (Lottig and Stanley, 2007).

1.2.5. Metabolism

Biological processes cycle organic matter and nutrients through the water column and hyporheic zone during downstream transport through stream networks. Net ecosystem metabolism (NEM) is the sum of the biological processes (autotrophic primary production and heterotrophic respiration) that produce and consume DOM in streams (Bott, 2007). NEM, also referred to as net daily metabolism (NDM), is calculated as the sum of 24-hr community respiration (CR_{24}) and gross primary production (GPP) over a 24-hr time span (Bott, 2007). Because NEM metrics are calculated as mass of oxygen per area (or volume) over time, negative values are associated with respiration because it consumes oxygen, while positive values are assigned to primary production because it creates oxygen. A negative NEM value corresponds with a ratio of GPP to CR_{24} (P/R) less than 1 and a heterotrophic system dominated by respiration. A positive NEM value corresponds to a P/R ratio greater than 1 and an autotrophic ecosystem that is operating as a net source of energy by creating

biomass through photosynthesis (Odum, 1955; Vannote et al., 1980). Streams reaches can continue to function with negative metabolic energy balances because they receive inputs from terrestrial sources (e.g. leaf litter), lateral groundwater inflow carrying organic matter, and upstream reaches where NEM values can differ (Vannote et al., 1980).

1.2.6. Open Water Methods

By definition, NEM estimates provide insight into the biological processes occurring in the entire stream ecosystem (Bott, 2007). This means a combination of processes occurring in the water column, and also in the hyporheic zone of the stream bed are included in estimates of NEM, GPP, CR_{24} , and P/R (Bott, 2007). This whole-system balance, especially in streams with an open or semi-open canopy, means the water column is dominated by autotrophic activity during daylight hours, while the hyporheic zone is consistently heterotrophic (Grimm and Fisher, 1984). Therefore, biological processes for a whole system are driven not only by individual factors influencing respiration (temperature, organic matter supply) and primary production (light, nutrient supply), but also by factors that define the boundaries for the system (e.g. hydrology, sediment composition) (Lottig and Stanley, 2007).

NEM, GPP, and CR_{24} are difficult to measure directly in the field, so methods have been developed to monitor changes in DO concentrations that are then used to estimate these metrics (Odum, 1955). Open water NEM estimation methods assume DO levels increase during daylight hours due to primary production driven by sunlight, and heterotrophic respiration remains constant over 24 hours (Bott, 2007). These assumptions allow for measurements made at night to be attributed solely to respiration

and then applied uniformly over the entire 24-hr monitoring period. Any departure in DO concentration observed from this constant value during the day can then be assumed to be the result of autotrophic primary production. This method cannot identify component contributions to each ecosystem process (e.g., the differences between GPP from phytoplankton, benthic algae, and macrophytes) (Grace and Imberger, 2006), and is designed for well-mixed stream segments with constant flow and low groundwater inputs. Groundwater inflow between monitoring stations can produce DO level changes not representative of the system, and stratified streams can produce varying results based on monitoring depth and lateral placement (Grace and Imberger, 2006).

First described by Odum (1955), open water measurements of diurnal changes in oxygen concentrations use either a single or a two-station method. Upstream and downstream locations can be used to assess stream metabolism of a slug of water as it moves downstream or a single station can be used if spatial variations in oxygen concentration are assumed to be negligible (Bott, 2006). Changes in oxygen concentration are corrected for exchange across the air/water interface (reaeration), and saturation concentrations are calculated based on water temperature, salinity, and barometric pressure (Bott, 2006). Rates of change not associated with physical drivers are assumed to be the result of biological activity, and analyses of those changes result in estimates of the metabolism metrics.

One of the most difficult parameters to obtain accurately in the open water methods is the reaeration coefficient (k). Reaeration can be determined using sulfur hexafluoride (SF_6) or propane injections, or through empirical models such as the surface renewal model (SRM) and energy dissipation model (EDM) (Owens et al., 1964;

Tsivoglou and Neal, 1976). The empirical methods (Marzolf et al., 1994; Young and Huryn, 1998) use velocity, stream depth, and channel slope to determine reaeration.

Rates of stream ecosystem metabolism are influenced by factors both in the stream channel and in the surrounding landscape. Light reaching the streambed, nutrient availability, temperature, organic matter availability, and geomorphology are some of the factors regulating stream metabolism (Young and Huryn, 1999; Mulholland et al., 2001). Along the length of a stream, rates of metabolism components can change due to hydrologic changes (Young and Huryn, 1996), changes in floodplain organic matter inputs (Meyer and Edwards, 1990), or geomorphic factors such as loose substrate, which does not provide stable habitat for benthic algae and that offers no protection against disturbance (Bott, 1983). Studies across different landscapes and stream orders have shown light reaching the streambed is the major driver of GPP (Mulholland et al., 2001), but high nutrient concentrations, specifically SRP, can also lead to increased GPP by autotrophic organisms (Lamberti and Steinman, 1997; Young and Huryn, 1999). Daily light changes in a stream can be attributed to cloud cover and turbidity in the water column, seasonal fluctuations of light can be regulated by canopy cover, and spatial variation of light can be influenced by cliffs or steep terrain shading a stream channel (Young and Huryn, 1999). Organic matter contributions are the primary control of CR_{24} (Young and Huryn, 1999). Reported rates also vary across studies and may be related to methodology, specifically reaeration estimation technique (Table 1.1).

1.2.7. In-Stream Carbon Dioxide Concentrations

Another metric for assessing the biological processes taking place in a stream and the surrounding landscape is measuring the amount of dissolved carbon dioxide

(CO₂) or excess partial pressure of carbon dioxide (*ep*CO₂). *ep*CO₂ is a measure of the saturation state of carbon dioxide in the water column above or below equilibrium levels. The state of saturation of dissolved CO₂ can be related to biological processes that produce (respiration) or consume (photosynthesis) CO₂ (Hamilton et al., 1995; Guasch et al., 1998). CO₂ concentrations in streamwater are also influenced by pH as dissolved inorganic carbon (DIC) components (CO₂, carbonate (CO₃²⁻), and bicarbonate (HCO₃⁻)) will reach equilibrium and partition between species based on pH (1.1; Emerson and Hedges, 2008).

$$\text{DIC} = \text{CO}_2 + [\text{CO}_3^{2-}] + [\text{HCO}_3^-] \quad (1.1)$$

CO₂ measurements can also provide information about the surrounding landscape (Johnson et al., 2008) and hyporheic system that contribute discharge to the stream (Tables 1.2 and 1.3). The hyporheic zone, directly in contact with the water column, can contribute over 75% of the CO₂-producing respiration component of stream metabolism measurements (Naegeli and Uehlinger, 1997; Fellows et al., 2001). Numerous studies have also shown streams and rivers across varying climates and eco-regions as a net source of CO₂ with diel outgassing curves being evident during periods of increased algal activity (Raymond et al., 1997; Guasch et al., 1998; Johnson et al., 2008; Butman and Raymond, 2011). Water moving in flow paths through microbially active organic soil layers can carry supersaturated concentrations of CO₂ from the landscape to streams via lateral flow, with higher concentrations moving from the landscape to surface waters during seasonally wet periods (Johnson et al., 2008)

and during warmer summer months (Jones and Mulholland, 1998). Aqueous CO₂ transported from watershed soils to streams through lateral flow and deep groundwater flow can account for a high percentage (> 70%) of the total carbon export from the landscape (Johnson et al., 2008).

1.2.8. Storm Flows

Numerous studies have investigated DOM concentration and composition in precipitation-driven stream discharge from non-glaciated watersheds in southeastern Alaska and other regions (Hinton et al., 1997; Hood et al., 2006; Fellman et al., 2008). In both forested and wetland covered watersheds, DOC concentrations increased during storm discharge increases (Fellman et al., 2009a; Inamdar et al., 2009). This increase is attributed to changes in flow paths and contributing sources of water flowing from the landscape to the stream channel. Changes in source also impact composition of DOM delivered to the stream channel during storms. Unlike DOC, normalized inorganic nitrogen concentrations often have an inverse relation to stream discharge increases (Goodale et al., 2009).

During storm events, some catchments can receive contributions to stream flow from different landscape sources at different times of the storm hydrograph. For example, DOC contributions from near-stream riparian areas can appear in the channel early in the event hydrograph, while DOC contributions from disconnected locations in the landscape can appear on the descending limb of the hydrograph (McGlynn and McDonnell, 2003). A similar pattern of early near-stream flushing of DOC has been observed with snowmelt, as riparian areas contribute DOC early in the melt season, while upslope landscapes contribute DOC later (Boyer et al., 1997).

In southeast Alaska, heavy precipitation coupled with small, steep coastal watersheds means rainfall-driven freshwater discharge can significantly influence the flux of freshwater and the associated organic matter and nutrient fluxes from the coastal landscapes to the GOA. In addition to concentration, bioavailability of DOC in the channel also increased during storm flows (Fellman et al., 2009a) because shallow flow paths can access recent DOM in the landscape with reduced opportunity for bioavailable fractions to be mineralized or incorporated into biomass.

On glaciated surfaces, seasonal discharge changes can impact flow paths in the sub-glacial environment as early contributions of snow and ice melt are more dispersed, while peak discharge regimes are characterized by channelized flow paths (Bhatia et al., 2011). This change in meltwater flow path may also occur over the course of a storm when event precipitation drives increased discharge from the glacial terminus on a shorter time scale.

1.2.9. Longitudinal Trends

As stream water transitions from low order, high-elevation headwater streams through the landscape to larger rivers, concentrations of nutrients, organic matter, and other solutes can change because of a combination of biotic (McTammany et al., 2003) and abiotic factors (Mulholland et al., 2001; Benner and Kaiser, 2011) in the watershed and can influence the water quality and organic matter in the water column. Glacial land cover and meltwater contributions can influence many of these factors, and therefore influence the processing of nutrients and organic matter during transport through the watershed (Uehlinger et al., 2010). Changes in soil temperature, water table dynamics,

and aerobic conditions all contribute to landscape retention or export of DOM to streams (D'Amore et al., 2010) at different points and times in the watershed.

In-stream biotic processes (respiration, primary production) also influence the cycling and retention of landscape inputs as they travel downstream to higher-order reaches. Stream nutrient concentrations have been linked to the activity of microbial communities reacting to external drivers such as increased sunlight or pulses of organic matter (Mulholland, 2004). Additional control on stream water NO_3^- concentration can come from denitrification of groundwater in the riparian zone, which like in-stream processes, can also be controlled by organic matter availability changes (Groffman et al., 1996) and temperature differences (Rasmussen et al., 2011; Ylla et al., 2012) from headwaters to valleys.

Streams in southeast Alaska transitioning from high elevation headwaters can start in open-canopied landscapes, transition to closed canopied reaches, and receive added sunlight as stream width increases downstream with increased discharge. In a longitudinal study of stream metabolism in a forested stream, rates of CR_{24} remained constant while GPP increased 3-fold downstream along a 37 km stretch of the Little Tennessee River (McTammany et al., 2003). Similar studies have also shown a shift toward a less heterotrophic system with increased stream order which can be attributed to more light reaching the stream through a decreasingly dense forest canopy (Bott et al., 1985).

1.2.10. Fluorescence Properties and Isotope Analysis

DOM Fluorescence

Insight into the composition of the organic matter pool in aquatic ecosystems can be obtained from fluorescence excitation-emission matrices (EEMs) of DOM, which can identify the contribution of specific fluorescent DOM compounds to the total DOM fluorescence (McKnight et al., 2001; Stedmon et al., 2003). This method cannot fully characterize the bulk DOM pool but can provide insight into relative sources.

Fluorescence emission peaks, determined by relaxation of molecules to a ground state following the absorption of light, are then corrected for background interference and modeled using the multivariate statistical method of parallel factor analysis (PARAFAC) (Stedmon et al., 2003). PARAFAC is used to quantitatively identify emission peaks and then group similar peaks (Fellman et al., 2009c). These groups, or components, can then be related to specific material in the bulk DOM pool and then related to source (microbial vs. terrestrial) based on location of the emission peak (McKnight et al., 2001). Protein-like fluorescence has been strongly correlated to bioavailable dissolved organic carbon (BDOC) in coastal streams in southeast Alaska (Fellman et al., 2009a).

Fluorescence spectroscopy has also been used to characterize the source and reactivity of DOC in glacial systems in Antarctica and Canada (Barker et al. 2006).

Glacial outflow samples produced emission peaks consistent with established values for microbial generation with protein-like contributions ranging from 88% - 90% of the DOM pool, while samples from a nearby watershed dominated by wetlands and conifer forest contained DOM with only 2% protein-like fluorescence (Stubbins et al., 2012).

Fluorescence Index

The fluorescence index (FI) is another metric used to gain information about the source and composition of DOM and, therefore, provide insight on the role DOM plays in larger ecosystem functions. The FI measures the relative drop in emission when wavelength increases from 450 to 500 nm, with larger decreases associated with microbially derived DOM and smaller decreases associated with terrestrial DOM (McKnight et al., 2001). Analyses of the FI has been used during studies of storm flows to show increases in aromatic lignin contributions (Vidon et al., 2008), during salmon spawning to show decreases in streamwater aromaticity (Hood et al., 2007), and in glacial systems to show the dominance of microbially based DOM (Lafreniere and Sharp, 2004). A FI value typically associated with streamwater dominated by microbial sources with low aromaticity is near 1.9, while DOM with terrestrial origins has values of FI near 1.4 (McKnight et al., 2001). Calculated FI values beyond that range have been measured elsewhere including wetlands in southeast Alaska (1.27) and in Antarctic lakes (2.82) (McKnight et al., 2001; Hood et al., 2007). When compared with DOC levels in glacial systems, FI values have been shown to decrease as DOC concentrations increase (Lafreniere and Sharp, 2004; Hood et al., 2006). These values can vary by landscape, but are useful in comparing treatments or end-members to one another and identifying the relative difference in DOM source contributions between different surface waters.

Isotope Analysis

Another technique to identify landscape source contributions to streams is the use of stable water isotopes oxygen-18 (^{18}O) and deuterium (D , ^2H). Water isotopes in

hydrology have been used to determine discharge source the based on residence time in the landscape, or the location in the landscape it fell as precipitation. These applications are based on the fundamental concepts that the isotope signature of water can only change through conservative mixing with water of a different isotopic composition, or through fractionation (McGuire and McDonnell, 2007). Isotope hydrology has been used for hydrograph separation during storms (Sklash and Flarvolden, 1979), hydrograph separation during snowmelt (Hooper and Shoemaker, 1986), and comparisons of glacier meltwater contributions to streams in southeast Alaska (Hood and Berner, 2009). Isotope analysis is done to determine how depleted or enriched a water sample is of the targeted isotope (^{18}O , D) from an established standard value of either Standard Mean Ocean Water (SMOW), or Vienna Standard Mean Ocean Water (VSMOW) (Kendall and Caldwell, 1998).

Differences in water isotopic composition are caused by the differences in the amount of energy required to change phase during fractionation. For example, a water molecule containing heavier ^{18}O requires more energy to transition from a liquid to a gas (evaporation) than a molecule with ^{16}O . This means the gas phase will be enriched in ^{16}O and depleted in ^{18}O , while the opposite description can be applied to the liquid phase. This can also be applied for water transitioning from a gas to a liquid (formation of precipitation). Heavier ^{18}O will fall out of the atmosphere first, while lighter ^{16}O requires less energy and can remain as water vapor longer. This results in areas further inland from the coast, at higher elevations, and with colder temperatures receiving precipitation that is depleted in the heavier water isotopes of ^{18}O and deuterium. Examples of this concept applied in the field include differences of $\delta^{18}\text{O}$ in glacial ice

and snow (-28.2 and -12.3 ‰) in Greenland show the glacial ice is more depleted with respect to the standard value (Bhatia et al., 2011) because it likely fell as precipitation at a higher elevation and at a colder temperature. In locations where stream water is generated from locations that differ in elevation, temperature, and distance from the coast (such as southeast Alaska) isotopic analysis can provide valuable insight into discharge contributions from various landscape sources.

Table 1.1: Estimated values of stream metabolism metrics. NEM, CR₂₄, GPP, reaeration coefficients (K_{O2}), depth, and discharge for selected studies across a range of stream sizes, environments, and K_{O2} estimation techniques.

Location	Depth (m)	Q (m ³ sec ⁻¹)	K _{O2} (d ⁻¹)	Method for K _{O2} Determination	Metabolism (g O ₂ m ⁻² d ⁻¹)			Reference
					GPP	CR ₂₄	NEM	
Darling R, Burtundy, NSW	1-2	5	0.22	From diel curve	2.1	-4.1	-2.1	Grace et al., MDBC, 2003
Giltner Springs Ck, WY, USA	0.12	0	32	SF6	16.8	-11.6	5.2	Hall & Tank, 2005
Necker R, Switzerland	0.25	18	1.2	SF6	2.5	-3.5	-1.0	Uehlinger & Naegeli, 1998
Grand R, MI, USA	0.58	32	5.5	Delta Method	9.9	-9.3	0.6	Chapra & DiToro, 1991
Hugh White Ck, NC, USA	0.03	0.018	240	Propane	0.1	-3.3	-3.2	Mulholland et al., 1997
Walker Branch, TN, USA	0.05	0.029	140	Propane & EDM	1.5	-6.0	-4.5	Mulholland et al., 2001
Sycamore Ck, AZ, USA	0.04	0.12	160	Propane & EDM	11.2	-8.0	3.2	Mulholland et al., 2001
Bear Brook, NH, USA	0.13	0.009	80	Propane & EDM	0.3	-7.0	-6.7	Mulholland et al., 2001
Gallina Ck, NM, USA	0.06	0.012	260	Propane & EDM	0.7	-7.2	-6.5	Mulholland et al., 2001
Eagle Ck, MI, USA	0.24	0.74	30	Propane & EDM	1.0	-6.2	-5.3	Mulholland et al., 2001
South Kings Ck, KS, USA	0.04	0.039	43	Propane & EDM	2.8	-2.1	0.7	Mulholland et al., 2001
Sutton Stream, NZ	0.17	0.88*	115*	Propane	0.9	-4.6	-3.7	Young & Huryn, 1999
Powder Ck, NZ	0.16	0.17*	130*	Propane	0.6	-5.4	-4.8	Young & Huryn, 1999
Lee Stream, NZ	0.38	1.84*	6*	Propane	1.1	-1.9	-0.8	Young & Huryn, 1999
Three O'Clock Stream, NZ	0.39	0.48*	29*	Propane	3.5	-2.7	0.8	Young & Huryn, 1999
Ditch Ck, WY, USA	0.14	0.88	98	SF6	2.0	-6.4	-4.5	Hall & Tank, 2003
Lizard Ck, WY, USA	0.11	0.10	48	SF6	0.6	-4.1	-3.5	Hall & Tank, 2003
Bailey Ck, WY, USA	0.1	0.44	70	SF6	1.0	-2.0	-1.0	Hall & Tank, 2003
Paintbrush Canyon Ck, WY, USA	0.06	0.015	59	SF6	0.3	-1.9	-1.5	Hall & Tank, 2003
Mangaone R, Waikato, NZ	0.66	1.53	8.5	From diel curve	3.6	-23.1	-19.5	Wilcock et al., 1998
Matahuru R, Waikato, NZ	0.54	1.27	2.8	From diel curve	9.2	-4.6	4.6	Wilcock et al., 1998
Opitonui R, Waikato, NZ	0.24	1.05	21	From diel curve	3.8	-9.1	-5.3	Wilcock et al., 1998
Oraka R, Waikato, NZ	0.57	2.72	9.5	From diel curve	2.3	-13.1	-10.8	Wilcock et al., 1998
Waitoa R, Waikato, NZ	0.53	1.36	13	From diel curve	46	-21	25	Wilcock et al., 1998
Goulburn R, Shepparton, Vic	1.4	NA	1.5	From diel curve	1.5	-6.7	-5.2	Grace, NEMP Phase 2, 2000
Dobson's Ck, Melbourne, Vic	0.11	0.005	5.1	From diel curve	0.2	-1.5	-1.3	Grace, CRCFE Project D210, 2003
Lyrebird Ck, Melbourne, Vic	0.08	0.007	17	From diel curve	0.0	-0.6	-0.6	Grace, CRCFE Project D210, 2003

(Continued)

Table 1.1 (continued): Estimated values of stream metabolism metrics. NEM, CR₂₄, GPP, reaeration coefficients (K_{O2}), depth, and discharge for selected studies across a range of stream sizes, environments, and K_{O2} estimation techniques.

Location	Depth (m)	Q (m ³ sec ⁻¹)	K _{O2} (d ⁻¹)	Method for K _{O2} Determination	Metabolism (g O ₂ m ⁻² d ⁻¹)			Reference
					GPP	CR	NEM	
Northern Spain	0.36-1.52	0.57-22.74	n.a.	Nighttime Regression	2.7 to 11.0	-6.30 to -42.6	-1.7 to -36.2	Izagirre et al., 2008
Switzerland	<0.2	n.a.	n.a.	SF6	1.2 to 10.8	-5.9 to -9.9	n.a.	Logue et al., 2004
Little Tenn River, NC	0.7-1.0	7.4-18.4	3.15-9.26	EDM	0.22 to 6.14	-0.85 to -7.28	-0.28 to -3.26	McTammany et al., 2003
Pocopson Creek, PA	0.21	0.09 - 0.16	16.5	Propane, EDM, SRM	2.6	-3.89	-1.29	Bott et al., 2006
Birch Run, PA	0.18	0.03 - 0.10	25.3	Propane, EDM, SRM	1.5	-2.31	-0.81	Bott et al., 2006
White Clay Creek, PA	0.14	0.03 - 0.10	43.4	Propane, EDM, SRM	1.85	-3.12	-1.28	Bott et al., 2006
Buck and Doe Run, PA	0.35	0.76 -3.37	8.3	Propane, EDM, SRM	1.67	-3.35	-1.68	Bott et al., 2006
Gallina Creek, NM	0.16	0.0008	n.a.	Propane	1.7	-14.7	-13.0	Fellows et al., 2001
Columbus, GA	0.04-0.15	0.003-00.026	2-341	Propane	<0.01 to 1.75	-0.1 to -16.3	n.a.	Houser et al., 2005
Ogeechee River, GA	>0.5	9.6-12.8	n.a.	SRM	0.02 - 1.21	-0.48 to -8.69	-0.44 to -8.14	Meyer and Edwards, 1990
River Necker, SZ	n.a.	4.6	n.a.	SF6	1.8 to 8.0	-4.6 to -7.8	n.a.	Naegeli and Uehlinger, 1997
Taieri River, NZ	n.a.	6.6-76.8	0.8-34	Night/Daytime Regression	<0.3 to 9.6	-0.7 to -9.8	-8.6 to 6.2	Young & Huryn, 1996

*Indicates mean value

Table adapted from: Grace and Imberger, 2006

GPP = gross primary production

CR₂₄ = 24-hour community respiration

NEM = net ecosystem metabolism

Q = discharge

m = meters

d⁻¹ = per day

K_{O2} = oxygen reaeration coefficient; EDM = energy dissipation model; SF6 = sulfur hexafluoride

g O₂ m⁻² d⁻¹ = grams of oxygen per square meter per day

Table 1.2: CO₂ flux from selected studies as described in Striegl et al. (2012).

Location	Areal CO ₂ Flux (mmol C m ⁻² day ⁻¹)	CO ₂ Emission (Tg C yr ⁻¹)	CO ₂ Yield (g C m ⁻² yr ⁻¹)	Reference
Sweden	387	0.85	1.9	Humborg et al., 2010
Amazon	189	470	68	Richey et al., 2002
Mississippi	270	10	3.4	Dubois et al., 2010
Xijiang River	189	0.16–0.30	0.5	Yao et al., 2007
Yukon River Basin	311	7.68	9	Striegl et al., 2007; Striegl et al., 2012
Boreal	913	40		Aufdenkampe et al., 2011
Global		560		Aufdenkampe et al., 2011
Conterminous U.S.	2370	96.8	12.4	Butman and Raymond, 2011; Stets and Striegl, 2012

Striegl et al., 2012

Table 1.3: CO₂ flux across landscapes and water bodies from selected studies.

Location	CO ₂ Flux	Unit	Description	Reference
Amazon	0.4	Mg CO ₂ -C ha ⁻¹ yr ⁻¹	Later CO ₂ flux from Soil to Stream	Johnson et al., 2008
Amazon	114 x 10 ¹²	g CO ₂ -C yr ⁻¹	1st Order Amazon Upland Streams	Johnson et al., 2008
Amazon	580 x 10 ¹²	g CO ₂ -C yr ⁻¹	Amazon Aquatic System	Johnson et al., 2008
Hudson River	10-162	g CO ₂ -C m ⁻² yr ⁻¹	Freshwater Portion of River System	Raymond et al., 1997
Interior AK, USA	360-739	g CO ₂ -C m ⁻² yr ⁻¹	Annual Soil CO ₂ Loss	Kane et al., 2006

1.3. References

- Aikenhead-Peterson, J. A., W. H. McDowell, and J. C. Neff. 2003. Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters. *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*, S.E.G. Findlay and R.L. Sinsabaugh. Academic Press: 26-59.
- AKRDC. 2013. Alaska Resource Development Council: Alaska's Fishing Industry. Available at: <http://www.akrdc.org>. Accessed 12 April 2013.
- Arendt, A. A., K. A. Echelmeyer, W. D. Harrison, C. S. Lingle, and V. B. Valentine. 2002. Rapid wastage of Alaska glaciers and their contribution to rising sea level. *Science* 297: 382–386.
- Baker, C. S., J. M. Straley, and A. Perry. 1992. Population characteristics of individually identified humpback whales in southeastern Alaska: Summer and fall 1986. *U.S. Fishery Bulletin* 90: 429-437.
- Bardgett, R. D., A. Richter, R. Bol, M. H. Garnett, R. Baumler, X. Xu, E. Lopez-Capel, D. A. C. Manning, P. J. Hobbs, I. R. Hartley, and W. Wanek. 2007. Heterotrophic microbial communities use ancient carbon following glacial retreat. *Biology Letters* 2: 487-490.
- Barker, J. D., M. J. Sharp, S. J. Fitzsimons, and R. J. Turner. 2006. Abundance and dynamics of dissolved organic carbon in glacier systems. *J. Arc. Ant. Alp. Res.* 38: 163–172.
- Benner, R., and K. Kaiser. 2011. Biological and photochemical transformation of amino acids and lignin phenols in riverine dissolved organic matter. *Biogeochemistry* 102: 209-222.
- Bhatia, M. P., S. B. Das, E. B. Kujawinski, P. Henderson, A. Burke, and M. A. Charette. 2011. Seasonal evolution of water contributions to discharge from a Greenland outlet glacier; insight from a new isotope-mixing model. *Journal of Glaciology* 57(205): 929-941.
- Bott, T. L. 1983. Primary productivity in streams. In *Stream Ecology*. New York, N.Y.: Plenum.
- Bott, T. L., J. T. Brock, C. S. Dunn, R. J. Naiman, R. W. Ovink, and R. C. Petersen. 1985. Benthic community metabolism in four temperate stream systems: An inter-biome comparison and evaluation of the river continuum concept. *Hydrobiologia* 123: 3-45.
- Bott, T. L., J. D. Newbold, and D. B. Arscott. 2006. Ecosystem metabolism in piedmont streams: Reach geomorphology modulates the influence of riparian vegetation. *Ecosystems* 9: 398-421.
- Bott, T. L. 2007. Primary productivity and community respiration. In *Methods in Stream Ecology*, second edition, 663-690. Burlington, MA. Elsevier, Inc.

- Boyer, E. W., G. M. Hornberger, K. E. Bencala, and D. M. McKnight. 1997. Response characteristics of DOC flushing in an alpine catchment. *Hydrological Processes* 11: 1653-1647.
- Compton, J. E., M. R. Church, S. T. Larned, and W. E. Hogsett. 2003. Nitrogen export from forested watersheds in the Oregon Coast Range: The role of N₂-fixing red alder. *Ecosystems* 6: 773–785.
- D'Amore, D. V., J. B. Fellman, R. T. Edwards, and E. Hood. 2010. Controls on dissolved organic matter concentrations in soils and streams from a forested wetland and sloping bog in southeast Alaska. *Ecohydrol.* 3: 249-261.
- Emerson, S. and J. Hedges. 2008. Chapter 4: Carbonate chemistry. In *Chemical oceanography and the marine carbon cycle*. Cambridge, U.K.: Cambridge University Press.
- Etherington L. L., P. N. Hodge, E. R. Hodge, and D. F. Hill. 2007. Oceanography of Glacier Bay, Alaska: Implications for biological patterns in a glacial fjord estuary. *Estuaries and Coasts* 30(6): 927-944.
- Fellows, C. S., H. M. Valett, and C. N. Dahm. 2001. Whole-stream metabolism in two montane streams: Contribution of the hyporheic zone. *Limnol. Oceanogr.* 46(3): 523-531.
- Fellman, J. B., E. Hood, R. T. Edwards, and D. V. D'Amore. 2008. Return of salmon-derived nutrients from the riparian zone to the stream during a storm in southeastern Alaska. *Ecosystems* doi: 10.1007/s10021-008-9139-y.
- Fellman, J. B., E. Hood, R. T. Edwards, and D. V. D'Amore. 2009a. Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. *Journal of Geophysical Research* 114: doi: 10.1029/2008JG000790.
- Fellman, J. B., E. Hood, D. V. D'Amore, R. T. Edwards, and D. White. 2009b. Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds. *Biogeochemistry*. 95: 277-293.
- Fellman, J. B., Miller, M. P., Cory, R. M., D'Amore, D. V., and D. White. 2009c. Characterizing dissolved organic matter using PARAFAC modeling of fluorescence spectroscopy: A comparison of two models. *Environ. Sci. Technol.* 43: 6228-6234.
- Fellman, J. B., R. G. M. Spence, P. J. Hernes, R. T. Edwards, D. V. D'Amore, and E. Hood. 2010. The impact of glacier runoff on the biodegradability and biochemical composition of terrigenous dissolved organic matter in near-shore marine ecosystems. *Marine Chemistry* 121: 112-122

- Findlay, S. E. G., and R. L. Sinsabaugh. 2003. *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*. Burlington, Massachusetts: Elsevier Science.
- Goodale, C. L., S. A. Thomas, G. Fredriksen, E. M. Elliott, K. M. Flinn, T. J. Butler, and M. T. Walter. 2009. Unusual seasonal patterns and inferred processes of nitrogen retention in forested headwaters of the Upper Susquehanna River. *Biogeochemistry* 93: 197-218.
- Grace, M. R., and S. J. Imberger. 2006. Stream metabolism: Performing and interpreting measurements. Water studies Centre Monash University, Murray Darling basin Commission and New South Wales Department of Environmental and Climate Change. Stream metabolism technical manual. Available at: www.sci.monash.edu.au/wsc/docs/tech-manual-v3.pdf. Accessed 1 December 2011.
- Grimm, N. B., and S. G. Fisher. 1984. Exchange between interstitial and surface water: Implications for stream metabolism and nutrient cycling. *Hydrobiologia* 111: 219-228.
- Groffman, P. M., P. Eagan, W. M. Sullivan, and J. L. Lemunyon. 1996. Grass species and soil type effects on microbial biomass and activity. *Plant Soil* 183: 61–67.
- Guasch, H., J. Armengol, E. Marti, and S. Sabater. 1998. Diurnal variation in dissolved oxygen and carbon dioxide in two low-order streams. *Water Resources* 32(4): 1067-1074.
- Hartmann, B., and G. Wendler. 2005. The significance of the 1976 Pacific climate shift in the climatology of Alaska. *Journal of Climate* 18: 4824.
- Hamilton, S. K., S. J. Sippel, and J. M. Melack. 1995. Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil. *Biogeochemistry* 30: 115-141.
- Hinton, M. J., S. L. Schiff, and M. C. English. 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. *Biogeochemistry* 36: 67-88.
- Hodson, A., P. Mumford, and D. Lister. 2004. Suspended sediment and phosphorus in proglacial rivers: Bioavailability and potential impacts upon the P status of ice-marginal receiving waters. *Hydro. Proc.* 18: 2409–2422.
- Hodson, A., P. Mumford, J. Kohler, and P. Wynn. 2005. The high Arctic glacial ecosystem: New insights from nutrient budgets. *Biogeochemistry* 72: 233–256.
- Hood, E., M. Gooseff, and S. Johnson. 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds. *J. Geophys. Res.* 111: G01007.
- Hood, E., J. Fellman, and R. T. Edwards. 2007. Salmon influences on dissolved organic matter in a coastal temperate brownwater stream: An application of fluorescence

- spectroscopy. *Limnology and Oceanography* 52: 1580–1587.
- Hood, E. and D. T. Scott. 2008. Riverine dissolved organic matter and nutrient yields in southeast Alaska affected by glacial coverage. *Nature Geoscience* 1: 583-587.
- Hood, E., and L. Berner. 2009. Effects of changing glacial coverage on the physical and biogeochemical properties of coastal streams in southeastern Alaska. *J. Geophys. Res.* 114, G03001: doi:10.1029/2009JG000971.
- Hood, E., J. Fellman, R. G. M. Spencer, P. J. Hernes, R. Edwards, D. D'Amore, and D. Scott. 2009. Glaciers as a source of ancient and labile organic matter to the marine environment. *Nature* 462: 1044-1047.
- Hooper, R. P., and C. A. Shoemaker. 1986. A comparison of chemical and isotopic hydrograph separation. *Water Resources Research* 22(10): 1444-1454.
- Inamdar, S., J. Rupp, and M. Mitchell. 2009. Groundwater flushing of solutes at wetland and hillslope positions during storm events in a small glaciated catchment in western New York, USA. *Hydrological Processes* 23: 1912-1926.
- Johnson, M. S., J. Lehmann, S. J. Riha, A. V. Krusche, J. E. Richey, J. P. H. B. Ometto, and E. G. Couto. 2008. CO₂ efflux from Amazonian headwater streams represents a significant fate for deep soil respiration. *Geophysical Research Letters* 35: doi: 10.1029/GL034619.
- Jones, J. B. Jr, and P. J. Mulholland. 1998. Influence of drainage basin topography and elevation on carbon dioxide and methane supersaturation of stream water. *Biogeochemistry* 40: 57-72.
- Kendall, C., E. A. and Caldwell. 1998. Fundamentals of Isotope Geochemistry, In: C. Kendall and J.J. McDonnell (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier Science, Amsterdam, pgs: 51-86.
- Lafreniere, M., and M. J. Sharp. 2004. The concentration and spectrofluorometric properties of DOC from glacial and non-glacial catchments. *J. Arc. Ant. Alp. Res.* 36: 156-165.
- Lamberti, G. A., and A. D. Steinman. 1997. A comparison of primary production in stream ecosystems. *Stream Organic Matter Budgets* 16: 95-104.
- Lottig, N. R., and E. H. Stanley. 2007. Benthic sediment influence on dissolved phosphorus concentrations in a headwater stream. *Biogeochemistry* 84: 297-309.
- Marzolf, E. R., Mulholland, P. J., and A. D. Steinman. 1994. Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Can. J. Fish. Aquat. Sci.* 51: 1591-1599.

- McGlynn, B. L., and J. J. McDonnell. 2003. Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. *Water Resources Research* 39(4): 1090, doi:10.1029/2002WR001525.
- McGuire, K., and J. McDonnell. 2007. Stable Isotope Tracers in Watershed Hydrology, in *Stable Isotopes in Ecology and Environmental Science*, Second Edition (eds R. Michener and K. Lajtha), Blackwell Publishing Ltd, Oxford, UK. doi: 10.1002/9780470691854.ch11
- McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Anderson. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanogr.* 46(1): 38-48.
- McTammany, M. E., J. R. Webster, E. F. Benfield, and M. A. Neatrour. 2003. Longitudinal patterns of metabolism in a southern Appalachian river. *J. N. Am. Benthol. Soc.* 22(3): 359-370.
- Meyer, J. L., and R. T. Edwards. 1990. Ecosystem metabolism and turnover of organic carbon along a blackwater river continuum. *Ecology* 71(2): 668-677.
- Mulholland, P. J., C. S. Fellows, J. L. Tank, N. B. Grimm, J. R. Webster, S. K. Hamilton, E. Marti, L. Ashkenas, W. B. Bowden, W. K. Dodds, W. H. McDowell, M. J. Paul, and B. J. Peterson. 2001. Inter-biome comparison of factors controlling stream metabolism. *Freshwater Biology* 46: 1503-1517.
- Mulholland, P. J. 2004. The importance of in-stream uptake for regulating stream concentrations and outputs of N and P from a forested watershed: evidence from long-term chemistry records for Walker Branch Watershed. *Biogeochemistry* 70: 403-426.
- Naegeli, M. W., and U. Uehlinger. 1997. Contribution of the hyporheic zone to ecosystem metabolism in a pre-alpine gravel-bed river. *J. N. Amer. Benthol. Soc.*, 16(4): 794-804.
- Neal, E. G., E. Hood, and K. Smikrud. 2010. Contribution of glacier runoff to freshwater discharge into the Gulf of Alaska. *Geophysical Research Letters* 37: L06404.
- NOAA. 2013. Alaska Climate Database: Juneau Airport. National Weather Service. Available at: <http://pajk.arh.noaa.gov/cliMap/akClimate.php>. Accessed 5 March 2013.
- Odum, H. T. 1955. Primary production in flowing waters. *Limnology and Oceanography*, 2, 85-97.
- Owens, M., R. W. Edwards, and J. W. Gibbs. 1964. Some reaeration studies in streams. *International Journal of Air and Water Pollution* 8: 469-486.

- Rasmussen, J. J., A. Baattrup-Pedersen, T. Riis, and N. Friberg. 2011. Stream ecosystem properties and processes along a temperature gradient. *Aquatic Ecology*, 45: 213-242.
- Raymond, P. A., N. F. Caraco, J. J. Cole. 1997. Carbon dioxide concentration and atmospheric flux in the Hudson River. *Estuaries* 20(2): 381-390.
- Sharp, M., J. Parkes, B. Cragg, I. J. Fairchild, H. Lamb, and M. Tranter. 1999. Widespread bacterial populations at glacier beds and their relationship to rock weathering and carbon cycling. *Geology*, 27(2): 107-110.
- Skidmore, M., J. M. Foght, and M. J. Sharp. 2000. Microbial life beneath a high Arctic glacier. *Applied and Environmental Microbiology* 66: 3214-3220.
- Sklash, M. G., R. N. Farvolden. 1979. The role of groundwater in storm runoff. *Journal of Hydrology* 43: 45-65.
- Stark, J. M. 1996. Modeling temperature response of nitrification. *Biogeochemistry* 35: 433-445.
- Stedmon, C., S. Markager, and R. Bro. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* 82: 239-254.
- Stubbins, A., E. Hood, P. A. Raymond, G. R. Aiken, R. L. Sleighter, P. J. Hernes, B. Butman, P. G. Hatcher, R. G. Striegl, P. Schuster, H. A. N. Abdulla, A. W. Vermilyea, D. T. Scott, and R. G. M. Spencer. 2012. Anthropogenic aerosols as a source of ancient dissolved organic matter in glaciers. *Nature Geoscience* doi:10.1038.
- Tranvik, L. J., and E. V. Wachenfeldt. 2009. Interactions of dissolved organic matter and humic substances. *Organic Compounds Elsevier*: 754-760.
- Tsivoglou, H. C., and L. A. Neal. 1976. Tracer measurement of reaeration: III, Predicting the reaeration capacity of inland streams. *Journal of the Water Pollution Control Federation* 489: 2669-2689.
- Uehlinger, U., C. T. Robinson, M. Hieber, and R. Zah. 2010. The physio-chemical habitat for periphyton in alpine glacial streams under a changing climate. *Hydrobiologia* 657: 107-121.
- Vannote, R. L., G. W. Minshall, K. W. Cummins, J. R. Sedell, and C. E. Cushing. 1980. The river continuum concept. *Can. J. Fish. Aquat. Sci.* 37: 130-137.
- Vidon, P., L. E. Wagner, and E. Soyeux. 2008. Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses. *Biogeochemistry* 88: 257-270.

- Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fuji, and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *En. Sci. Tech.* 37: 4702-4708.
- Ylla, I., A. M. Romani, and S. Sabater. 2012. Labile and recalcitrant organic matter utilization by river biofilm under increasing water temperature. *Microb. Ecol.* 64: 593-604.
- Young, R. G., and A. D. Huryn. 1996. Interannual variation in discharge controls ecosystem metabolism along a grassland river continuum. *Can. J. Fish. Aquat. Sci.* 53: 2199-2211.
- Young, R. G., and A. D. Huryn. 1998. Comment: Improvements to the diurnal upstream-downstream dissolved oxygen change technique for determining whole-stream metabolism in small streams. *Can. J. Fish. Aquat. Sci.* 55: 1784-1785.
- Young, R. G., and A. D. Huryn. 1999. Effects of land use on stream metabolism and organic matter turnover. *Ecological Applications* 9(4): 1359-1376.

Chapter 2: In-Stream Metabolism Estimates

2.1. Abstract

Stream metabolism estimates and biological activity were compared in two coastal streams in southeast Alaska draining (1) a non-glacial catchment and (2) a glaciated catchment. Open-water oxygen-based metabolism estimates revealed increased rates of gross primary production (GPP) and 24-hr community respiration (CR_{24}) in the glacial stream compared to the non-glacial site. Cloud cover resulted in rates of GPP, CR_{24} , and net ecosystem metabolism (NEM) in the glacial stream to be similar to rates calculated for the non-glacial forested stream. *In situ* carbon dioxide (CO_2) monitoring indicated the non-glacial stream contained dissolved CO_2 at over twice the equilibrium concentration, while the glacial stream had CO_2 levels near equilibrium during the study period. Findings from *in situ* CO_2 monitoring suggest streams and contributing watersheds that drain glacial catchments process less organic carbon and release less CO_2 than streams in non-glacial forested catchments. Additionally, in-stream estimates of NEM indicate glacial streams with little riparian vegetation have potentially higher rates of GPP and CR_{24} when streambeds are stable enough to support microbial communities and photosynthetic biomass and light can penetrate the water column reaching the growing surface. These findings suggest large streams receiving high inputs of glacial meltwater during the summer melt season are less capable of cycling carbon and nutrients than non-glacial streams with stable sediments and warmer water temperatures. The decreased processing observed in the glacial stream in this study suggest organic matter and nutrients in glacial meltwater are likely

delivered with minimal biological processing to downstream water bodies such as the Gulf of Alaska (GOA).

2.2. Introduction

Over the past 50 years, Alaskan glaciers contributed more freshwater to coastal zones than any other group of glaciers in the world (Arendt et al., 2002). During the summer melt season, coastal glacial meltwater contributions carry a unique combination of organic matter and nutrients to the Gulf of Alaska (GOA) compared to freshwater from forested watersheds (Hood and Scott, 2008; Hood and Berner, 2009; Bhatia et al., 2013). In addition to the unique composition of dissolved organic matter (DOM) and nutrients carried in glacial meltwater, glaciated watersheds have decreased yields of dissolved organic carbon (DOC) and increased yields of soluble reactive phosphorus (SRP) (Hood and Scott, 2008). With the rate of glacial thinning in Alaska increasing (Arendt et al., 2002), export of organic matter and nutrients from glaciated coastal watersheds to the GOA will continue to change.

Although existing data indicate glacial recession may affect the total flux and bioavailability of DOM in these coastal streams (Hood and Scott, 2008; Bhatia et al., 2013), little is known about the in-stream uptake and mineralization of DOM in glacial streams prior to reaching the GOA. This study focuses on the impact of glacial meltwater contributions on the biological in-stream processes of photosynthesis and respiration. Biologically driven in-stream processes influence not only the DOM dynamics of the stream channel, but also the near-shore marine environment receiving contributions from freshwater streams. Changes to the physical and chemical characteristics of streamwater attributed to glacial recession can impact the in-stream microbial communities (Wilhelm et al., 2013), thereby influencing the biological processes occurring in the stream channel. In conjunction with microbial uptake and

adsorption in terrestrial soils, in-stream processing regulates the amount and form of DOM and nutrients that reach receiving water bodies such as the GOA. Both biotic and abiotic factors influence the in-stream processing of DOM and nutrients, and many of these factors are affected by glacier meltwater contributions including water temperature, suspended sediment loads, and stream discharge (Rasmussen et al., 2011; Uehlinger et al., 2010). For example, fine sediments associated with glacial streams retain SRP through mostly abiotic sorption reactions, while streams with coarse sediments retain more SRP through biotic uptake (Lottig and Stanley, 2007).

Coastal streams along the GOA transport glacial meltwater to near-shore marine ecosystems, which are productive fisheries as well as ecologically important nurseries and migratory corridors for many species (Baker et al., 1992). Biological processes cycle organic matter and nutrients through the water column and hyporheic zone as they move downstream from the coastal mountains to the GOA. Ecosystem metabolism is the sum of the biological processes of autotrophic primary production and heterotrophic respiration that regulate DOM and nutrients in aquatic environments. This research aims to contrast the impact of glaciated and forested landcover end members on ecosystem metabolism in streams representative of those draining watersheds along the southeastern coast of Alaska.

Rates of stream ecosystem metabolism are influenced by factors in the stream channel and in the surrounding landscape that differ both between watersheds, and along the length of a single stream (Vannote et al., 1980). Light reaching the streambed, nutrient availability, and geomorphology are some of the factors regulating stream metabolism (Mulholland et al., 2001). Organic matter contributions are the primary

control of community respiration (CR) rates (Young and Huryn, 1999), while light (influenced by riparian vegetation, water clarity) drives gross primary production (GPP).

Along the length of a stream, rates of metabolism components can change due to hydrologic changes (Young and Huryn, 1996), changes in floodplain organic matter inputs (Meyer and Edwards, 1990), or geomorphic factors such as loose substrate (Bott, 1983). In a longitudinal study of stream metabolism, rates of 24-hr community respiration (CR_{24}) remained constant, while GPP increased 3-fold along a 37 km stretch of the Little Tennessee River resulting in a less heterotrophic system (McTammany et al., 2003). Similar studies have also shown a shift toward decreased heterotrophy with increased stream order as a result of more light reaching the stream because of decreased shading (Bott et al., 1985). This pattern of increasing stream order resulting in increased light reaching the streambed and higher ratios of gross primary production to community respiration (P/R) is expected to reverse as deeper, more turbid rivers, restrict light and lower the P/R ratio (Vannote et al., 1980). Surface light levels above $200 - 250 \mu\text{mol m}^{-2} \text{s}^{-1}$ have been shown to create light saturation of GPP in streams (Young and Huryn, 1996; Young and Huryn, 1999), but open channel net ecosystem metabolism (NEM) estimates have not found evidence of excess surface light resulting in photoinhibition of GPP (Young and Huryn, 1996).

Even though light has a strong positive correlation with GPP, other factors including inorganic nutrient concentrations influence GPP. High nutrient concentrations, specifically SRP, can lead to increased GPP by autotrophic organisms (Lamberti and Steinman, 1997; Young and Huryn, 1996). Nutrient uptake also responds to light and exhibits a diurnal signal because the activities of photosynthetic organisms are

controlled by sunlight (Fellows et al., 2006). NEM, primary production, and biomass also influence nitrogen retention within streams, as increased nitrogen uptake is closely linked to succession and recovery of biomass after disturbance (Grimm, 1997).

Another metric for assessing biological processes taking place in a stream and the surrounding landscape is the concentration of dissolved carbon dioxide (CO_2) or excess partial pressure of carbon dioxide ($ep\text{CO}_2$). $ep\text{CO}_2$ is a measure of the saturation state of CO_2 in the water column above or below equilibrium levels. The state of saturation of dissolved CO_2 can be related to biological processes that produce (respiration) or consume (photosynthesis) CO_2 (Guasch et al., 1998; Hamilton et al., 1995). Numerous studies have also shown streams and rivers across varying climates and eco-regions as a net source of CO_2 with diel outgassing curves being evident during periods of increased algal activity (Raymond et al., 1997; Guasch et al., 1998; Johnson et al., 2008; Butman and Raymond, 2011; Striegl et al., 2012).

CO_2 measurements can also provide information about the surrounding landscape (Johnson et al., 2009) that contributes discharge to the stream and hyporheic zone of the channel. Water moving in flow paths through microbially active organic soil layers can carry supersaturated concentrations of CO_2 from the landscape to streams via lateral flow, with higher concentrations moving from the landscape to surface waters during seasonally wet periods (Johnson et al., 2008), and during warmer summer months (Jones and Mulholland, 1998). The production of CO_2 and consumption of O_2 from respiration in the hyporheic zone can constitute over 75% of the community respiration component of NEM estimates (Naegeli and Uehlinger, 1997; Fellows et al., 2001).

The objective of this study was to quantify in-stream reactivity (ecosystem metabolism, nutrient uptake) differences between streams receiving glacial meltwater and nearby non-glacial streams. Rates of GPP and CR_{24} will provide insight on organic matter processing potential in pro-glacial and forested streams. Additional metabolism metrics and nutrient uptake measurements will further identify differences between streams draining forested and glaciated landcover.

2.3. Methodology

2.3.1. Site Description

The study watersheds were located in southeast Alaska near Juneau (Figure 2.1). Study sites were selected to target landscape end member streams (Table 2.1) draining (1) a glaciated watershed and (2) a forested watershed. Herbert River (glacial) and Lake Creek (forested, non-glacial) are both located in the Tongass National Forest in southeast Alaska along the Juneau road system. Average sea level air temperatures range from January lows of -6.3°C to July highs of 17.9°C , with an average annual air temperature of 5.5°C . Total annual precipitation averages 1480 mm, with the wettest month (October) averaging 211 mm and the driest month (April) averaging 75 mm (NOAA, 2005). Snowmelt contributions fill streams during the drier spring, with glacial meltwater dominating summer stream discharge in glaciated catchments. Glacial meltwater is the dominant freshwater discharge source, accounting for 47% of all freshwater contributions to the GOA (Neal et al., 2010).

The reach directly below the Herbert Glacier terminus was selected to evaluate the glaciated landscape end member with no riparian shading and a mix of fine glacial sediment and larger (<1cm) sediment. The glacial study reach had an average discharge of 0.22 m³/sec, average width of 4.3 m, and average depth of 16 cm. The glacial study reach was located on a shallow braided channel offset from the main channel. This location was selected because it had decreased velocity and a more stable substrate compared to the main channel, allowing for the assessment of potential processing and also allowing for the detection of biological indicators of metabolism. The second study reach, Lake Creek, was within a forested watershed, with a closed riparian canopy and heterogeneous streambed ranging from small pebbles (1 to 2 cm) to larger rocks (< 25 cm). The Lake Creek study reach had an average discharge of 0.02 m³/sec, average width of 3.9 m, and average depth of 12.5 cm.

2.3.2. Field Methods

Dissolved oxygen (concentration and percent saturation) and water temperature were recorded at 10-min increments for three days with a YSI optical dissolved oxygen (ODO) probe (YSI, Inc., Yellow Springs, Ohio, USA) at each study reach. Water depth was recorded at 10-minute intervals with an In-Situ level logger (In-Situ, Inc., Ft. Collins, Colorado, USA) at the upstream location of each study reach for the duration of the data collection period. Supplemental cross-sectional measurements of water depth, width, and velocity were made along both study reaches. Velocity and discharge were measured with a Sontek Flowtracker handheld ADV (Sontek/YSI, San Diego, California, USA).

Photosynthetically active radiation (PAR) and CO₂ were measured at 10-minute intervals for three days at each study site. Carbon dioxide concentrations were measured using Vaisala *in situ* CO₂ probes (Vaisala, Helsinki, Finland). A single carbon dioxide probe measured dissolved CO₂ levels at the up-stream location of each site. Calculation of stream *ep*CO₂ values were made by correcting raw dissolved CO₂ concentrations for temperature and barometric pressure at 10-min intervals. Average probe depth and atmospheric concentrations of CO₂ were used to normalize measured values to the ambient environment. Prior to deployment, CO₂ probes were waterproofed using a gas-permeable polytetrafluoroethylene (PTFE) membrane as described by Johnson et al. (2010). Light was measured at each site using a Solar Light PMA1132 Quantum detector (Solar Light Company, Inc., Glenside, Pennsylvania, USA) that measures PAR from a wavelength of 400 to 700 nm. PAR values recorded in the field were reported as daily totals (mol photons m⁻² day⁻¹).

2.3.3. In-Stream Metabolism Estimates

Net ecosystem metabolism (NEM) was estimated using the single-station open-water method as described in Hauer and Lamberti (2007) with a reaeration coefficient estimated using the surface renewal model (SRM) method (Owens et al., 1964). Briefly, dissolved oxygen concentrations were normalized using simultaneously collected temperature and pressure data to obtain hourly surplus/deficit values with respect to dissolved oxygen saturation under the same environmental conditions. Changes in oxygen concentrations were corrected for reaeration across the air/water interface (2.1) using the SRM (2.2) and normalized for temperature (2.3), leaving only in-stream biological processes (respiration and photosynthesis) to account for the remaining

changes in dissolved oxygen. Average hourly values of nighttime respiration rates were estimated and applied across a 24-hr period to calculate 24-hr community respiration (CR_{24}). GPP was calculated as the difference of the measured change in oxygen concentration during the daylight hours from average hourly CR. NEM was then calculated by subtracting CR_{24} from GPP (2.4).

$$Reaeration = O_2 \text{ surplus or deficit} \times f_{(t^{\circ}C)} \quad (2.1)$$

where: $f_{(t^{\circ}C)}$ = mass transfer coefficient at stream temperature

$$f_{(20^{\circ}C)} = 50.8 \times V^{0.67} \times H^{-0.85} \quad (2.2)$$

where: $f_{(20^{\circ}C)}$ = mass transfer coefficient at 20°C (cm/hr)

V = velocity (cm/s) for $3 \leq V \leq 150$ cm/s

H = depth (cm) for $12 \leq H \leq 335$ cm

$$f_{(t^{\circ}C)} = f_{(20^{\circ}C)} \times 1.024^{(t-20)} \quad (2.3)$$

where: t = stream temperature (°C)

$$NEM = GPP - CR_{24} \quad (2.4)$$

Carbon-based areal CO_2 flux values were calculated as the product of the concentration difference across the water-air interface and the gas transfer velocity (2.5) (Striegl et al., 2012).

$$\text{Flux} = (C_{\text{sw}} - C_{\text{a}}) \times k \quad (2.5)$$

where: Flux = areal CO₂ flux (CO₂-C mol m⁻² day⁻¹)

C_{sw} = average concentration of CO₂ -C in stream (mol C m⁻³)

C_a = average concentration of CO₂ -C in air at site (mol C m⁻³)

k = CO₂ gas transfer velocity (m day⁻¹)

CO₂ concentrations in aquatic systems are also influenced by the pH of the water. Unpublished data collected at glacial and non-glacial sites near Juneau showed a diurnal pH pattern where in-stream pH measurements varied by 0.05 during a 24-hr period with pH peaks occurring near 12:00 and low values recorded near 00:00. Glacial streams were observed to have pH values ranging from 6.7 to 6.9, and non-glacial streams had pH values ranging from 6.5 to 6.6. CO₂ values are expected to decrease with increasing pH, but the daily variation in the study streams never exceeded 0.05. Because the studies were performed under constant flow regimes and with near constant water quality conditions, chemical forcing of inorganic carbon species concentrations was assumed to be minimal during the monitoring period and CO₂ concentration patterns to be a result of biological processes.

2.3.4. Laboratory Sample Analysis

Water samples were collected during the first 24-hr period of stream monitoring at each study reach to verify steady-state background stream chemistry across a diurnal cycle. Samples were filtered through a 0.45 µm in-line filter and individually bottled on-site for analysis of DOC, dissolved inorganic carbon (DIC), nutrients, and turbidity. Additional samples were collected approximately every 6 hr at a location upstream of

the oxygen, CO₂, and temperature probes. Samples for DOC, DIC, and total dissolved nitrogen (TDN), were collected in pre-combusted 40 mL amber glass vials, refrigerated, and analyzed on a Shimadzu TOC-V carbon analyzer (Shimadzu Corporation, Kyoto, Japan) within 3 days of collection. Twenty-six triplicate samples of DOC and TDN, and five duplicate samples of DIC had sample standard deviation values of 8.9, 1.7, and 6.3 µmol/L, respectively. Inorganic nitrogen and phosphorus samples were collected in 60 mL amber HDPE bottles, frozen, and analyzed within 3 months on a SEAL segmented-flow nutrient analyzer (Seal Analytical, Mequon, Wisconsin, USA). Five laboratory duplicate samples of NH₄⁺ and PO₄³⁻ produced average instrument precision limitation values of 0.26 and 0.01 µmol/L, respectively.

Raw data used in NEM calculations, daily PAR data, and hourly NEM results are presented in Appendix A. Supplemental data including CO₂-based open-water metabolism estimates, mesocosm CO₂ production and NEM estimates, and nutrient uptake calculations are also presented in Appendix A.

2.4. Results

2.4.1. Net Ecosystem Metabolism Estimates

Net ecosystem metabolism estimates were calculated for three days at each study site using the open water SRM method and dissolved oxygen concentrations (Table 2.2). In-stream estimates of 24-hr community respiration in the non-glacial stream reach ranged from 0.79 to 1.10 g O₂ m⁻² d⁻¹ over 72 hr (Figure 2.2), with higher

respiration rates estimated in the glacial stream (1.71 to $2.92 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$) (Figure 2.3). Primary production in the glacial stream reach ranged from 1.20 to $3.16 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$, while rates of GPP in the non-glacial forested stream ranged from 0.45 to $0.72 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$. GPP in the non-glacial stream increased each day of the study, while GPP estimates in the glacial stream varied with PAR values. NEM estimates for the glacial stream ranged from -1.27 to $0.78 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$, with positive values estimated for days with little cloud cover. NEM estimates for the non-glacial forested stream showed little variation during the study period and ranged from -0.48 to $-0.34 \text{ g O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (Figure 2.4).

P/R values in the glacial stream varied across the 3 d study with values ranging from 0.49 to 1.46 based on cloud cover (Table 2.3). As with other metabolism metrics, P/R values in the non-glacial stream varied little and ranged from 0.54 to 0.67 . Recorded PAR values (Figure 2.5) showed the effect of the open canopy along the glacial river with values ranging from 10 to $44 \text{ mol m}^{-2} \text{ d}^{-1}$. The closed canopy along the non-glacial stream decreased day-to-day PAR variation, with values ranging from 26 to $32 \text{ mol m}^{-2} \text{ d}^{-1}$.

2.4.2. In-Stream CO₂

Estimates of $ep\text{CO}_2$ at each site indicated the non-glacial stream had CO₂ concentrations more than double the glacial site (Figure 2.6). During the study, $ep\text{CO}_2$ in forested Lake Creek averaged 2.21 (more than double the equilibrium value), while glacial Herbert River averaged 0.98 (near the equilibrium value of 1). A diurnal signal of similar magnitude was observed in both streams with $ep\text{CO}_2$ levels peaking at night

and reaching a minimum by approximately 12:00hrs. Daytime levels of $epCO_2$ at the glacial site were below saturation, while $epCO_2$ values at night were above saturation levels for the stream. Non-glacial Lake Creek remained supersaturated with CO_2 during the entire 3 d monitoring period. CO_2 gas transfer velocity calculations using the SRM method resulted in a higher average value for the glacial stream (9.8 m d^{-1}) than the non-glacial stream (7.0 m d^{-1}). CO_2 areal flux calculations based on measured CO_2 equilibrium saturation concentration and gas transfer velocity values resulted in a low (and gaining value) for the glacial stream of $-10 \text{ mmol C m}^{-2} \text{ d}^{-1}$, and a net carbon export from the non-glacial stream of $242 \text{ mmol C m}^{-2} \text{ d}^{-1}$.

2.5. Discussion

2.5.1. Net Ecosystem Metabolism Estimates

The results of open-water ecosystem metabolism estimates suggest organic matter and nutrients in glacial meltwater have the potential to be processed through biological activity. Dissolved O_2 -based estimates of open-water metabolism comparing a glacial and non-glacial stream show increased rates of respiration and primary production in the proglacial stream. These findings were unexpected because the low temperatures recorded in the glacial stream are associated with lower stream metabolism metrics (Rasmussen et al., 2011).

Previous studies have shown carbon in glacial streams to be more bioavailable than carbon in non-glacial streams (Hood et al., 2009, Fellman et al., 2010; Bhatia et al., 2013), which may account for the higher than expected respiration rates in water with

lower temperatures. Substantial biomass was also observed in the glacial study site, which suggests GPP rates could be higher than the forested reach during periods of prolonged sunlight. Bioavailable glacially-derived DOM has also been suggested as source of organic carbon processing, including CO₂ generation in proglacial streams (Singer et al., 2012). Additionally, the location of the oxygen sensor on the glacial study reach was approximately 200 m downstream of the monitored channel's split from the main channel, allowing for an increase in water temperature because of solar warming of the shallow stream.

Primary production differences (observed as increased oxygen and decreased carbon dioxide) were more strongly correlated to increased light in the open-canopied glacial stream ($R^2 = 0.86$) than in the closed-canopied non-glacial stream ($R^2 = 0.34$) (Figure 2.7). This increase in GPP during periods of sun exposure resulted in the glacial stream reach shifting from a heterotrophic system to a net autotrophic system. Other studies in headwater, open-canopied streams have shown consistently heterotrophic systems (Logue et al., 2004), while net autotrophy has been associated with open-canopied systems with high SRP concentrations (Mulholland et al., 2001). A shift from autotrophic to heterotrophic states has also been observed in cryoconite holes on glacier surfaces during the meltseason (Telling et al., 2011). As with the open-water respiration estimates, GPP values in this study are likely not representative of GPP rates in a large glacial channel. Larger glacial streams may have a less clear relationship between PAR and GPP because deeper streams would be subject to decreased light passing through the water column to the streambed because of increased turbidity associated with glacial streams (Hood and Berner, 2009). The

shallow glacial study reach was selected based on suitability to open-water reaeration estimates and the ability to evaluate biological processing potential. Additionally, the higher discharge and water velocities associated with large glacial rivers also inhibit the type of aquatic vegetation establishment that was observed in this study reach (Merritt and Wohl, 2002).

2.5.2. In-Stream CO₂

In-stream measurements of CO₂ made in the glacial and non-glacial stream showed increased concentrations of dissolved CO₂ in the stream draining the non-glacial forested watershed (62 µmol/L) compared to the glaciated watershed (42 µmol/L). These results carry over to DIC values, which averaged 245 µmol/L in the forested stream and 138 µmol/L in the glacial stream. Assuming consistent alkalinity over time and between both sites, this indicates CO₂ makes up an equivalent portion of the DIC pool in the glacial stream but at lower concentrations compared the non-glacial stream. Evidence of increased heterotrophic microbial respiration in the form of higher average values of *ep*CO₂ was observed in the forested stream throughout the monitoring period. The CO₂ levels in the stream reflect biological (contributions from both respiration in the stream and the surrounding organic soil layers of the watershed) and abiotic processes in the streambed and the surrounding contributing landscape (Jones and Mulholland, 1998; Johnson et al., 2008).

The near equilibrium *ep*CO₂ in the glacial stream further supports evidence from the metabolism estimates that the in-stream production and landscape contributions of biologically produced CO₂ are much less in the glacial landscape than in the non-glacial

system. The diel curve of $epCO_2$ during periods of steady discharge in both streams showed peaks correspond with times of decreased light and lower values corresponded to daylight hours (Figure 2.6). Assuming respiration rates are constant in the stream channel and contributing soil layers over a 24-hr period, lower $epCO_2$ values during the day are likely the result of increased in-stream primary production and CO_2 consumption, while higher values at night reflect lower rates of primary production and decreased CO_2 consumption. This diurnal cycle of CO_2 concentrations in the glacial system is evidence that biological activity and carbon mineralization is occurring even in extreme environmental conditions. Despite the near-equilibrium saturation of CO_2 in the glacial system, glaciers (specifically the surface areas) have been observed to act as sources of biologically respired CO_2 (Stibal et al., 2012).

A calculation of the areal flux of CO_2 -C from the streams reinforces both the metabolism and $epCO_2$ data. The $242 \text{ mmol C m}^{-2} \text{ d}^{-1}$ flux from the non-glacial site is slightly lower than values reported from the Yukon River of $311 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (Striegl et al., 2012) and Mississippi River of $270 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (Dubois et al., 2010) but higher than values reported from the Amazon River of $189 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (Richey et al., 2002). The flux calculated from the glacial site was negligible and suggests glaciated watersheds and streams retain and transport carbon downstream more readily than non-glacial systems.

The transfer velocity of CO_2 in the study streams averaged 7.0 m d^{-1} at the proglacial site and 9.8 m d^{-1} at the forested site. The near equilibrium CO_2 levels in the glacial stream suggest either extremely high gas-transfer velocities are releasing CO_2 to the atmosphere before concentrations in the water exceed equilibrium, low

concentrations of CO₂ are introduced from the landscape through lateral flow, or low amounts of CO₂ are produced in the stream channel. In tributaries of the Yukon River, transfer velocity values for CO₂ were calculated to range from 3.9 to 6.9 m d⁻¹ and from 0.3 - 4.5 m d⁻¹ in the Yukon River's main channel (Striegl et al., 2012). Broader ranges have been calculated in other streams in the United States ranging from 2.5 m d⁻¹ in the Mississippi to 18 m d⁻¹ in mountain headwater streams (Butman and Raymond, 2011). The calculated values for the sites in this study are within the range of CO₂ transfer velocities reported in other studies with excess in-stream CO₂, indicating the low in-stream CO₂ recorded in the glacial stream was the result of low biological production of CO₂ in the surrounding landscape and stream channel.

2.5.3. Conclusions

Higher rates of GPP in the braided glacial reach, along with higher respiration rates suggest carbon and nutrients in glacial meltwater have the potential to be processed and assimilated into biomass if environmental factors in glacial streams allow for autotrophic organisms and heterotrophic microbial communities to become established in the channel. The bioavailable characteristics of glacially-derived DOM can be exported downstream to marine ecosystems if in-stream environmental conditions are not suitable for processing during the short travel length from the coastal mountains to the GOA. Despite the increased bioavailability associated with glacial DOM, the combination of in-stream respiration and landscape carbon mineralization in non-glacial watersheds results in these soil/water systems functioning as a net source of CO₂ to the environment.

Decreased glacial meltwater contributions resulting in improved environmental conditions (lower turbidity, lower flow, warmer water temperatures) can result in a more robust aquatic biota presence including increased periphyton biomass (Uehlinger et al., 2010), and increased micro-organisms and macroinvertebrates (Milner et al., 2009) in glacial streams. Because glacial drainages often originate in high-elevation areas of watersheds, the hydrodynamic heterogeneity of these streams may also promote exchange between the water column and hyporheic zone of the streambed and result in increased activity of the microbial community (Battin, 2000). Increased levels of CO₂ observed during in-stream monitoring suggest carbon in forested streams and watersheds is processed more rapidly than in glacial systems. These findings indicate water bodies receiving glacial meltwater, such as the GOA, are also receiving DOM and nutrients that are not cycled to the same extent as those only receiving freshwater from forested watersheds. This material is likely more bioavailable when it reaches the coastal areas of the GOA, and can support biological activity more readily than material that has undergone more processing. As glacier volume loss increases and watersheds shift from rock and ice to forest and wetlands, the in-stream processing of organic matter and nutrients in freshwater streams flowing into the GOA will transition from CO₂ neutral systems to a source of CO₂ to the atmosphere.

Table 2.1: Background and characterization of glacial Herbert River and non-glacial Lake Creek near Juneau, Alaska. All values provided represent averages over 3 consecutive precipitation-free days of monitoring during the summer melt season. Lake Creek 7/21/2011 to 7/23-2011; Herbert River 7/13/2011 to 7/15/2011.

	Non-Glacial: Lake Creek	Glacial: Herbert River
DOC ($\mu\text{mol/L}$)	377	19.7
TDN ($\mu\text{mol/L}$)	16.9	2.32
PO_4^{3-} ($\mu\text{mol/L}$)	0.04	0.05
DIC ($\mu\text{mol/L}$)	245	138
$\delta^{18}\text{O}$ (‰)	-13.2	-16.2
Glacier Coverage (%)	0	40
PAR ($\text{mol m}^{-2} \text{d}^{-1}$)	29.2	31.1
Q (m^3/sec)	0.024	0.216
Turbidity (NTU)	1	135
Temp ($^{\circ}\text{C}$)	11.9	2
Width (m)	3.9	4.3
Depth (cm)	12.5	16
Reach Travel Time (min)	9.5	7

Table 2.2: Metabolism estimates from non-glacial Lake Creek and glacial Herbert River using in situ dissolved O₂ concentrations. All values are calculated from single station, open water measurements and corrected for temperature. Reaeration was estimated with the surface renewal model (SRM), and NEM was calculated as GPP – CR₂₄. All values are reported in g O₂ m⁻² d⁻¹.

Date	CR ₂₄	GPP	NEM
Non-Glacial			
7/21/2011	0.79	0.45	-0.34
7/22/2011	1.04	0.56	-0.48
7/23/2011	1.10	0.72	-0.38
Glacial			
7/13/2011	1.71	2.50	0.78
7/14/2011	2.46	1.20	-1.27
7/15/2011	2.92	3.16	0.23

Table 2.3: Net ecosystem metabolism P/R ratios for glacial Herbert River and non-glacial Lake Creek during the summer melt season near Juneau Alaska. In forested Lake Creek estimates were made for July 21 to 23, 2011, and in glacial Herbert River measurements were for July 13 to 15, 2011. Metabolism metrics were calculated using dissolved oxygen concentrations with the single station open water method using the surface renewal model (SRM).

Location	P/R		
	Day 1	Day 2	Day 3
Lake Creek	0.60	0.55	0.67
Herbert River	1.46	0.49	1.08

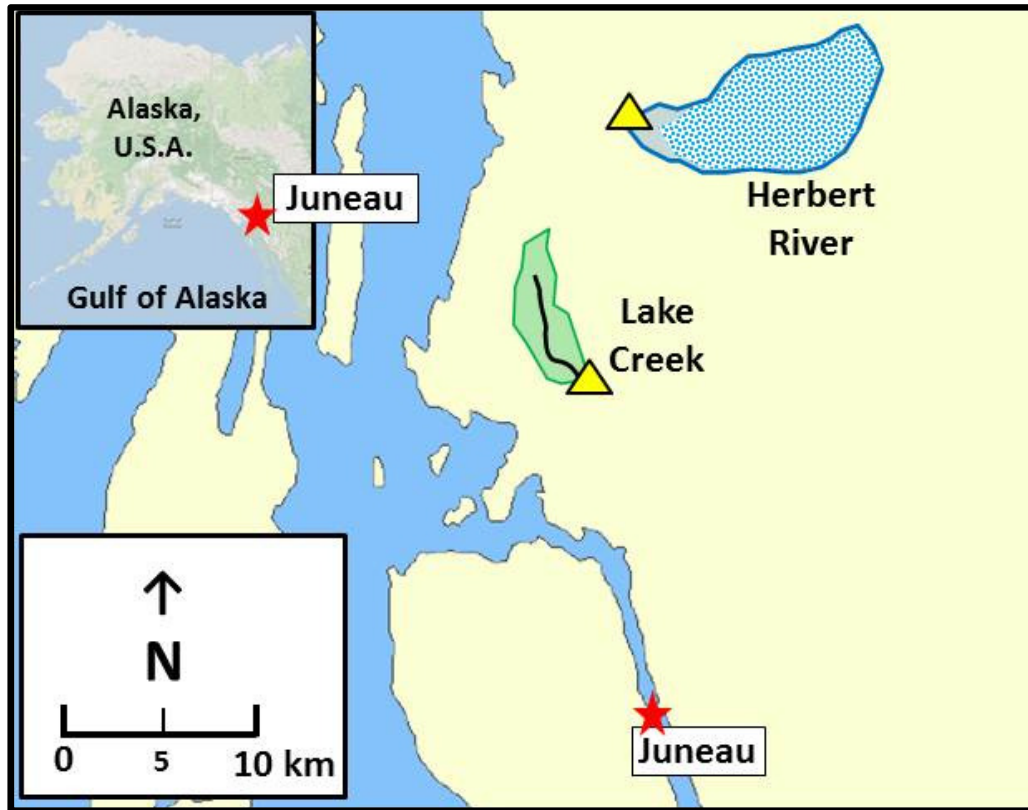


Figure 2.1: Watershed map showing contributing areas to study reaches in the non-glacial Lake Creek and glacial Herbert River watersheds in coastal southeast Alaska. Location of in-stream NEM data collection, water sampling, and injection experiment at each stream denoted with triangle.

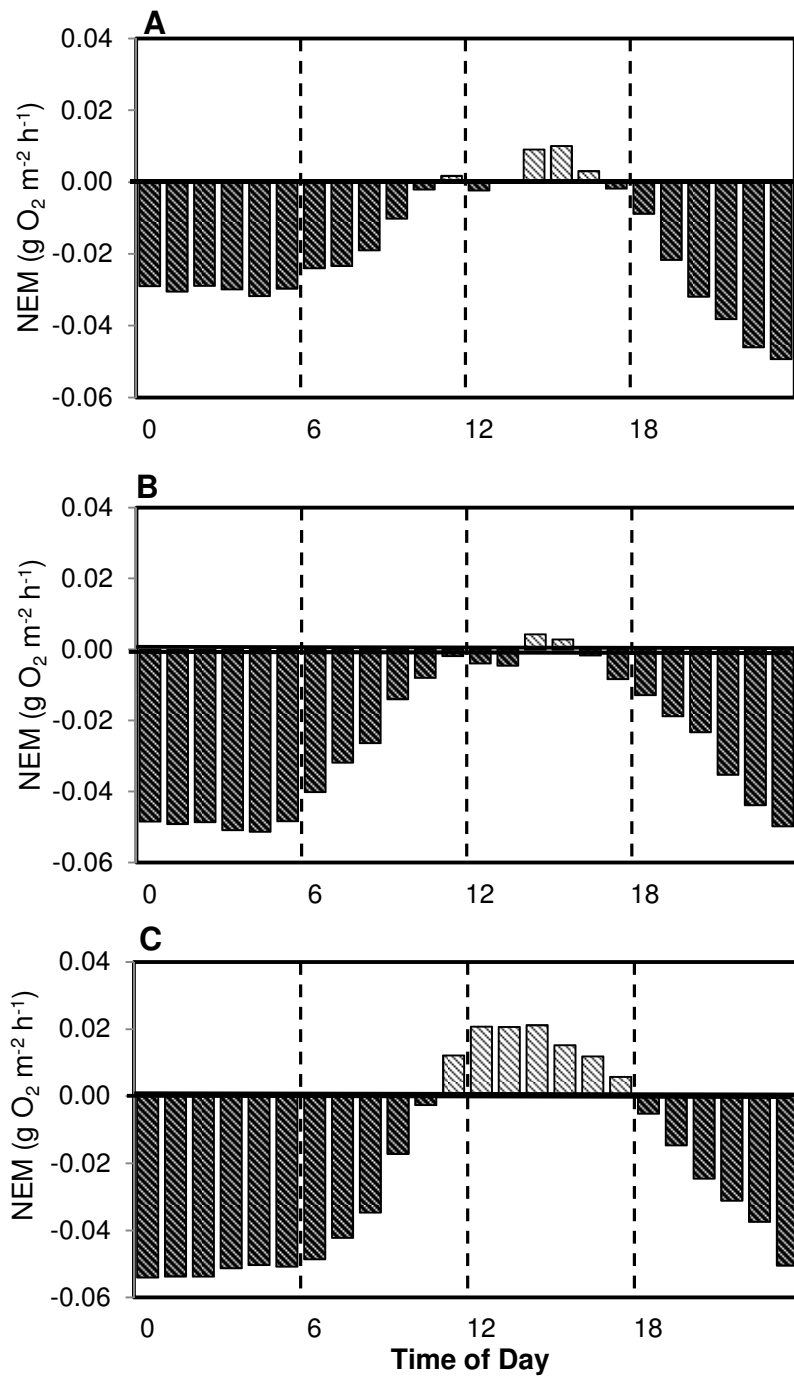


Figure 2.2: Diurnal hourly patterns of net ecosystem metabolism (NEM) from dissolved oxygen measurements for in the non-glacial forested study site (Lake Creek) on July 21st (A), July 22nd (B) and July 23rd (C) 2011. NEM values presented as net dissolved oxygen change on an area basis corrected for temperature and reaeration using the surface renewal model (SRM).

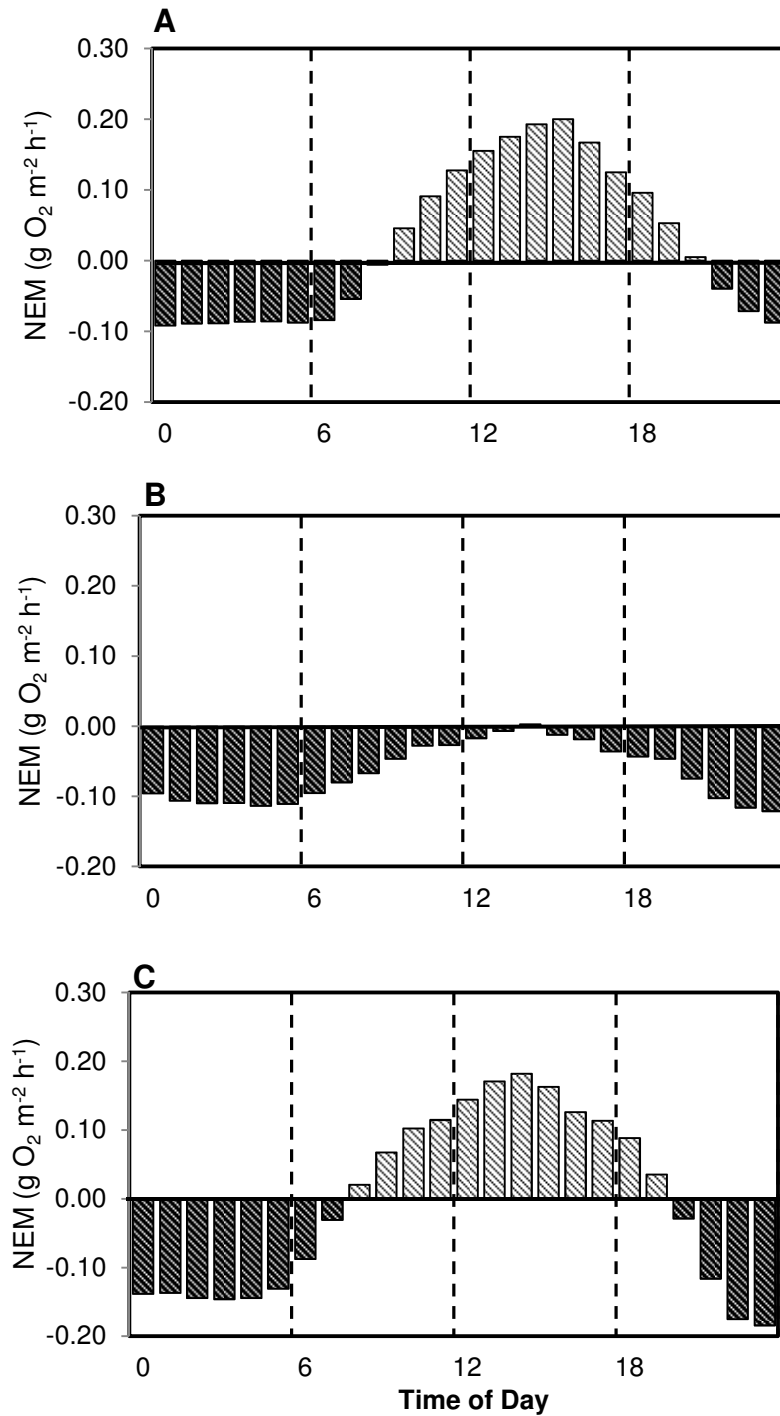


Figure 2.3: Diurnal hourly patterns of net ecosystem metabolism (NEM) from dissolved oxygen measurements for the glacial study stream (Herbert River) from July 13th (A), July 14th (B), and July 15th (C) 2011. NEM values presented as net dissolved oxygen change on an area basis corrected for temperature and reaeration using the surface renewal model (SRM).

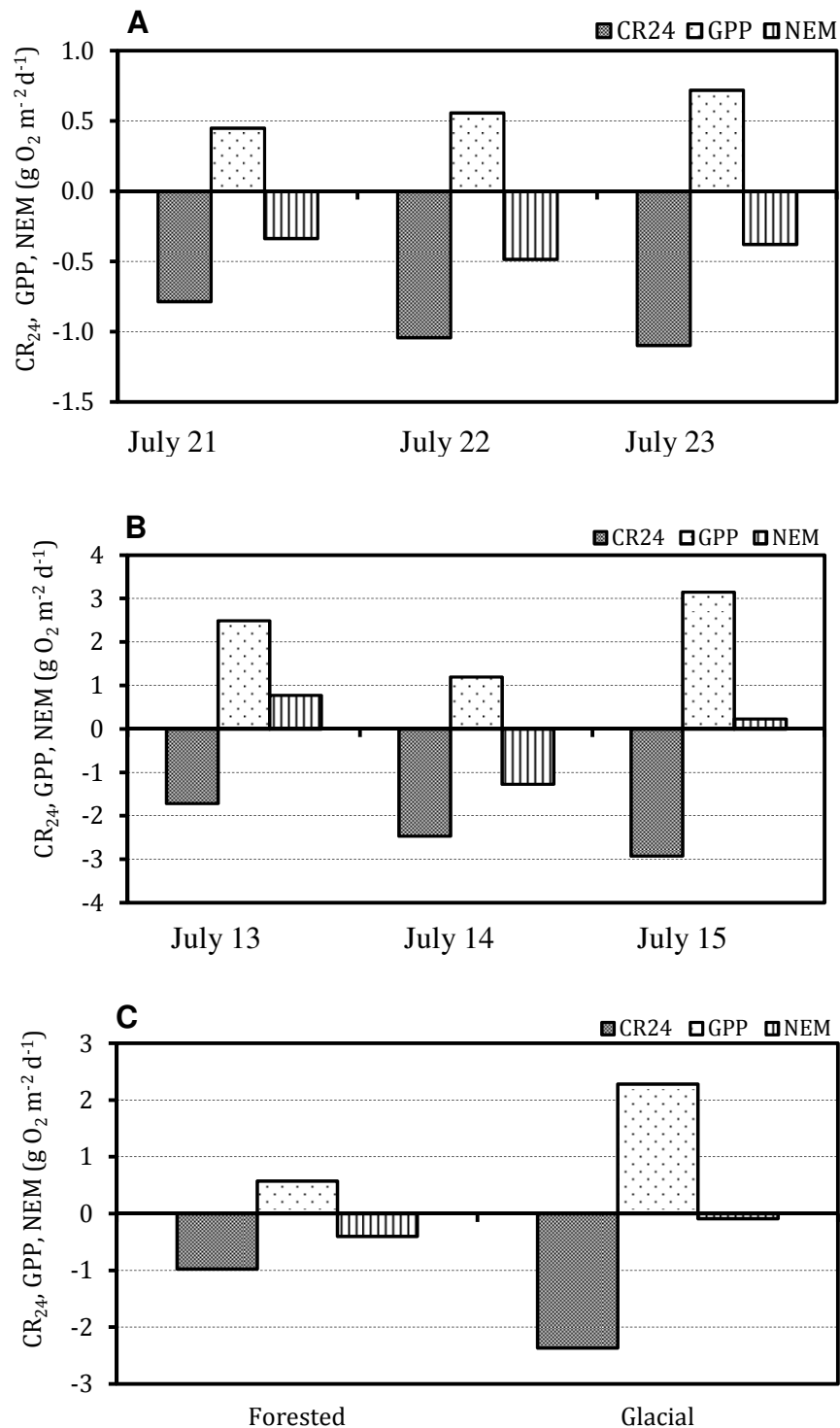


Figure 2.4: Daily net ecosystem metabolism estimates for non-glacial Lake Creek (A) and glacial Herbert River (B), and site averages (C) during the summer melt season near Juneau Alaska. Values calculated using the single station, dissolved oxygen, open water method with reaeration calculated using the surface renewal model (SRM).

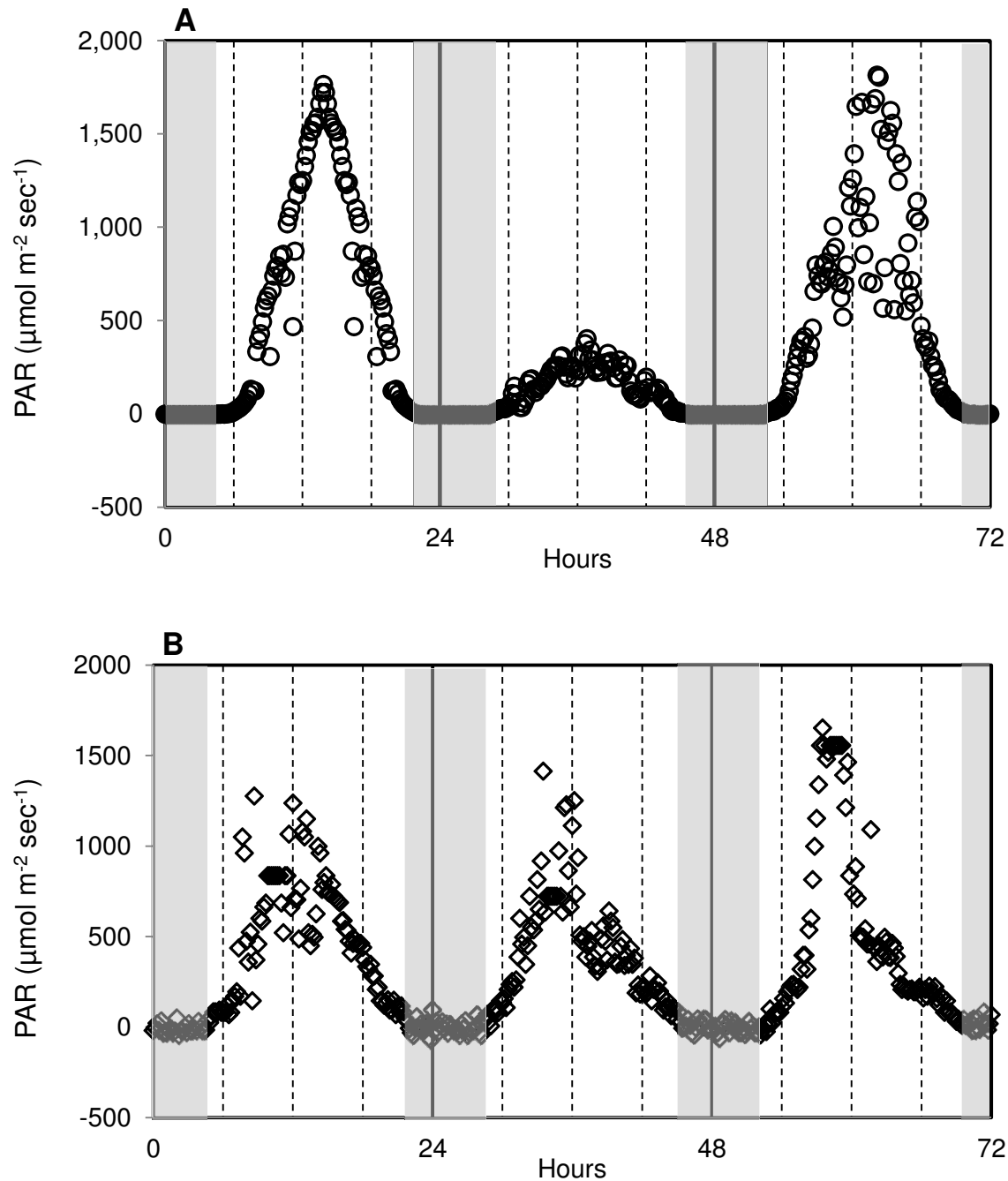


Figure 2.5: Stream bank PAR values for glacial Herbert River (A) and forested Lake Creek (B). Light was measured on the stream bank at 10-minute intervals during the 3-day monitoring period spanning July 13-15, 2011 at the proglacial stream and July 21-23, 2011 at the forested stream. The forested stream had a closed canopy and the proglacial stream had an open canopy with no riparian shading. Topography did not significantly impact shading at either site as the sun crossed the southern portion of the sky, and the coastal mountains were north of both study sites.

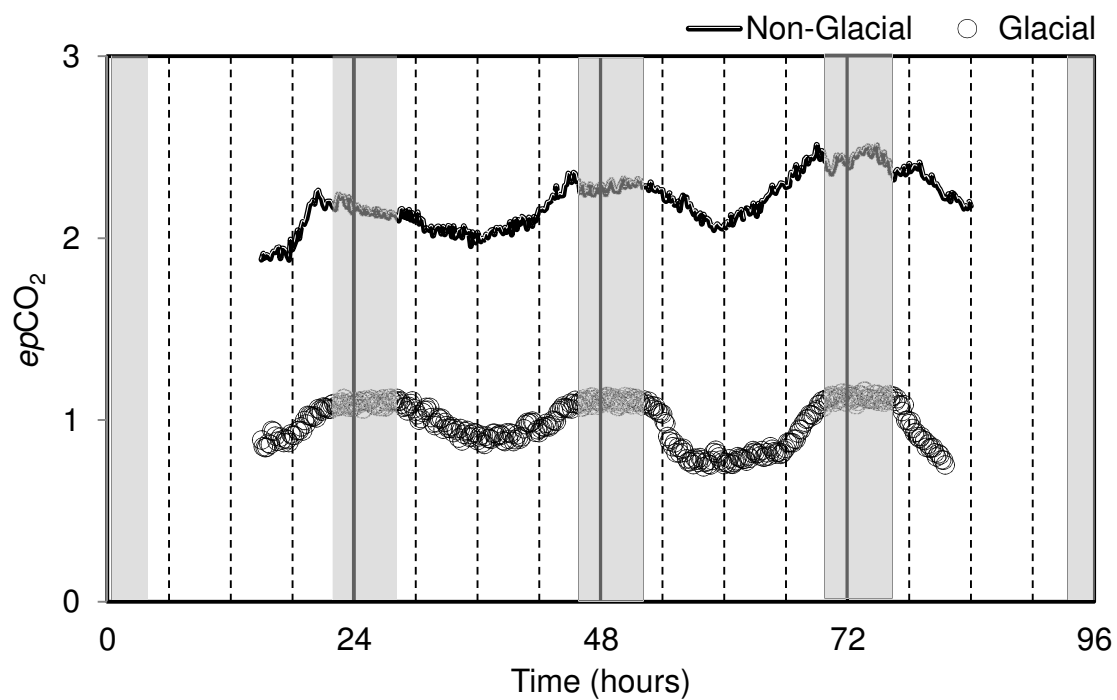


Figure 2.6: In-stream $epCO_2$ values for non-glacial Montana Creek and glacial Herbert River. Values corrected for temperature and depth. $epCO_2$ values greater than 1 indicate supersaturated water, shading indicates periods without sunlight.

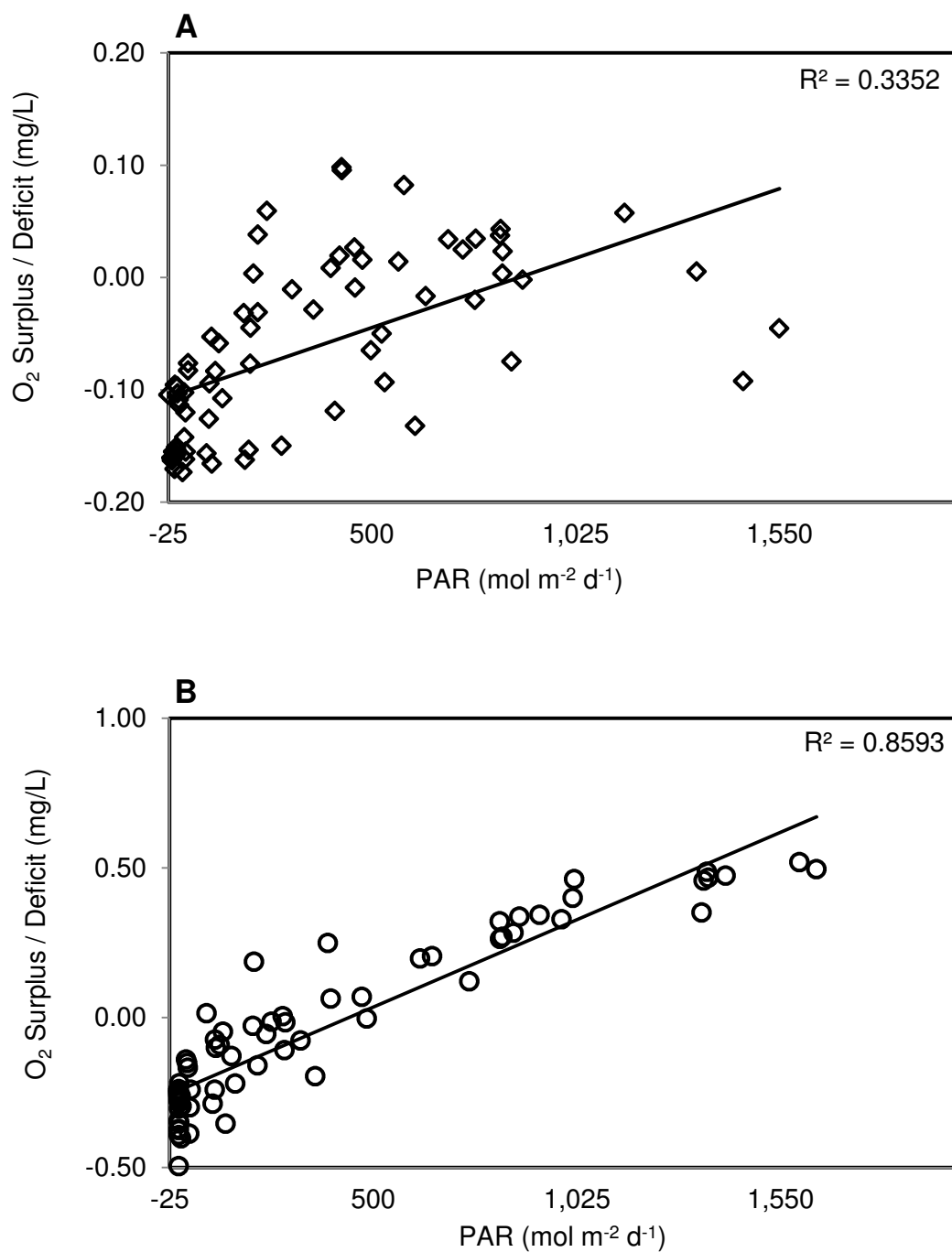


Figure 2.7: Dissolved oxygen concentrations vs. PAR values in non-glacial Lake Creek (A) and glacial Herbert River (B) during summer melt season near Juneau Alaska. PAR values recorded on stream bank for duration of 3-day study period at each. PAR values recorded at Lake Creek from July 21 to 23, 2011, and at Herbert River from July 13 to 15, 2011. Oxygen values corrected for temperature.

2.6 References

- Arendt, A. A., K. A. Echelmeyer, W. D. Harrison, C. S. Lingle, and V. B. Valentine. 2002. Rapid wastage of Alaska glaciers and their contribution to rising sea level. *Science* 297: 382–386.
- Baker, C. S., J. M. Straley, and A. Perry. 1992. Population characteristics of individually identified humpback whales in southeastern Alaska: Summer and fall 1986. *U.S. Fishery Bulletin* 90: 429-437.
- Battin, T. J. 2000. Hydrodynamics is a major determinant of streambed biofilm activity: From the sediment to the reach scale. *Limnol. Oceanogr.* 45(6): 1308-1319.
- Bhatia, M. P., S. B. Das, L. Xu, M. A. Charette, J. L. Wadham, E. B. Kujawinski. 2013. Organic carbon export from the Greenland ice sheet. *Geochimica et Cosmochimica Acta* 109: 329-344.
- Bott, T. L. 1983. Primary productivity in streams. In *Methods in Stream Ecology*, 29-53. J. R. Barnes and G. W. Minshall, Plenum, New York, NY.
- Bott, T. L., J. T. Brock, C. S. Dunn, R. J. Naiman, R. W. Ovink, and R. C. Petersen. 1985. Benthic community metabolism in four temperate stream systems: An inter-biome comparison and evaluation of the river continuum concept. *Hydrobiologia* 123: 3-45.
- Bott, T. L., J. D. Newbold, and D. B. Arscott. 2006. Ecosystem metabolism in piedmont streams: Reach geomorphology modulates the influence of riparian vegetation. *Ecosystems* 9: 398-421.
- Bott, T. L. 2007. Primary productivity and community respiration. In *Methods in Stream Ecology*, second edition, 663-690. Burlington, MA. Elsevier, Inc.
- Butman, R., and P. A. Raymond. 2011. Significant efflux of carbon dioxide from streams and rivers in the United States. *Nature Geoscience* 1294: DOI: 10.1038.
- Etherington L. L., P. N. Hodge, E. R. Hodge, and D. F. Hill. 2007 Oceanography of Glacier Bay, Alaska: Implications for biological patterns in a glacial fjord estuary. *Estuaries and Coasts* 30(6): 927-944.
- Fellman, J. B., R. G. M. Spencer, P. J. Hernes, R. T. Edwards, D. V. D'Amore, E. Hood. 2010. The impact of glacier runoff on the biodegradability and biochemical composition of terrigenous dissolved organic matter in near-shore marine ecosystems. *Marine Chemistry* 121: 112-122.
- Fellows, C. S., H. M. Valett, and C. N. Dahm. 2006. Whole-stream metabolism in two-montane streams: Contribution of the hyporheic zone. *Limnol. Oceanogr.* 46(3):

523-531.

- Fellows, C. S., H. M. Valett, C. N. Dahm, P. J. Mulholland, and S. A. Thomas. 2006. Coupling nutrient uptake and energy flow in headwater streams. *Ecosystems* 9:788-804.
- Grace, M., and S. Imberger. 2006. Stream metabolism: Performing and interpreting measurements. Water studies Centre Monash University, Murray Darling basin Commission and New South Wales Department of Environmental and Climate Change.
- Guasch, H., J. Armengol, E. Marti, and S. Sabater. 1998. Diurnal variation in dissolved oxygen and carbon dioxide in two low-order streams. *Water Research* 32(4): 1067-1074.
- Hamilton, S. K., S. J. Sippel, and J. M. Melack. 1995. Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil. *Biogeochemistry* 30: 115-141.
- Hill, B. H., and J. R. Webster. 1982. Periphyton production in an Appalachian river. *Hydrobiologia* 97: 275-280.
- Hood, E., J. Fellman, and R. T. Edwards. 2007. Salmon influences on dissolved organic matter in a coastal temperate brownwater stream: An application of fluorescence spectroscopy. *Limnology and Oceanography* 52: 1580–1587.
- Hood, E. and D. T. Scott. 2008. Riverine dissolved organic matter and nutrient yields in southeast Alaska affected by glacial coverage. *Nature Geoscience* 1: 583-587.
- Hood, E., and L. Berner. 2009. Effects of changing glacial coverage on the physical and biogeochemical properties of coastal streams in southeastern Alaska, *J. Geophys. Res.* 114, G03001, doi: 10.1029/2009JG000971.
- Hood, E., J. Fellman, R. G. M. Spencer, P. J. Hernes, R. Edwards, D. D'Amore, and D. Scott. 2009. Glaciers as a source of ancient and labile organic matter to the marine environment. *Nature* 462: 1044-1047.
- Houser, J. N., P. J. Mulholland, and K. O. Maloney. 2005. Catchment disturbance and stream metabolism: Patterns in ecosystem respiration and gross primary production along a gradient of upland soil and vegetation disturbance. *J. N. Am. Benthol. Soc.* 24(3): 538-552.
- Johnson, M. S., J. Lehmann, S. J. Riha, A. V. Krusche, J. E. Richey, J. P. H.B. Ometto, and E. G. Couto. 2008. CO₂ efflux from Amazonian headwater streams represents a significant fate for deep soil respiration. *Geophysical Research Letters* 35: doi: 10.1029/GL034619.

- Johnson, M. S., M. F. Billett, K. J. Dinsmore, M. Wallin, K. E. Dyson, and R. S. Jassal. 2010. Direct and continuous measurement of dissolved carbon dioxide in freshwater aquatic systems – method and applications. *Ecohydrology* 3: 68-78.
- Jones, J. B. Jr., and P. J. Mulholland. 1998. Influence of drainage basin topography and elevation on carbon dioxide and methane supersaturation of stream water. *Biogeochemistry* 40: 57-72.
- Lamberti, G. A., and A. D. Steinman. 1997. A comparison of primary production in stream ecosystems. *Stream Organic Matter Budgets* 16: 95-104.
- Logue, J. B., C. T. Robinson, C. Meier, and J. R. Van der Meer. 2004. Relationship between sediment organic matter, bacteria composition, and the ecosystem metabolism of alpine streams. *Limnol. Oceanogr.* 49(6): 2001-2010.
- Lottig, N. R., and E. H. Stanley. 2007. Benthic sediment influence on dissolved phosphorus concentrations in a headwater stream. *Biogeochemistry* 84: 297-309.
- McTammany, M. E., J. R. Webster, E. F. Benfield, and M. A. Neatrour. 2003. Longitudinal patterns of metabolism in a southern Appalachian river. *J. N. Am. Benthol. Soc.* 22(3):359-370.
- Merritt, D. M., and E. E. Wohl. 2002. Processes governing hydrochory along rivers: hydraulics, hydrology, and dispersal phenology. *Ecological Applications* 12(4): 1071-1087.
- Meyer, J. L., and R. T. Edwards. 1990. Ecosystem metabolism and turnover of organic carbon along a blackwater river continuum. *Ecology* 71(2): 668-677.
- Milner, A. M., L. E. Brown, and D. M. Hannah. 2009. Hydroecological response of river systems to shrinking glaciers. *Hydrological Processes* 23: 62-77.
- Moore, R. D. 2004. Introduction to salt dilution gauging for streamflow measurement, Part 2: Constant-rate injection. *Streamline Watershed Management Bulletin* 8(1): 11-14.
- Mulholland, P. J., C. S. Fellows, J. L. Tank, N. B. Grimm, J. R. Webster, S. K. Hamilton, E. Marti, L. Ashkenas, W. B. Bowden, W. K. Dodds, W. H. McDowell, M. J. Paul, and B. J. Peterson. 2001. Inter-biome comparison of factors controlling stream metabolism. *Freshwater Biology* 46: 1503-1517.
- Naegeli, M. W., and U. Uehlinger. 1997. Contribution of the hyporheic zone to ecosystem metabolism in a pre-alpine gravel-bed river. *J. N. Amer. Benthol. Soc.* 16(4): 794-804.

- Neal, E. G., E. Hood, and K. Smikrud. 2010. Contribution of glacial runoff to freshwater discharge into the Gulf of Alaska. *Geophysical Research Letters* 37: doi: 10.1029.
- Owens, M., R. W. Edwards, and J. W. Gibbs. 1964. Some reaeration studies in streams. *International Journal of Air and Water Pollution* 8: 469-486.
- Rasmussen, J. J., A. Baattrup-Pedersen, T. Riis, and N. Friberg. 2011. Stream ecosystem properties and processes along a temperature gradient. *Aquat. Ecol.* 45: 213-242.
- Raymond, P. A., N. F. Caraco, J. J. Cole. 1997. Carbon dioxide concentration and atmospheric flux in the Hudson River. *Estuaries* 20(2): 381-390.
- Singer, G. A., C. Fasching, L. Wilhelm, J. Niggemann, P. Steier, T. Dittmar, and T. J. Battin. 2012. Biogeochemically diverse organic matter in alpine glaciers and its downstream fate. *Nature Geoscience* 5: doi: 10.1038/NGEO1518.
- Stibal, M., M. Sabacka, and J. Zarsky. 2012. Biological processes on glacier and ice sheet surfaces. *Nature Geoscience* 5: doi: 10.1038/NGEO1611.
- Telling, J., A. M. Anesio, M. Tranter, M. Stibal, J. R. Hawkings, T. D. L. Irvine-Fynn, A. Hodson, C. Butler, M. Yallop, and J. Wadham. 2011. Controls on the autochthonous production and respiration of organic matter in cryoconite holes on High Arctic glaciers. *J. Geophys. Res.* doi: 10.1029/2011JG001828.
- Uehlinger, U., C. T. Robinson, M. Hieber, and R. Zah. 2010. The physic-chemical habitat for periphyton in alpine glacial streams under a changing climate. *Hydrobiologia* 657: 107-121.
- Vannote, R. L., G. W. Minshall, K. W. Cummins, J. R. Sedell, and C. E. Cushing. 1980. The river continuum concept. *Can. J. Fish. Aquat. Sci.* 37: 130-137.
- Wilhelm, L., G. A. Singer, C. Fasching, T. J. Battin, and K. Besemer. 2013. Microbial biodiversity in glacier-fed streams. *International Society of Microbial Ecology*: 1-10.
- Young, R. G., and A. D. Huryn. 1996. Interannual variation in discharge controls ecosystem metabolism along a grassland river continuum. *Can. J. Fish. Aquat. Sci.* 53: 2199-2211.
- Young, R. G., and A. D. Huryn. 1999. Effects of land use on stream metabolism and organic matter turnover. *Ecological Applications* 9(4): 1359-1376.

Chapter 3: Longitudinal Stream Analysis

3.1. Abstract

Longitudinal sampling of a proglacial and a non-glacial stream was conducted during the glacial melt season in southeast Alaska to assess changes to the physical and chemical characteristics of meltwater as it travels through the landscape. Study streams drained short, steep watersheds that discharged freshwater, organic matter, and sediment to near-shore areas of the Gulf of Alaska. Results indicate increases of dissolved organic carbon, nutrients, temperature, and turbidity along the non-glacial stream with increasing watershed area and distance from the headwaters. This is in contrast to changes in the glacial meltwater in the upper reaches of the watershed followed by steady concentrations in the lower reaches of the proglacial stream. Parallel factor analysis (PARAFAC) modeling also revealed protein contributions to the DOM pool decreased at a greater rate in the non-glacial stream than in the proglacial stream, and decreased more rapidly when deciduous forest /muskeg landcover was included in the watershed. Analysis of tributaries of each stream indicated lower elevation landscapes had more control over water quality parameters in the non-glacial watershed, while the upper reaches of the watershed had greater control on the glacial stream. This was likely a function of the disproportionate amount of discharge the glacial landcover contributes to the proglacial stream, and the controls low water temperatures and high amounts of fine sediments exert on biological activity in the glacial stream. These findings suggest coastal proglacial streams transport the physical and chemical characteristics of headwater streams from high elevation reaches to near-shore marine ecosystems more conservatively than non-glacial streams. Because

glacial meltwater contains DOM that is highly biologically available, these results suggest coastal regions in the Gulf of Alaska receiving discharge from glacial streams are also receiving bioavailable DOM contributions similar to those seen in higher elevation headwater streams. This information will provide further insight into in-stream processes impacting transport of organic matter from terrestrial to aquatic pools in the changing landscape of southeast Alaska.

3.2. Introduction

Glacial recession and thinning along the southeastern coast of Alaska has resulted in changes in the export of freshwater, nutrients, and dissolved organic matter (DOM) from coastal watersheds to the Gulf of Alaska (GOA) (Hood and Scott, 2008). The GOA is an ecologically important resource (Baker et al., 1992) and supports a fishing industry that catches 4.1 billion pounds of fish and shellfish annually, worth over \$1.3 billion (AKRDC, 2009). Over the last half of the 20th century, melting Alaskan glaciers contributed more freshwater to the coastal ocean than any other group of glaciers in the world (Arendt et al., 2002). Furthermore, the rate of glacial thinning in southeastern Alaska is increasing (Arendt et al., 2002).

An estimated 78% of the freshwater contributions, including glacial meltwater, to the GOA originate from small drainages along the coast (Neal et al., 2010). Streams in these watersheds start in the coastal mountains and quickly descend along short flow paths to the GOA. As streams transition from low order, high-elevation headwater streams through the watershed to higher order rivers, concentrations of nutrients, organic matter, and other solutes can change because of a combination of biotic (McTammany et al., 2003) and abiotic factors (Mulholland et al., 2001; Benner and Kaiser, 2011). Landscape controls (e.g., landcover and meltwater contributions) can influence many biotic and biotic factors, and therefore influence the processing of nutrients and organic matter during transport through these transitioning watersheds (Uehlinger et al., 2010). The impact glacial recession has on the in-stream processing of DOM and nutrients is unknown.

Studies of coastal streams in glaciated and non-glaciated catchments during base flow conditions revealed differences in organic matter, nutrients, and the physical characteristics of the water at analogous points in the watershed (Lafreniere and Sharp, 2004; Hood et al., 2009b). Glacial meltwater contributions decrease water temperatures (Hood and Berner, 2009), which can decrease in-stream processing of DOM (Rasmussen et al., 2011; Ylla et al., 2012). Increased meltwater contributions also increase stream water turbidity (Hood and Berner, 2009), which decreases light penetrating the water column. Decreased light in water column can directly impact primary production (Mulholland et al., 2001) and photodegradation of DOM (Benner and Kaiser, 2011). Higher discharge associated with glacial streams during the summer melt season (Hood and Berner, 2010) can also influence stream metabolism (Young and Huryn, 1996) and, therefore, impact biological processing of organic matter.

Glacial meltwater carries a unique combination of nutrients and organic matter from the landscape to receiving water bodies (Hood et al., 2009; Hood and Berner, 2009). DOM derived from glacial sources is older and more bioavailable than DOM from forested catchments in streams along GOA (Hood et al., 2009), and may come from aerosol deposits of fossil fuel burning (Stubbins et al., 2012). Glacial meltwater contributions result in streams having lower dissolved organic carbon (DOC) concentrations during the summer melt seasons than non-glacial streams (Hood and Scott, 2008; Hood and Berner, 2009), but higher percent bioavailable dissolved organic carbon (BDOC) levels (Fellman et al., 2010), suggesting glacier-derived DOM can be readily used by downstream ecosystems (e.g., coastal waters, GOA).

Insight on the composition of the organic matter pool in aquatic ecosystems can be obtained from fluorescence excitation-emission matrices (EEMs) of DOM, which identifies the contribution of specific fluorescent DOM compound classes to the total DOM fluorescence (McKnight et al., 2001; Stedmon et al., 2003). EEM analysis cannot fully characterize every component of the bulk DOM pool, but provides insight into the source (terrestrial vs. microbial) of aquatic DOM (McKnight et al., 2001; Stedmon et al., 2003). Protein-like fluorescence has been strongly correlated to BDOC in coastal streams in southeast Alaska (Fellman et al., 2009a). Fluorescence spectroscopy has also been used to characterize the source and reactivity of DOM in glacial systems in Antarctica and Canada (Barker et al. 2006).

This research aimed to determine the effect of glacial landcover and meltwater contributions on the longitudinal patterns of organic matter and nutrient dynamics along the length of a proglacial stream. This study investigated if the unique physical and chemical signature of glacial meltwater is transported conservatively downstream from high-elevation glacial headwaters to the ecologically and economically valuable coastal zone of the GOA. A proglacial stream was compared to a stream draining a high-elevation, non-glacial landscape to determine if the physical and chemical characteristics of the streams were influenced differently by downstream contributions from landscapes dominated by alpine vegetation, conifer forest, deciduous forest, and muskegs.

3.3. Methodology

3.3.1. Site Description

The proglacial Lemon Creek and non-glacial Montana Creek watersheds are located in southeast Alaska near Juneau between the GOA and the Juneau Icefield (Figure 3.1). The GOA drainage basin has an area of 420,230 km² including 75,640 km² (18%) of glacier ice coverage (Neal et al., 2010). Juneau air temperatures average 5.5°C at sea level and range from January averages of -6.3°C to July averages of 17.9°C. Total annual precipitation in this region averages 1475 mm including 2360 mm of snow each year, with the wettest month (October) averaging 210 mm, and the driest month (April) averaging 75 mm. Montana Creek, which drains a non-glacial, forested watershed contains no glacial land cover while Lemon Creek receives glacial meltwater from Lemon, Thompson, and Ptarmigan glaciers.

The 57.2 km² Lemon Creek watershed ranges in elevation from 22 to 1410 m, includes 16.3 km² of glacial landcover (28%), and contains three non-glacial tributaries (Sawmill Creek, Canyon Creek, and an unnamed tributary) on the southern half of the watershed that drain 15.5 km². Several small, unnamed streams drain the northern half of the watershed bounded by Heintzleman Ridge and the main channel, but were not accessible to field personnel. Lower elevations of this watershed are covered by coastal temperate rainforests, with conifers (Sitka spruce and western hemlock) as the dominate vegetation (15%), and alder concentrated near the riparian zone of the channel (Figure 3.2). Lemon Creek was sampled along 12 km of the main channel, at 2 discharge sources of adjacent and contributing glaciers, and in the 3 southern tributaries.

The studied extent of non-glacial Montana Creek watershed (41.4 km²) ranges in elevation from 19 to 1400 m and is covered by approximately 50% conifer forest. The primary tributary, McGinnis Creek, drains an area of high elevation snowfields including Mts. McGinnis and Stroller White. This watershed also contains alpine/sub-alpine vegetation (28%), deciduous forest / muskeg (7%), and another 14% of the watershed is covered by unvegetated rock. During the study, the McGinnis Creek tributary was considered the upper extent of the main channel upstream of the confluence with Montana Creek. This was done to better represent a stream draining a high-elevation, non-glaciated catchment (ranging in elevation from 19 to 1400 m) with a tributary (main stem Montana Creek) draining lower elevation forested areas and wetlands. Montana Creek was sampled along 9.7 km of the main channel and 0.6 km of the low elevation tributary.

3.3.2. Field Methods

Samples were collected at multiple locations in the main channel, upstream and downstream of the intersection of major tributaries, and in the tributaries upstream of the confluence with the main channel along both study streams (Figure 3.3). Water was collected from a well-mixed location in the stream channel starting from the upstream most location in each watershed and moving downstream in a single day. Sample collection occurred in 2011 between 12:05 and 15:30 on July 28th in the non-glacial stream and between 14:00 and 22:57 on July 29th in the glacial stream. Samples were individually bottled for analysis of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN), dissolved inorganic carbon (DIC), inorganic nitrate – nitrogen (NO₃⁻),

inorganic ammonium – nitrogen (NH_4^+), phosphate (PO_4^{3-}), water isotopes ($\delta^{18}\text{O}$), organic matter fluorescence properties.

Samples were collected using either a peristaltic Geopump fitted with silicon tubing and an in-line capsule 0.20 μm glass fiber filter or a 60 mL syringe fitted with a 0.20 μm disc filter. DOC, DIC, TDN, and samples for fluorescence analysis were collected in 40 mL amber glass bottles and refrigerated. Inorganic nutrients (NO_3^- , NH_4^+ , PO_4^{3-}), chloride, and sulfate samples were collected in 25 mL HDPE scintillation vials and frozen. Isotope samples were collected in 30 mL glass vials with conical polyseal lids with no headspace and stored at room temperature. Water quality measurements, including temperature, turbidity, pH, and specific conductivity were recorded with a YSI ProPlus handheld multiparameter meter at each sampling location.

3.3.3. Laboratory Sample Analysis

Samples for DOC/TDN and DIC were analyzed on a Shimadzu TOC-V carbon analyzer (Shimadzu Corporation, Kyoto, Japan) within 3 days of collection. Twenty-three field triplicate samples of DOC and TDN, and five field duplicate samples of DIC had standard deviation values of 4.2, 0.7, and 6.7 $\mu\text{mol/L}$, respectively. NH_4^+ and phosphorus samples were analyzed within 3 months on a SEAL segmented-flow nutrient analyzer (Seal Analytical, Mequon, Wisconsin, USA). Two duplicate field samples of NH_4^+ , and PO_4^{3-} had precision values of 0.46, and 0.02 $\mu\text{mol/L}$, respectively. NO_3^- samples were analyzed on a Dionex 8000 ion chromatograph (Dionex Corporation, Sunnydale, California, USA) within 3 months of collection. Four instrument duplicates of NO_3^- resulted in an instrument precision value of 0.63 $\mu\text{mol/L}$.

Fluorescence analysis of DOM was performed on a FluoroMax spectrofluorometer (Horbia Scientific, Kyoto, Japan) by building EEMs between excitation values of 240 and 450 nm at every 4 nm and within an emission range of 300 – 600 nm at every 5 nm. Values were corrected for background interference and normalized using a water Raman peak at an excitation of 350 nm. EEMs were then modeled in MATLAB (Stedmon et al., 2003; Stedmon and Bro, 2008) using parallel factor analysis (PARAFAC) with samples from other glacial and non-glacial streams in southeast Alaska. The fluorescence index (FI) was calculated as the ratio of emission intensity from 450 to 500 nm at an excitation of 370 nm (McKnight et al., 2001).

3.3.4. Watershed Analysis

Results from sample analyses were related to watershed location and landscape type through analysis of landcover and watershed area. Contributing watershed area at each sampling location was classified as glacier, unvegetated rock, alpine / sub-alpine, conifer forest, or deciduous forest / muskeg (Table B.4). GIS analysis of the study watersheds confirmed the Montana Creek watershed did not contain glacier landcover and the Lemon Creek watershed did not contain deciduous forest / muskeg landcover. Discharge was estimated at each sampling location in non-glacial Montana Creek based on average discharge contribution per watershed area at the USGS Montana Creek gage. This method provides a rough estimation of discharge throughout the watershed, but does not account for discharge variation based on landcover (e.g. forest vs. snowfield).

Discharge estimates for glacial Lemon Creek were based on discharge values from gages in the upper reach (15052000) 7.2 km upstream of the mouth in Gastineau

Channel, and lower reach (15052009) 1.6 km upstream of the mouth in Gastineau Channel. These gages were maintained non-concurrently by the USGS since 1951. Because of the influence of precipitation and air temperature on meltwater contributions and total discharge in glacial Lemon Creek, years with similar monthly temperature, precipitation, and discharge from the beginning of the meltseason until the study (May-July) were selected for analysis to more accurately estimate discharge contributions (Tables B.6 and B.7). Differences in discharge contribution per watershed area between the upper (current) USGS Lemon Creek gage and the lower USGS gage were calculated based on the average discharge differences for the month of July during the selected analogous years and contributing watershed areas at each gage (Table B.8). Because the difference in discharge between these gages originated from non-glacial sources, this value was used to estimate discharge throughout the watershed based on non-glacial watershed area.

3.4. Results

Discharge in the non-glacial stream increased from an estimated $3.2 \text{ m}^3/\text{s}$ at the upstream most location draining 16.4 km^2 of steep terrain and snowfields, to an estimated $8.0 \text{ m}^3/\text{s}$ at the downstream most sampling location upstream of the confluence with the Mendenhall River (Table 3.1). The estimated contributions from the McGinnis Creek branch ($3.6 \text{ m}^3/\text{s}$) and upper Montana Creek branch ($1.8 \text{ m}^3/\text{sec}$) align with previous USGS instantaneous discharge measurements that showed McGinnis Creek contributed at least 66% of the discharge to the main channel of Montana Creek during 75% of data collection efforts (Trout Unlimited, 2006). The proglacial stream

increased in discharge from 8.0 m³/s at the glacier terminus, to 13.8 m³/s at the bottom of the sampled reach. During the sampling window, discharge varied at the USGS gage in the glacial stream from 11.3 to 12.6 m³/s and in the forested stream from 6.5 to 7.8 m³/s. Both streams had decreasing discharge, and precipitation did not occur during the sampling window.

DOC in the main channel of the non-glacial stream ranged from 30 µmol/L at the upstream most sampling location, to 167 µmol/L at the downstream most location (Figure 3.4). The low elevation branch draining wetlands and forested hillsides had DOC concentrations above any location in the main channel, ranging from 239 to 285 µmol/L. Both sampled sites in the branch draining wetlands had higher DOC concentrations than the steep forested hillslope. The overall increase in the main channel of the forested stream from the upstream most location to the downstream confluence with the Mendenhall River was 137 µmol/L (458%). The main channel of the glacial stream had DOC concentrations ranging from 13 µmol/L at the glacier terminus to 28 µmol/L at the downstream most sampling location. All three sampling locations draining glacial surfaces (Thompson, Ptarmigan, and Lemon Creek Glaciers) had DOC concentrations below 23 µmol/L. Sampled tributaries draining high elevation snowfields and forested hillsides all had DOC concentrations above 37 µmol/L with the low elevation tributary having a DOC concentration of 72 µmol/L. The overall increase in the glacial stream from the glacier terminus to the downstream most sampled location in the valley was 15 µmol/L (127%).

TDN concentrations in the forested stream ranged from 5.7 µmol/L at the upstream most sampling location to 9.6 µmol/L at the downstream most location

(Figures 3.5). The branch draining low elevation wetlands and forested hillsides had TDN concentrations ranging from 4.5 to 7.7 $\mu\text{mol/L}$. The overall increase in the main channel of the forested stream from sampled headwaters to the downstream most sampled location was 3.9 $\mu\text{mol/L}$ (68%). The main channel of the glacial stream had TDN concentrations ranging from 0.4 $\mu\text{mol/L}$ at the glacier terminus to 4.1 $\mu\text{mol/L}$ at the downstream most sampling location. Sampled tributaries all had TDN concentrations above 3.75 $\mu\text{mol/L}$, with Sawmill Creek having a TDN concentration of 17 $\mu\text{mol/L}$. The overall increase in the glacial stream from the glacier terminus to the downstream most sampled location in the valley was 3.7 $\mu\text{mol/L}$ (860%).

NH_4^+ concentrations in the forested stream ranged from 0.7 $\mu\text{mol/L}$ upstream of the branch confluence to 2.0 $\mu\text{mol/L}$ at the downstream most location, an increase of 1.3 $\mu\text{mol/L}$ (178%) (Figure 3.6). Concentrations of NH_4^+ in the glacial stream and its tributaries ranged from 0.43 to 0.93 $\mu\text{mol/L}$ and all were within reporting error range. The only exception was the Sawmill Creek tributary, which had an NH_4 concentration of 1.22 $\mu\text{mol/L}$. NO_3^- concentrations in the forested stream decreased from 5.7 to 5.2 $\mu\text{mol/L}$ throughout the watershed (Figure 3.6). NO_3^- was not detected at any high-elevation sample locations near the glacier terminus. A maximum main channel concentration of 3.0 $\mu\text{mol/L}$ was recorded in the valley and the low-elevation tributary had a NO_3^- concentration of 17.6 $\mu\text{mol/L}$.

Measured levels of PO_4^{3-} in the main channel of the forested stream ranged from 0.04 $\mu\text{mol/L}$ to 0.11 $\mu\text{mol/L}$ at the downstream most sampling location (Figure 3.6). Tributary concentrations were equivalent to main channel levels with the exception of the sampled location upstream of the confluence (0.13 $\mu\text{mol/L}$). The main channel

showed an increase of PO_4^{3-} of $0.07 \mu\text{mol/L}$ 175% from the headwaters to the Mendenhall River confluence. Concentrations of PO_4^{3-} in the main channel of the glacial stream and its tributaries did not vary beyond the range of reporting error with a minimum value of $0.01 \mu\text{mol/L}$ and a maximum value of $0.05 \mu\text{mol/L}$.

DIC concentrations increased in the non-glacial stream from a minimum value of $300 \mu\text{mol/L}$ in the headwaters, to a maximum value of $365 \mu\text{mol/L}$ near the Montana Creek USGS gaging station (Figure 3.6). Samples from tributaries draining forested hillslopes and wetlands all had DIC values above the main channel and ranged from 405 to $509 \mu\text{mol/L}$. DIC samples from the glacial stream ranged from a minimum of $133 \mu\text{mol/L}$ at the glacier terminus to a maximum value of $266 \mu\text{mol/L}$ at the downstream most sampling location. Non-glacial tributaries all had DIC values above the main channel, with values ranging from $331 \mu\text{mol/L}$ at the high elevation tributary to $642 \mu\text{mol/L}$ at the low elevation tributary.

FI values decreased in the forested stream from a peak value of 1.4 at the upstream most location of McGinnis Creek to a minimum of 1.3 at the USGS gage (Figures 3.7). Sampled tributaries reflected similar values as the main channel at equivalent locations in the watershed ranging from 1.26 to 1.30 . FI values in the main channel of the forested stream decreased 0.16 (13%) from the headwaters to the confluence with the Mendenhall River. In the glacial stream, FI values ranged from a maximum of 2.95 to a minimum of 1.40 . The three main tributaries reflected similar values as the main channel at equivalent locations in the watershed ranging from 1.36 to 1.44 . FI values in the main channel of the glacial stream decreased 79% from the headwaters to the valley.

MATLAB analysis of DOM fluorescence EEMs resulted in a 7-component PARAFAC model. Protein content of the DOM pool in the non-glacial stream was highest at the upstream most sample location (27%), decreased rapidly until the confluence with the low elevation branch, and then continued to decrease at a lower rate throughout the watershed (Figure 3.8). Protein content of the DOM pool in non-glacial stream decreased by a total of 23% as it traveled through the non-glacial watershed. Protein contributions in the glacial stream main channel varied from 25% to 45% along the length of the stream, with the exception of an outlier upstream of the unnamed tributary. Throughout the glacial watershed, protein contributions to the DOM pool decreased by a total of 8.9%.

Additional data are presented in Appendix B including land cover classifications and coverage areas and historical records of average monthly air temperature, precipitation and Lemon Creek discharge. Raw data from water samples and probes are presented in Tables B.2 and B.3. PARAFAC components and sample leverage are presented in Figures B.1 and B.2.

3.5. Discussion

The transport of carbon and nutrients from coastal landscapes to near shore marine waters is an important process that influences both the water quality in freshwater streams (Hood and Berner, 2009) and the marine coastal waters where highly bioavailable exports (Hood et al., 2009; Fellman et al., 2010) mix with ocean water and support ecologically important zones. This research studied landscape

controls on DOM, nutrients, and other water quality parameters along the length of a non-glacial forested stream and nearby proglacial stream adjacent to the Gulf of Alaska.

DOC and TDN concentrations in the non-glacial stream increased throughout the watershed, but concentrations of both analytes were heavily influenced by contributions of the low elevation branch (Montana Creek) downstream of the confluence with the high-elevation branch (McGinnis Creek) (Figures 3.4 and 3.5). Below the confluence, contributions from wetlands and deciduous forest landcover increased at a greater rate, while contributions for conifer forest and alpine / sub-alpine vegetation became a smaller portion of the total contributing landscape. The contributions from muskegs and deciduous forest landcover had a consistent positive correlation with both DOC and TDN concentrations in the non-glacial stream throughout the watershed. Conifer forest was also positively correlated to both DOC and TDN, but this correlation varied from upstream to downstream of the confluence suggesting conifer forest landcover exerts less control on these analytes than deciduous forest and muskeg wetlands.

DOC and TDN concentrations in the glacial stream also increased throughout the watershed showing both a positive correlation to forest cover and a negative correlation to contributions from glacial landcover (Figures 3.4 and 3.5). The inverse relationship of both DOC and TDN to glacial landcover has been documented across watersheds along a gradient of glacial landcover in southeast Alaska (Hood and Berner, 2009), and within glacial watersheds in other regions (Williams et al., 2001). The three sampled tributaries with DOC concentrations above levels in the main channel did not impact stream DOC concentrations in the glacial stream as strongly as the tributary with high DOC and TDN concentrations affected the non-glacial stream.

The lack of a significant increase in DOC and TDN in the glacial stream is likely a function of the dominant discharge contribution from the glacier meltwater when compared to discharge contributions from non-glacial landscape components. Discharge at the glacial study site during the summer is strongly driven by discharge from Lemon, Thompson, and Ptarmigan Glaciers. This results in the reduced influence of non-glacial tributaries with lower specific discharge. Discharge estimates during the study suggest outflow from glacial landcover contributes 58% of the stream discharge to the proglacial stream, even though glacial landcover only makes up 28% of the watershed at the downstream location.

Nutrient concentrations in the non-glacial stream exhibited a changing pattern of NH_4^+ and PO_4^{3-} concentrations through the watershed and overall increases in DIC and steady concentrations of NO_3^- . NH_4^+ and PO_4^{3-} concentrations increased at the lower reach of the non-glacial stream after a decline from the upstream-most sampling location. This increase is likely the result of salmon-derived nutrient (SDN) additions to the stream. Non-glacial Montana Creek is pristine spawning habitat for Pink, Coho, and Chum salmon during the summer. Nutrient additions to streams from spawning salmon have been documented in nearby Peterson Creek (Fellman et al., 2008) and in streams supporting salmon runs in other regions (Mitchell and Lamberti, 2005). Spawning activities increase streamwater concentrations of both NH_4^+ and PO_4^{3-} , with no impact on NO_3^- (Mitchell and Lamberti, 2005).

Nutrient concentrations in the proglacial stream were within the expected range of values observed in other glacial streams in southeast Alaska (Hood and Berner, 2009). DIC and NO_3^- concentrations in the glacial stream increased throughout the

watershed, while NH_4^+ and PO_4^{3-} varied only within the range of sample precision. The low values of NO_3^- in the glacial stream are likely a function of both the dominance of glacial meltwater flow. Low water temperatures combined with light-limiting glacial flour and high, bed-scouring discharge make glacial streams less suitable for established biological communities to alter stream DOM (Young and Huryn, 1996; Rasmussen et al., 2011). The overall increase in NO_3^- at this site is likely the result of contributions to the stream channel from the landscape and not from autochthonous sources. Previous studies in this watershed (Hood and Berner, 2009) have noted the presence of nitrogen fixing alder which can increase NO_3^- concentrations in streams when present in the riparian zone or contributing upland areas of the watershed (Compton et al., 2003).

Increases in DIC along the glacial stream, especially in the lower elevations, are likely from groundwater contributions flowing through increasingly organic soil layers throughout the watershed. As thin soils and rock in the higher elevations are replaced by deeper organic soils in the lower reaches, soil microbial respiration contributes more CO_2 to the stream through lateral flow from the riparian zone and shallow groundwater flow in the lower elevations.

The analysis of DOM composition through PARAFAC EEM modeling indicates both streams start with similar contributions from protein DOM components. The non-glacial study site quickly shifts to less protein contributions as it transitions from snowmelt dominance to groundwater moving through organic soil layers. The glacial stream values varied throughout the length of the stream and, despite an overall decreasing trend in protein content of the DOM pool, an increase in values was modeled in the lower reaches. Overall, protein content decreased by 0.93% with every 1

km² increase in watershed area to the non-glacial stream, and only decreased 0.2% to a similar increase in watershed size in the proglacial stream. Landcover, specifically the deciduous forest/muskeg landcover and glacial landcover had opposite impacts on the composition of the DOM pool. Protein contributions decreased by 4.3% with a 1% increase in deciduous forest and muskeg landcover, which is in contrast to a 0.15% increase with an equivalent increase in glacial landcover.

Both the glacial and non-glacial stream showed initial decreases in FI values from the upstream-most sampling locations in each watershed. This initial decrease was followed by nearly consistent values throughout the remainder of each watershed. Furthermore, the glacial watershed retained a higher FI value throughout the length of the channel, indicating a more microbial source of streamwater DOM. In both study streams, FI decreased with increasing DOC values, a trend observed in other studies of both glacial and non-glacial systems (Lafreniere and Sharp, 2004) suggesting organic matter additions at lower reaches are from terrestrial sources and not autochthonously produced in the channel. In the glacial stream, FI values from the upstream most samples (2.9, 2.5) are higher than most reported values in other studies (Lafreniere and Sharp, 2004; Hood et al., 2006), but are comparable to maximum values found in the surface water on Antarctic lakes (McKnight et al., 2001). Samples resulting in these high values are from locations that contain 1% or less conifer forest landcover and drain landscapes dominated by glacier ice and unvegetated rock, suggesting low DOM aromaticity indicated by higher FI values are likely an accurate representation of the DOM pool.

This data set indicates streams receiving glacial meltwater are uniform in DOM composition and physical characteristics after initial changes immediately downstream of the glacier terminus. This is in contrast to continuing and sometimes increasing shifts in the physical and chemical composition of streamwater flowing through un-glaciated catchments. The likely reasons for this difference are 1) the dominance of glacial meltwater discharge as the primary component of stream flow throughout the watershed, 2) short travel times from the headwaters to the mouth of these coastal streams, and 3) the physical controls of glacial discharge on autochthonous DOM production and processing including low water temperatures and fine glacial sediment that limits light penetration in the water column and creates unstable substrate for microbial communities in the channel.

Because DOM and nutrients in glacial meltwater are transported more conservatively to near-shore ecosystems with less influence of low elevation landscapes than streamwater from high-elevation non-glacial landscapes, the unique and highly bioavailable DOM associated with glacial meltwater (Hood and Scott, 2008; Hood et al., 2009) is also delivered to the GOA with minimal change. Because marine microbes process glacial DOM more readily than DOM from forested watersheds in this region (Fellman et al., 2010), the DOM pool delivered to coastal waters during the summer glacier melt season is likely an important component of the aquatic food web in the summer. Increased loss of glacier mass in this region (Arendt et al., 2002), and changes in the timing and magnitude of meltwater discharge to the GOA will likely impact this source of DOM.

Table 3.1: Discharge estimates for sampling points along glacial Lemon Creek and non-glacial Montana Creek near Juneau Alaska. Calculations for Montana Creek based on average landscape discharge contributions from watershed area and discharge at USGS gaging station. Calculations for Lemon Creek based on average July discharge contribution per watershed area differences from the current USGS gage 3.8 km downstream of the glacier and a previously monitored gage at a lower. Because differences in discharge between these gages are assumed to originate from non-glacial sources, this value was used to estimate discharge throughout the watershed. USGS gage locations in bold.

Glacial ID	Dist. Upstream (km)	Area (km²)	Q (m³/sec)	Glacial Q (%)	Location
LC-1	0.0	57.2	13.8	58%	Main Channel
LC-4	3.2	52.3	13.5	59%	Main Channel
LC-5	5.1	48.5	13.3	60%	Main Channel
LC-6	6.3	46.7	13.2	61%	Main Channel
LC-8	6.4	42.5	13.0	62%	Main Channel
LC-9	7.9	39.1	12.8	63%	Main Channel
LC-11	8.5	29.4	12.26	66%	Main Channel
LC-12	12.5	12.3	8.0	99%	Main Channel
LC-13	n.a.	n.a.	n.a.	n.a.	Headwaters
LC-14	n.a.	n.a.	n.a.	n.a.	Headwaters
LC-3	n.a.	2.8	0.2	0%	Tributary
LC-7	n.a.	4.0	0.2	0%	Tributary
LC-10	n.a.	8.6	0.5	0%	Tributary
Non-Glacial ID	Dist. Upstream (km)	Area (km²)	Q (m³/sec)	Glacial Q (%)	Location
MC-1	0.0	41.4	8.0	0%	Main Channel
MC-2	2.5	37.5	7.04	0%	Main Channel
MC-3	7.0	30.3	5.8	0%	Main Channel
MC-4	9.5	26.6	5.1	0%	Main Channel
MC-8	9.6	18.7	3.6	0%	Main Channel
MC-9	11.1	16.4	3.2	0%	Main Channel
MC-5	n.a.	9.2	1.8	0%	Tributary
MC-7	n.a.	8.1	1.6	0%	Tributary
MC-6	n.a.	0.4	0.1	0%	Tributary

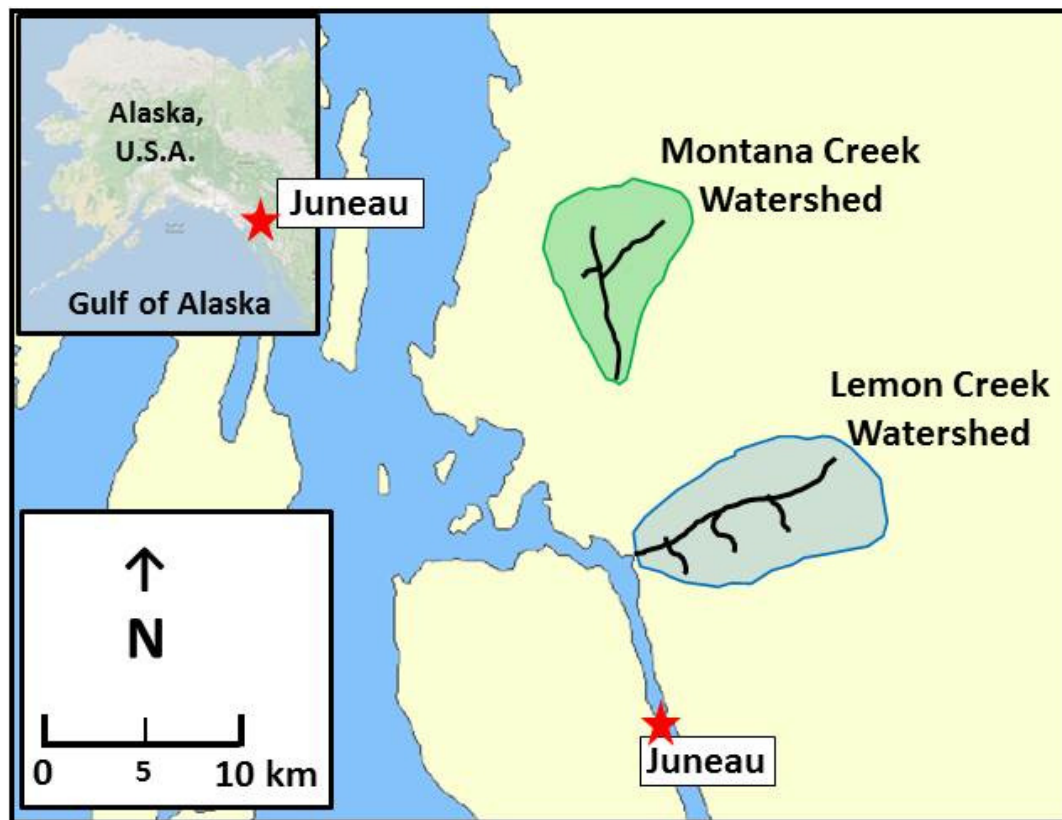


Figure 3.1: Location of non-glacial Montana Creek and glacial Lemon Creek in the southeast Alaska panhandle. Watersheds boundaries and contributing area for each study stream is highlighted along with the main channel and sampled tributaries.

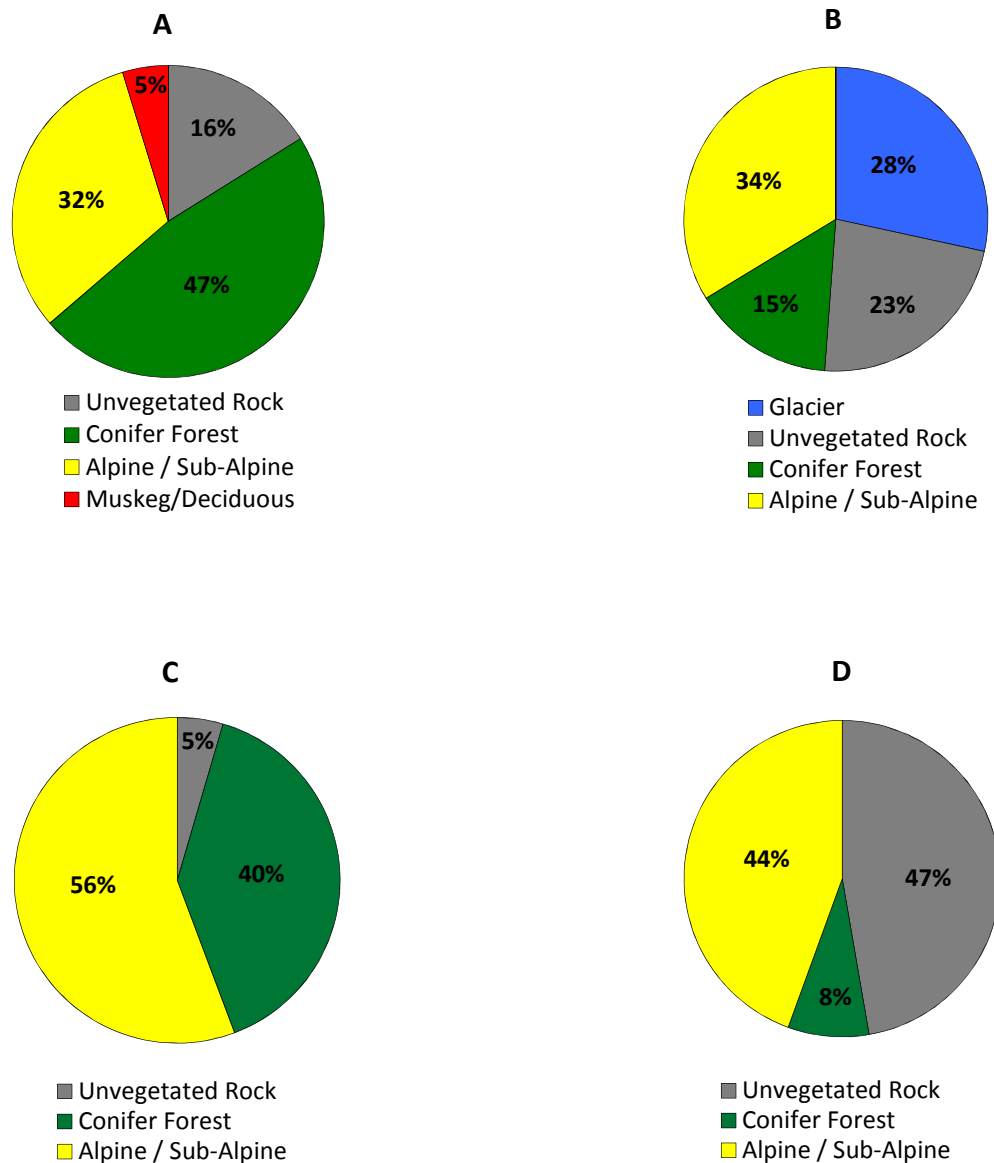
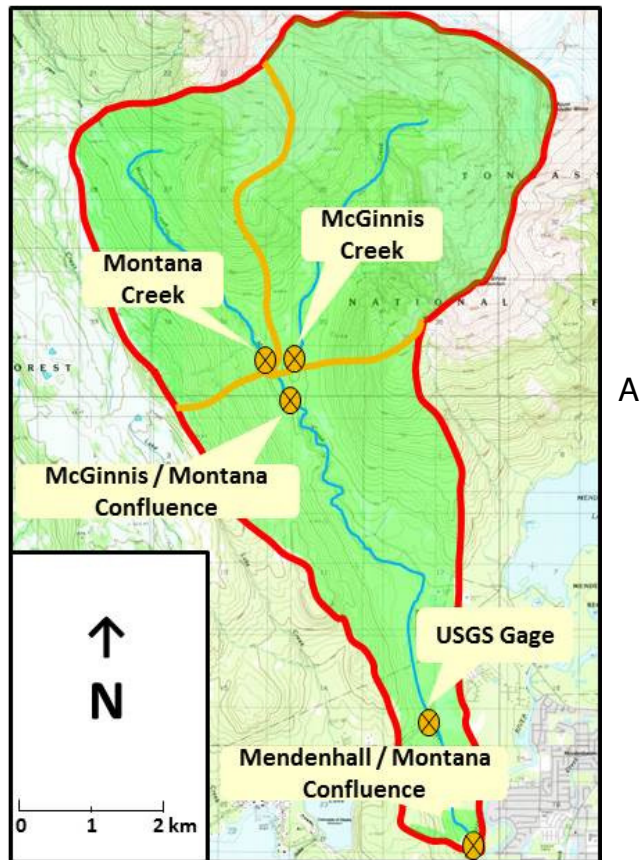
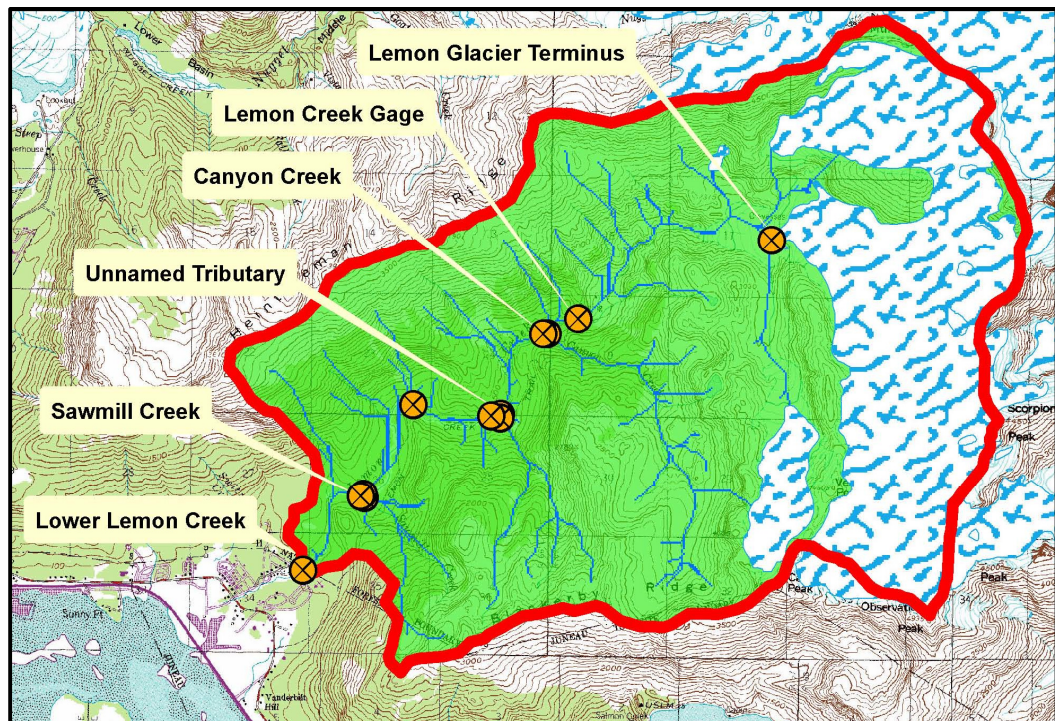


Figure 3.2: Watershed landcover at the downstream most sampling location for non-glacial Montana Creek (A) and glacial Lemon Creek (B) near Juneau Alaska. Non-glacial tributaries of Lemon Creek draining low elevation (C) and high elevation (D) sub-watersheds. Values obtained through GIS analysis did not include Muskeg or Deciduous landcover in the Lemon Creek Watershed, but field observations noted deciduous cover in the riparian zone of the main channel, and small dispersed muskegs in slope breaks throughout the watershed.



A



B

Figure 3.3: Watershed map and sampling locations in non-glacial Montana Creek (A) and glacial Lemon Creek (B) and near Juneau Alaska.

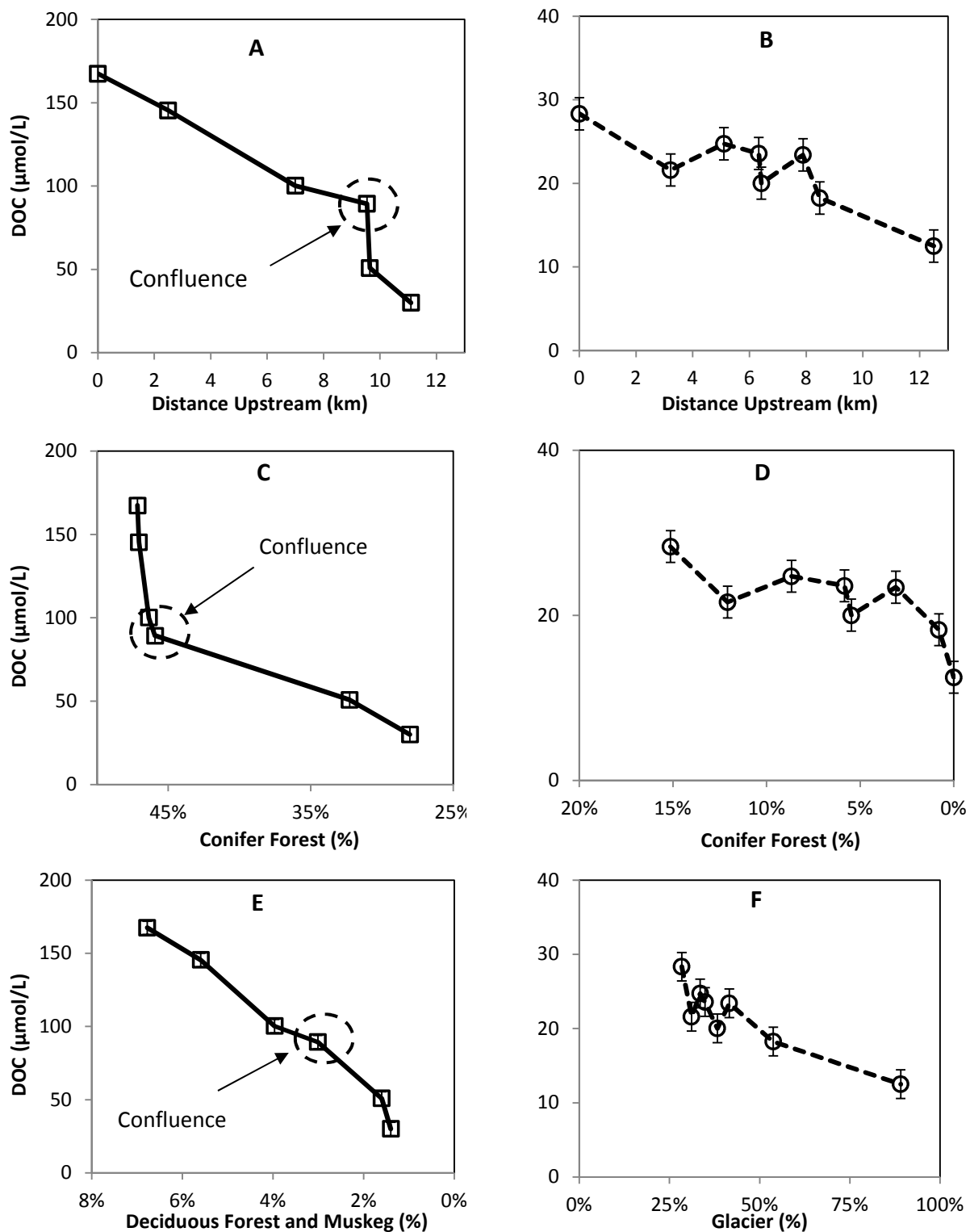


Figure 3.4: Dissolved organic carbon (DOC) vs. distance upstream (A, B), % conifer forest landcover (C, D), % deciduous forest and muskeg landcover (E), and % glacial landcover (F) in non-glacial Montana Creek (A, C, E) and glacial Lemon Creek (B, D, F) in southeast Alaska. Values obtained from longitudinal sampling of each study stream from a well-mixed location of the main channel. Error bars indicate ± 1 S.E., $N = 3$.

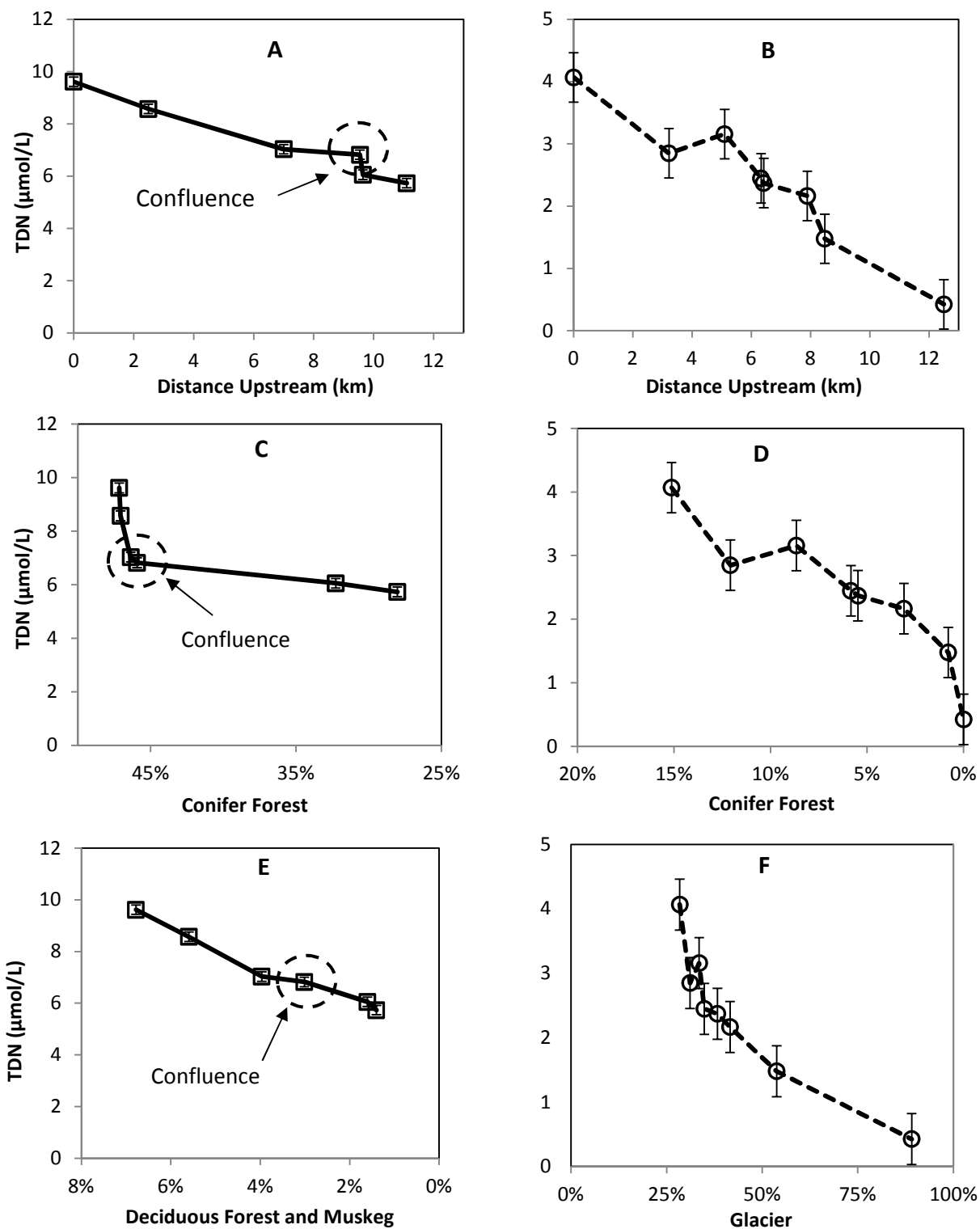


Figure 3.5: Total dissolved nitrogen (TDN) vs. distance upstream (A, B), % conifer forest landcover (C, D), % deciduous forest and muskeg landcover (E), and % glacial landcover (F) in non-glacial Montana Creek (A, C, E) and glacial Lemon Creek (B, D, F) in southeast Alaska. Values obtained from longitudinal sampling of each study stream from a well-mixed location of the main channel. Error bars indicate ± 1 S.E., $N = 3$.

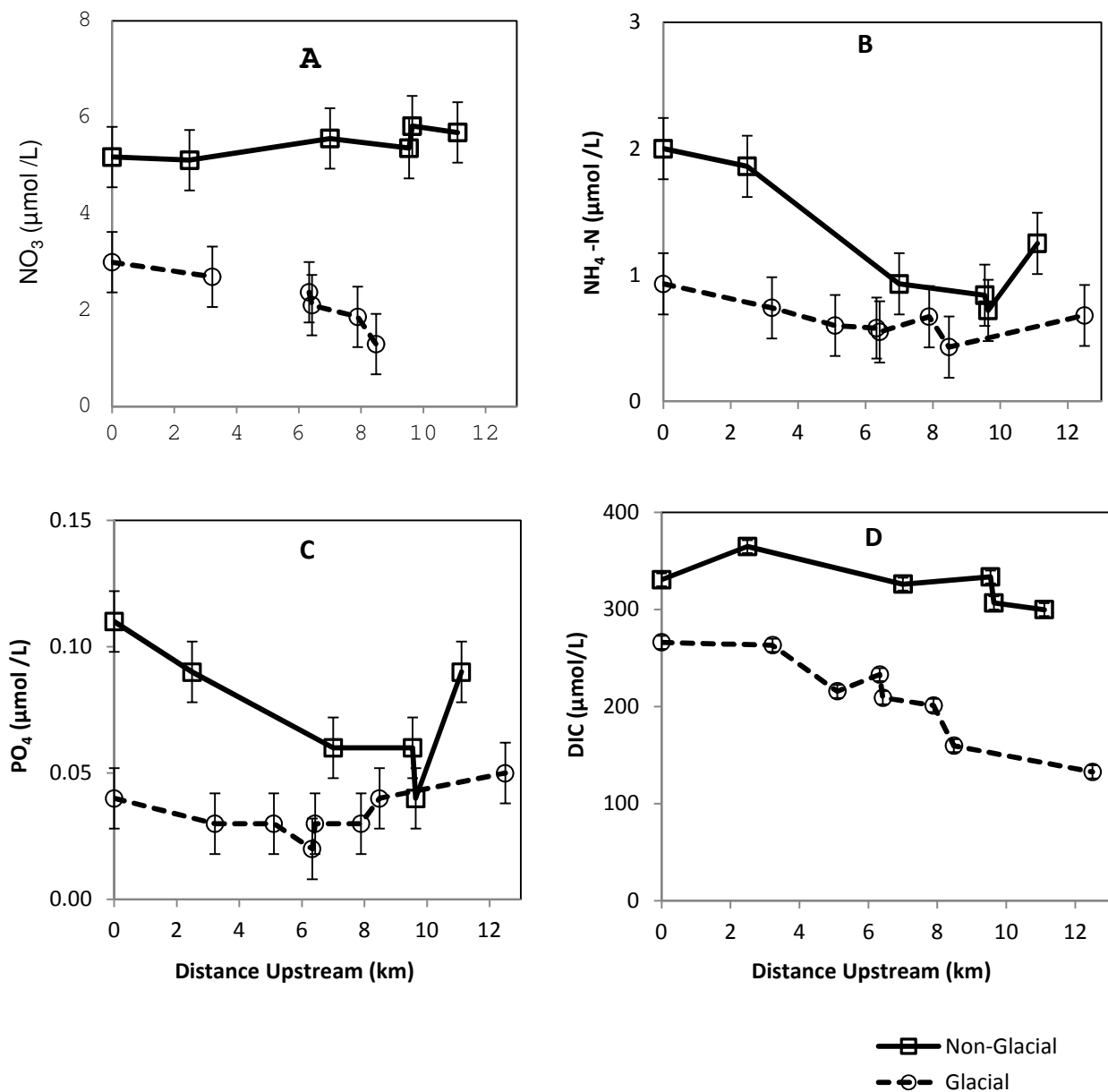


Figure 3.6: Distance upstream vs. nitrate nitrogen (NO_3^-) (A), ammonium nitrogen (NH_4^+) (B), phosphate (PO_4^{3-}) (C), and dissolved inorganic carbon (DIC) (D) in non-glacial Montana Creek and glacial Lemon Creek in southeast Alaska. Values obtained from longitudinal sampling of each study stream from a well-mixed location of the main channel. Error bars indicate instrument precision.

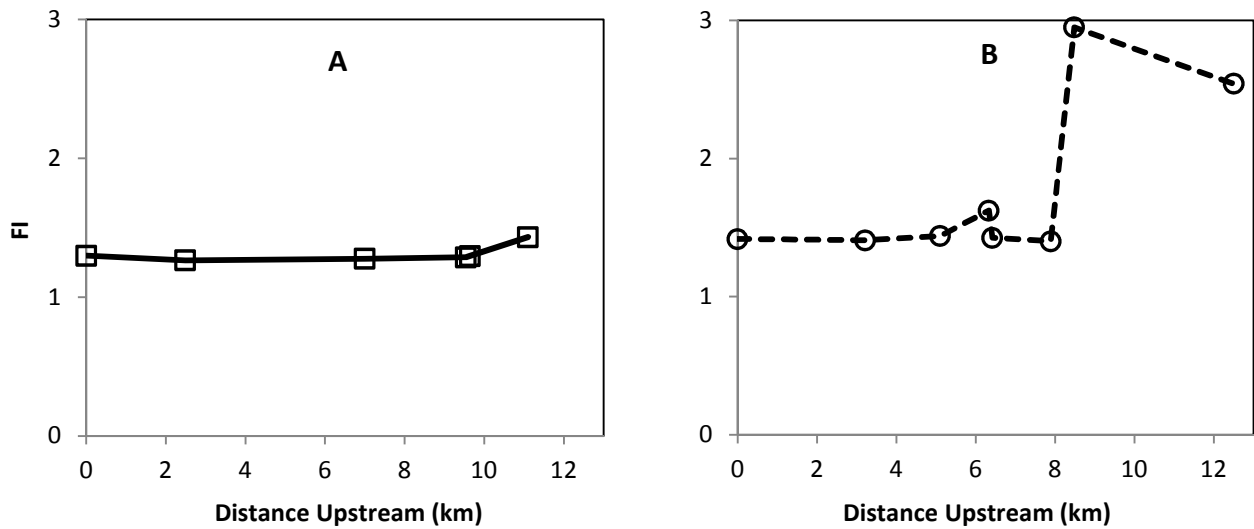


Figure 3.7: Distance upstream vs. fluorescence index (FI) in non-glacial Montana Creek (A) and glacial Lemon Creek (B) in southeast Alaska. Values obtained from longitudinal sampling of each stream from a well-mixed location of the main channel.

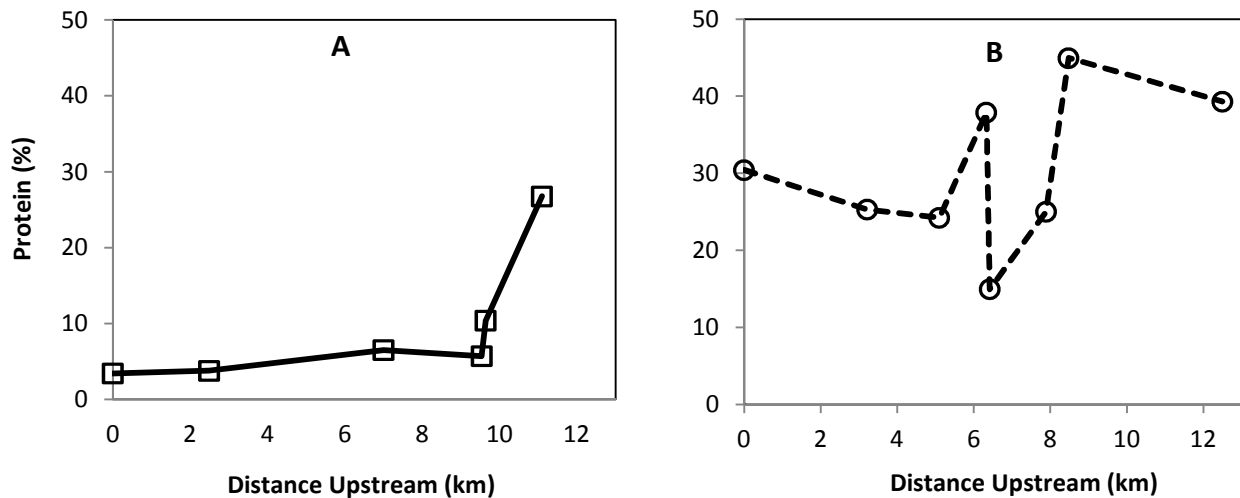


Figure 3.8: Distance upstream vs. fluorescence index (FI) values in streams in non-glacial Montana Creek (A) and glacial Lemon Creek (B) in southeast Alaska. Values obtained from longitudinal sampling of each stream from a well-mixed location of the main channel.

3.6 References

- Arendt, A. A., Echelmeyer, K. A., Harrison, W. D., Lingle, C. S. & Valentine, V. B. 2002. Rapid wastage of Alaska glaciers and their contribution to rising sea level. *Science* 297: 382–386.
- AKRDC. 2013. Alaska Resource Development Council: Alaska's Fishing Industry. Available at: <http://www.akrdc.org>. Accessed 12 April 2013.
- Baker, C. S., J. M. Straley, and A. Perry. 1992. Population characteristics of individually identified humpback whales in southeastern Alaska: Summer and fall 1986. *U.S. Fishery Bulletin* 90: 429-437.
- Barker, J. D., Sharp, M. J., Fitzsimons, S. J. & Turner, R. J. 2006. Abundance and dynamics of dissolved organic carbon in glacier systems. *J. Arc. Ant. Alp. Res.* 38: 163–172.
- Benner, R., and K. Kaiser. 2011. Biological and photochemical transformation of amino acids and lignin phenols in riverine dissolved organic matter. *Biogeochemistry* 102: 209-222.
- Fellman, J., E. Hood, D. D'Amore, and R. Boone . 2008a. Fluorescence characteristics and biodegradability of DOM in forest and wetland soils from coastal temperate watersheds. *Biogeochemistry* doi:10.1007/s10533-008-9203-x
- Fellman, J., E. Hood, R. Edwards, and D. D'Amore. 2008b. Return of salmon-derived nutrients from the riparian zone to the stream during a storm in southeastern Alaska. *Ecosystems* 11: 4.
- Fellman, J. B., E. Hood, R. T. Edwards, and D. V. D'Amore. 2009a. Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. *J. Geophys. Res.* 114 G01021, doi:10.1029/2008JG000790.
- Fellman, J. B., E. Hood, D. V. D'Amore, R. T. Edwards, and D. White. 2009b. Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds. *Biogeochemistry*. 95: 277-293.
- Fellman, J. B., R. G. M. Spence, P. J. Hernes, R. T. Edwards, D. V. D'Amore, and E. Hood. 2010. The impact of glacier runoff on the biodegradability and biochemical composition of terrigenous dissolved organic matter in near-shore marine ecosystems. *Marine Chemistry* 121: 112-122.
- Findlay, S. E. G., and R. L. Sinsabaugh. 2003. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Burlington, Massachusetts: Elsevier Science.

- Hood, E. and D. T. Scott. 2008. Riverine dissolved organic matter and nutrient yields in southeast Alaska affected by glacial coverage. *Nature Geoscience* 1: 583-587.
- Hood, E., J. Fellman, R. G. M. Spencer, P. J. Hernes, R. Edwards, D. D'Amore, and D. Scott. 2009. Glaciers as a source of ancient and labile organic matter to the marine environment. *Nature* 462: 1044-1047.
- Hood, E., and L. Berner. 2009. Effects of changing glacial coverage on the physical and biogeochemical properties of coastal streams in southeastern Alaska, *J. Geophys. Res.* 114, G03001, doi:10.1029/2009JG000971.
- McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Anderson. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanogr.* 46(1): 38-48.
- McTammany, M. E., J. R. Webster, E. F. Benfield, and M. A. Neatrour. 2003. Longitudinal patterns of metabolism in a southern Appalachian river. *J. N. Am. Benthol. Soc.* 22(3):359-370.
- Neal, E. G., E. Hood, and K. Smikrud. 2010. Contribution of glacier runoff to freshwater discharge into the Gulf of Alaska. *Geophysical Research Letters* 37: L06404.
- NLCD. 2011. National land cover database 2011. Available at: <http://www.mrlc.gov/nlcd2001.php>. Accessed 22 February 2011.
- NOAA. 2013. Alaska Climate Database: Juneau Airport. National Weather Service. Available at: <http://pajk.arh.noaa.gov/cliMap/akClimate.php>. Accessed 5 March 2013.
- Rasmussen, J. J., A. Baattrup-Pedersen, T. Riis, and N. Friberg. 2011. Stream ecosystem properties and processes along a temperature gradient. *Aquatic Ecology* 45: 213-242.
- Stedmon, C., S. Markager, and R. Bro. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* 82: 239-254.
- Stubbins, A., E. Hood, P. A. Raymond, G. R. Aiken, R. L. Sleighter, P. J. Hernes, B. Butman, P. G. Hatcher, R. G. Striegl, P. Schuster, H. A. N. Abdulla, A. W. Vermilyea, D. T. Scott, and R. G. M. Spencer. 2012. Anthropogenic aerosols as a source of ancient dissolved organic matter in glaciers. *Nature Geoscience* doi:10.1038.

- Uehlinger, U., C. T. Robinson, M. Hieber, and R. Zah. 2010. The physic-chemical habitat for periphyton in alpine glacial streams under a changing climate. *Hydrobiologia* 657: 107-121.
- USGS. 2013. 1502800 Montana C NR Auke Bay AK. U.S. Geological Survey. Available at: waterdata.usgs.gov/ak/uv/?site_no=15052800&PARmeter_cd=00065,00060. Accessed 5 March 2013.
- Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, and R. Fuji, and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *En. Sci. Tech.* 37: 4702-4708.
- Williams, M. W., E. H. Hood, G. Ostberg, B. Francou, and R. Galarraga. 2001. Synoptic survey of surface water isotopes and nutrient concentrations, Paramo high-elevation region, Antisana ecological Reserve, Ecuador. *Artic, Antarctic, and Alpine Research* 33(4): 397-403.
- Ylla, I., A. M. Romani, and S. Sabater. 2012. Labile and recalcitrant organic matter utilization by river biofilm under increasing water temperature. *Microb. Ecol.* 64: 593-604.
- Young, R. G., and A. D. Huryn. 1996. Interannual variation in discharge controls ecosystem metabolism along a grassland river continuum. *Can. J. Fish. Aquat. Sci.* 53: 2199-2211.

Chapter 4: Precipitation-Driven Landscape Flushing Analysis

4.1. Abstract

Discharge and dissolved organic matter (DOM) from a glaciated and forested catchment in southeast Alaska were monitored during an August storm event in the 2011 melt season. Increases in dissolved organic carbon (DOC) concentrations in the non-glacial stream were positively correlated to increasing discharge, while DOC concentrations in the glacial outflow did not change. Inorganic nutrient concentrations (e.g. ammonium (NH_4^+) and phosphate (PO_4^{3-})) in the non-glacial catchment decreased with increasing discharge, while remaining constant throughout the storm event in the glaciated catchment. Water isotope data collected from both locations and from precipitation indicated the increased discharge in the forested stream was from event water, while the increased discharge from the glacial surface was from glacial meltwater. Decreased specific conductivity levels in the forested catchment during peak flow indicated decreased routing through deeper bedrock and increased flow through shallow organic soil layers. Increasing specific conductivity values in the glacial outflow indicated increased contact with rock surfaces. These findings suggest precipitation-driven increases in discharge from glaciers result in the flushing of subsurface meltwater pools and do not change the dissolved organic matter signature of the outflow. Significantly higher specific discharge from the glaciated surface resulted in higher yield of allochthonous carbon, nitrogen, and phosphorus than from the forested watershed. When normalized to watershed area, the forested watershed yielded more carbon and nitrogen per unit area. Because southeast Alaska receives high amounts of precipitation (1480 mm annually), storm-driven discharge regimes account for an

important part of the melt season flux of freshwater from the landscape to the Gulf of Alaska (GOA). Findings from this study indicate frequent precipitation in southeast Alaska on glaciated land cover results in an increased yield of dissolved organic matter to the GOA from the flushing of previously melted glacier ice and not because of increased DOM concentrations from the flushing of disconnected organic matter pools in the landscape.

4.2. Introduction

Frequent rainfall during the meltseason in southeast Alaska is often associated with coastal storms that release moisture when they encounter high elevation mountain ranges near the coast. This heavy precipitation falls on small, steep coastal watersheds flushing dissolved organic matter (DOM) from the landscape to streams, and eventually to the Gulf of Alaska (GOA). Increased discharge from storms can significantly influence the total flux of freshwater and organic matter from terrestrial landscapes to the ecologically and economically productive GOA ecosystem.

Proglacial streams have been studied during base flow conditions revealing differences in organic matter, nutrients, and other water quality parameters compared to non-glacial systems (Lafreniere and Sharp, 2004; Hood and Berner 2009; Hood et al., 2009b). Specific conductivity of coastal streams is negatively correlated with watershed glacial coverage, while turbidity increases with increasing watershed glacial coverage (Hood and Berner, 2009). Glacial meltwater contributions decrease water temperatures in the summer, while temperatures are consistently near freezing for streams in both glacial and non-glacial watersheds in the winter (Hood and Berner, 2009).

Proglacial streams have higher discharge and lower dissolved organic carbon (DOC) concentrations than streams in non-glacial watersheds during the summer melt seasons (Hood and Scott, 2008; Hood and Berner, 2009). Although glacier meltwater has low DOC concentrations, streams receiving glacial meltwater have a high amount of biodegradable DOC (BDOC) (Fellman et al., 2010), suggesting glacier-derived DOC can be readily used by downstream ecosystems (e.g., coastal waters, GOA). The energy budgets, nutrient availability, and species diversity in downstream aquatic

ecosystems are partially regulated by the bioavailability and composition of organic matter delivered by contributing sources (Findlay et al., 2003). Therefore, the timing, concentration, and composition of freshwater exported from the landscape are critical factors influencing the GOA ecosystem.

In addition to lower DOC levels, dissolved organic nitrogen (DON) concentrations in proglacial streams are lower than non-glacial streams during the summer melt season (Hood and Berner, 2010). This relationship also extends to dissolved inorganic nitrogen (DIN) and the C:N ratio of the DOM pool. This is in contrast to concentrations of soluble reactive phosphorus, that increases with watershed glacier coverage (Hood and Scott, 2008; Hood and Berner, 2009). Increased phosphorus yields have been associated with erosive forces acting on bedrock at the glacier-rock interface, with high concentrations observed at points of discharge at the glacier terminus and then decreasing downstream (Williams et al., 2001).

Precipitation-driven stream discharge in non-glaciated watersheds in southeastern Alaska was evaluated for DOC concentration and composition (Fellman et al., 2009). In both forested and wetland covered watersheds, DOC concentrations increased during storm events (Fellman et al., 2009). This increase is attributed to changes in flow paths and contributing sources of water flowing from the landscape to the stream channel. The bioavailability of DOC in the channel also increased during storm flows because reduced residence time in the landscape reduced opportunity for bioavailable fractions to be mineralized or incorporated into biomass (Fellman et al., 2009). The total export of DOC from non-glacial watersheds during summer storms averages 31% BDOC (Fellman et al., 2009).

Analysis of the export of dissolved organic matter (DOM) from the landscape during storms from other forested watersheds indicate unique sources of DOM in the watershed contribute to the stream DOM pool when these sources become connected to the stream (Inamdar et al., 2004). Precipitation-driven increases in streamwater DOC concentrations can vary across landscapes and throughout the year (Hinton et al., 1997). The increased contribution during a storm can occur because of changes in subsurface flow paths (e.g., deep vs. shallow), or increased surface runoff. The saturation state of different landscape source pools can also influence the contribution of nutrients when flow paths connect these sources to the stream channel (Inamdar et al., 2007). The location within watershed with respect to the stream channel of unique landscape sources can also influence the amount and timing of contributions. Riparian areas contribute more during the rising limb of the hydrographs, while upland areas often have delayed contributions (McGlynn and McDonnell, 2003). Landscape source and flow path variability is a function of landscape components unique to different watersheds, and the antecedent conditions of the watershed before the storm (Hinton et al., 1997).

Previous research has both characterized glacial meltwater and explored non-glacial landscape responses to precipitation-driven flushing of DOM and nutrients. This research aimed to evaluate changes in precipitation-driven DOM and nutrient flushing from a glaciated watershed and an adjacent forested watershed during a storm event. Specifically, this study aimed to determine if precipitation on the glacier surface alters the DOM concentration and composition and the nutrient concentrations in outflow from a glacial watershed in contrast to a representative forested stream. Because of the high

amount of precipitation received by landscapes in southeast Alaska, this research will provide unique information about the response of changing landscapes to frequent precipitation.

4.3. Methodology

4.3.1. Site Description

The co-located watersheds of Mendenhall Glacier and Montana Creek are in southeastern Alaska near Juneau along the coast of the GOA (Figure 4.1). Glaciers cover 18% of the entire 420,230 km² GOA drainage basin (Neal et al., 2010), including 83% of the Mendenhall Glacier watershed (Hood et al., 2009; Hood and Berner, 2009). These study watersheds are representative of the small coastal watersheds responsible for the majority (74%) of the freshwater discharge to the GOA (Wang et al., 2004). Less than a quarter of the freshwater contributions to the GOA originate from large rivers draining interior portions of Alaska and Canada (Neal et al., 2010). These small coastal watersheds are disproportionately responsible for discharge to the GOA due to the high specific discharge associated with glacial landscapes (Figure C.6) during the meltseason, and because of orographic precipitation along the coastal mountains of southeast Alaska.

Average sea level air temperatures in Juneau range from January lows of -6.3°C to July highs of 17.9°C, with an average annual air temperature of 5.5°C. Total annual precipitation averages 1480 mm, with the wettest month (October) averaging 211 mm and the driest month (April) averaging 75 mm (NOAA, 2013). During the melt season, which typically begins in May, coastal streams are first controlled by snowmelt with

glacial meltwater, then controlling discharge in proglacial streams throughout the summer (Motyka et al., 2002). Streams in southeast Alaska generally experience peak discharge in the late summer or fall when large frontal storms from the GOA deliver heavy rainfall across the region (Hood and Berner, 2009).

The 155 km² Mendenhall Glacier watershed drains 128 km² (83%) of ice surface and only 0.5 km² (0.34%) of forested land cover. A USGS gaging station (15052500) for the Mendenhall River is located in Mendenhall Lake and includes discharge contributions from the Mendenhall Glacier watershed via the glacier terminus in the lake, meltwater from the Nugget Creek Glacier via Nugget Creek, and discharge from non-glacial sources including Steep Creek from the south and additional small non-glacial streams from the north. The lower reaches of the Mendenhall River are used as a corridor for spawning Sockeye and Chum salmon traveling to non-glacial Steep Creek. No salmon activity occurred upstream of the sampling location at the Mendenhall Glacier terminus. Average annual specific discharge in the Mendenhall River at the USGS gaging station is 0.98 mm/hr, with a maximum monthly average occurring in August (2.64 mm/hr), and an average monthly low occurring in February (0.07 mm/hr) (Neal and Host, 1999). Data and sample collection occurred at the Mendenhall Glacier terminus at a location elevated from the lake where glacial meltwater emerged from the ice surface to a small pool prior to dropping into Lake Mendenhall. Discharge from the glacier at this location was estimated as accounting for approximately 30% of the discharge from the glacier to the lake. This site was selected because runoff and meltwater coming from the Mendenhall Glacier could be isolated from water of different sources draining into the lake.

The Montana Creek watershed, where the forested end-member data were collected, covers 37 km² of non-glacial land adjacent to the Mendenhall Glacier watershed. This watershed is dominated by forested land cover (47%), with additional land cover comprising vegetated alpine (18%), sub-alpine (14%), and unvegetated rock (13%). The primary tributary, McGinnis Creek, drains an area of high elevation snowfields including Mt. McGinnis. Discharge on Montana Creek is monitored at a USGS gaging station (15052800) and drains into the Mendenhall River below Mendenhall Lake. Montana Creek supports runs of spawning Coho, Chum, and Pink salmon throughout the summer and early fall in both the upper branch of Montana Creek and the McGinnis Creek branch. Average annual specific discharge (Figure 4.2) in Montana Creek at the USGS gaging station is 0.28 mm/hr, with a maximum monthly average (0.49 mm/hr) occurring in September, and an average monthly low (0.11 mm/hr) occurring in February (USGS, 2012). Data and sample collection on Montana Creek occurred in a well-mixed portion of the stream channel at the USGS gaging station.

4.3.2. Field Methods

A proglacial lake, at the terminus of the study glacier, prevented direct measurement of glacier. Discharge was estimated using the USGS stream gages on the Mendenhall River, Montana Creek, and nearby Salmon Creek as well as historical data from Nugget Creek. Stage data from the USGS gages and stage measurements from a pressure transducer in the elevated outflow pool above the lake surface. Stage in the outflow pool was monitored to provide an estimate of lag time of peak discharge from the glacial surface to peak discharge at the USGS Mendenhall River gage.

To estimate outflow from the glacier, specific discharge at each USGS gaging station was calculated using 15-min data over the sampling period. A calculation relating discharge per unit area of Salmon Creek to Nugget Creek from historical data during the summer months of June, July, and August was used to estimate the contribution to Mendenhall Lake from the Nugget Creek watershed (4.1) (Vermilyea et al., In Press). This relationship had a coefficient of determination (R^2) of 0.70, and was used to estimate an average of 14% of the total discharge. Discharge per unit area from the adjacent, non-glacial Montana Creek watershed was used as a proxy for the non-glacial contributions of the Mendenhall Lake watershed not included in the Mendenhall Glacier or Nugget Creek watersheds (4.2). The glacier contribution was then estimated as the Mendenhall River discharge minus Nugget Creek and the remaining non-glacial land cover (4.3). This calculation estimated average glacial discharge into Mendenhall Lake as 85.9% of the discharge recorded at the Mendenhall River gaging station over the sampling period. Finally, a lag time of 9 hrs based on peak discharge at the USGS gaging station and a pressure transducer at the glacier terminus accounted for discharge differences between the glacier terminus and the USGS gaging station on the Mendenhall River.

$$Q_{nugget} = Q_{salmon} \times a + b \quad (4.1)$$

where: Q_{Nugget} = Nugget Creek discharge (ft^3/sec)

Q_{Salmon} = Salmon Creek discharge (ft^3/sec)

$a = 6.5335$

$b = 90.648$

$$Q_{NonGlacial} = \frac{Q_{Montana\ Creek}}{Area_{Montana\ Creek\ Watershed}} \times Area_{NonGlacial} \quad (4.2)$$

$$Q_{Glacier} = Q_{Mendenhall\ River} - Q_{Nugget\ Creek} - Q_{NonGlacial} \quad (4.3)$$

Samples were collected for analysis of dissolved organic carbon (DOC), total dissolved nitrogen (TDN), inorganic nitrogen – ammonium (NH_4^+), phosphate (PO_4^{3-}), water isotopes (deuterium), and carbon composition. Samples were collected using a peristaltic Geopump fitted with silicon tubing and an in-line capsule 0.20 μm glass fiber filter. DOC, TDN, and sample fluorescence were collected in 40 mL pre-combusted amber glass bottles, stored in the dark at 4°C, and analyzed within 3 days. Nutrient samples (NH_4^+ , PO_4^{3-}) were collected in 25 mL HDPE scintillation vials, frozen and analyzed within 2 months. Isotope samples were collected in 30 mL glass vials with conical polyseal lids with no headspace and analyzed within 2 months. Specific conductivity was recorded with a YSI multiparameter sonde at 5-minute increments for the duration of the study.

Background samples were collected prior to the start of the precipitation event to establish baseline conditions in both the forested stream and the glacier outflow. Sample frequency increased during the peak rainfall and discharge regimes, and decreased after discharge at each site decreased. Sample collection occurred every 2 to 4 hrs during the peak storm discharge and decreased in frequency to daily sampling for 3 d following the storm event when discharge levels at both the Mendenhall River

and Montana Creek gaging stations returned to pre-event levels. Rainwater was collected at the UAS campus (29 m above sea level), near both Montana Creek (2.1 km) and Mendenhall Glacier (7 km). Rainwater samples were analyzed for deuterium, DOC, and TDN.

4.3.3. Laboratory Sample Analysis

Samples for DOC and TDN were analyzed on a Shimadzu TOC-V carbon analyzer (Shimadzu Corporation, Kyoto, Japan). Twenty-six triplicate samples of DOC and TDN had standard deviation values of 2.1 and 0.5 $\mu\text{mol/L}$, respectively. NH_4^- and PO_4^{3-} samples were analyzed on a SEAL segmented-flow nutrient analyzer (Seal Analytical, Mequon, Wisconsin, USA). Four duplicate samples of NH_4^+ and PO_4^{3-} had instrument precision values of 0.14 and 0.02 $\mu\text{mol/L}$, respectively. Isotope samples were analyzed on a Picarro Isotopic Water Analyzer (Picarro, Inc., Santa Clara, California, USA). Replicates of calibration standards resulted in an average instrument precision value for δD of 0.73 ‰.

4.3.4. Flux Calculations

Area-weighted flux estimates of DOC, TDN, NH_4^+ , and PO_4^{3-} during the storm event were calculated using continuous discharge data and analysis of grab samples during the monitoring period. Linear interpolation of concentration-discharge values between each sample point for each analyte was used to estimate analyte concentrations between grab samples at each 15-min discharge value. Point-by-point concentration-discharge relationships were developed because the hysteresis observed during the storm event between many of the target analytes and stream discharge would have resulted in a flux estimate that did not accurately represent the physical

system. Area-weighted flux of DOC, TDN, NH_4^+ , and PO_4^{3-} was estimated by dividing the total mass exported during the storm by the watershed area. Area-weighted specific flux was then estimated by dividing the area-weighted flux by the specific discharge for the storm period.

4.4. Results

Approximately 19 mm of rainfall resulted in discharge in the non-glacial stream to increase by 176% and discharge from the glaciated landscape to increase by 34% during the monitored period from August 3rd to August 7th 2011 (Figure 4.2). This rain event was selected because it provided the opportunity to isolate a discrete precipitation event that started when stream discharge reflected baseflow conditions, lasted less than 24 hr, and allowed discharge to return to baseflow prior to another precipitation event. This rain event produced 12% of the average August rainfall for Juneau, but only 7% of the 2011 August rainfall total (NOAA, 2013). Discharge from the glacier surface started to increase immediately after the beginning of the precipitation and returned to pre-storm discharge levels 63 hr after the discharge began to increase. Discharge in the non-glacial stream did not respond to precipitation until 8 hr after the storm started and returned to pre-storm discharge levels after 61 hr. Discharge at both sites continued to decline beyond pre-event levels until the next rain event 5 d after the monitored period of this study.

Estimates of glacier discharge indicated contributions from the glacier averaged 86% of the total discharge for the Mendenhall River during the storm event, with maximum contributions (89%) occurring before and after the storm and minimum

contributions (75%) occurring when stream discharge peaked on the rising limb of the glacier hydrograph. Specific discharge from the glaciated surface averaged 1.50 mm/hr (max: 1.87 mm/hr, min: 1.14 mm/hr), while specific discharge from the forested watershed averaged 0.21 mm/hr (max: 0.47 mm/hr, min: 0.13 mm/hr).

Concentrations of DOC in the forested non-glacial stream averaged 123 $\mu\text{mol/L}$ and nearly tripled from background levels (72 $\mu\text{mol/L}$) to peak discharge (221 $\mu\text{mol/L}$) during the storm (Figure 4.3). DOC levels returned to near background levels following the storm, with both increases and decreases lagging behind changes in discharge. Concentrations of DOC in the glacier outflow averaged 14.7 $\mu\text{mol/L}$ and decreased from a pre-storm concentration of 18.7 $\mu\text{mol/L}$ to a minimum of 13.0 $\mu\text{mol/L}$. The magnitude of the observed decrease was within the concentration range associated with instrument reporting error.

Concentrations of nutrients in the non-glacial stream decreased with increasing discharge. TDN levels in the non-glacial stream averaged 11.9 $\mu\text{mol/L}$ and also decreased from background concentrations by approximately 25% (max: 14.5 $\mu\text{mol/L}$, min: 9.7 $\mu\text{mol/L}$) (Figure 4.4 A, NH_4^+ averaged 4.3 $\mu\text{mol/L}$ (max: 6.0 $\mu\text{mol/L}$, min: 2.7 $\mu\text{mol/L}$) (Figure 4.4 C), and PO_4^{3-} averaged 0.17 $\mu\text{mol/L}$ (max: 0.22 $\mu\text{mol/L}$, min: 0.14 $\mu\text{mol/L}$) in the non-glacial stream (Figure 4.4 E).

Nutrients in the glacial outflow remained at near constant concentrations with changing discharge. TDN concentrations in the glacier outflow averaged 0.8 $\mu\text{mol/L}$ and decreased beyond the range associated with laboratory precision (max: 1.1 $\mu\text{mol/L}$, min: 0.4 $\mu\text{mol/L}$) (Figure 4.4 B). Because background levels were very low (~ 1.1 $\mu\text{mol/L}$), this change was negligible. Concentrations of NH_4^+ averaged 0.7 $\mu\text{mol/L}$ in the

glacier outflow and remained unchanged beyond differences associated with laboratory precision (all values collected were below 1 $\mu\text{mol/L}$) (Figure 4.4 D). PO_4^{3-} levels in the glacier outflow averaged 0.06 $\mu\text{mol/L}$, and showed a small decrease during peak discharge (max: 0.08 $\mu\text{mol/L}$, min: 0.04 $\mu\text{mol/L}$), but this decrease was within the range of laboratory precision (Figure 4.4 F).

The calculated average fluorescence index (FI) for the non-glacial stream was 1.3, with a maximum of 1.5 and a minimum of 1.2. FI values for the glacial outflow averaged 1.9 with a maximum of 2.3 and a minimum of 1.6 (Figure 4.5). An outlier value of 4.4 was calculated for a sample collected on the rising limb of the hydrograph, but was not considered a valid measure of the fluorescence index, and was beyond the range of values associated with this system.

Specific conductivity in the non-glacial stream decreased with increasing stream discharge, showing a strong inverse relationship (Figure 4.6). A minimum value in the non-glacial stream during the monitoring period was 40 $\mu\text{S/cm}$, with values above 50 $\mu\text{S/cm}$ both before and after the storm hydrograph. Specific conductivity in the glacial outflow doubled over the monitoring period, increasing from a minimum value of 7 $\mu\text{S/cm}$ to 14 $\mu\text{S/cm}$ after the storm.

Deuterium analyzed during this study showed values changing at both sites during the storm event (Figure 4.7). The isotopic signature of δD in the precipitation during this storm event ranged from -93 to -85 ‰. The δD in the non-glacial stream water averaged -104 ‰ (δD) over the storm with no significant variation with changes in discharge. In the glacier outflow, discharge became more depleted with increasing discharge during the rain event. The values in the glacier outflow water averaged -114

‰ (δD) during the storm event and did not return to pre-event levels by the end of the monitoring period.

Area-weighted flux (kg km^{-2}) and area-weighted flux per specific discharge ($\text{kg km}^{-2} \text{mm}^{-1}$) of carbon and nutrients were calculated for both sites during the storm event (Table 4.1). Higher specific discharge was estimated from glacier surface (137 mm) than from the forested watershed (20 mm). The forested watershed had a higher yield of DOC (34 kg km^{-2}) than the glacial surface (22 kg km^{-2}). The total dissolved nitrogen yield from the forested watershed (3.4 kg km^{-2}) was over 2 times that of the glacier surface (1.5 kg km^{-2}). Similar values of NH_4^+ were recorded for the forested watershed (1.2 kg km^{-2}) and the glacial surface (1.3 kg km^{-2}), while PO_4^{3-} levels were 2 times as high in the glacier outflow (0.24 kg km^{-2}) than the forested stream (0.12 kg km^{-2}).

Discharge values and sample times for both study streams are presented in Appendix C. Additional data including stream physical and chemical characteristics and estimated continuous analyte concentrations are also presented in Appendix C.

4.5. Discussion

The findings in this study suggest rainfall on glaciated surfaces mixes with large subsurface pools of meltwater, unlike rainfall on forested watersheds, which flush shallow organic soil layers as the water table rises. This difference in flow path and contact with the unique glacial landscape elements accounts for the different responses to precipitation observed in the two study watersheds.

Because the hydrograph for the non-glacial stream increased and decreased more rapidly than the glacier outflow hydrograph (Figure 4.2), the rain contributions to

the glacial watershed were likely attenuated in sub-surface glacier meltwater pools. The delayed response in the non-glacial hydrograph to precipitation was likely a result of unsaturated soil layers and wetlands becoming saturated during the early portion of the storm, and then contributing to stream flow after the storage capacity of the landscape was reached. Rain near the terminus likely resulted in outflow from the glacier almost immediately because the glacier is already fully primed with no capacity for storage. This lack of landscape storage capacity is also expressed through a higher increase of specific discharge across the glacial surface (0.73 mm/hr) than in the forested watershed (34 mm/hr).

The discharge estimates for Mendenhall Glacier were an approximation of both the volume and timing of meltwater and precipitation coming from the glacier surface. Because the non-glacial components of the discharge estimates were calculated from an adjacent watershed of similar elevation and landcover, and because the estimated watershed contributions not coming from Mendenhall Glacier (Nugget Creek and Mt. McGinnis) only contributed a combined average of 14% of the discharge to the Mendenhall River gage, these estimates are a reasonable approximation of the system and were consistent with field observations of changing discharge at the glacier terminus. The ability of non-glacial landscapes to attenuate more precipitation than glaciated surfaces suggests decreased glacial landscape coverage in coastal Alaska could decrease freshwater input to the GOA not only because of decreased meltwater contributions, but also because of decreased storm runoff.

Increases in DOC associated with higher discharge in the non-glacial stream are likely a function of increased stream flow from landscape runoff through shallow organic

soils as the watershed becomes saturated during the storm event. This activation results in flushing of DOC from organic soils in the landscape with high concentrations observed during the ascending limb of the storm (Figure C.1). This hysteresis of DOC and discharge has been observed in forested streams in southeast Alaska and other regions (Hood et al., 2006). Samples from this study show similar trends as previous studies that concluded higher concentrations of DOC and nutrients are found in forested streams compared to glacial streams (Hood and Berner, 2009; Hood et al., 2009b; Fellman et al., 2010). The consistency of DOC concentrations between this study and others suggest watersheds sampled during the storm event were representative of common melt season watersheds where forested end-members have lower percent BDOC (Hood et al., 2009a), higher amounts of lignin (associated with vascular plants), and lower protein content (associated with microbial material) than glaciated end-members.

The decreases in nutrient concentrations in the non-glacial stream on the ascending limb of the hydrograph are likely a function of a dilution of nutrient contributions when event water enters the landscape (Figure 4.4), or the loss of salmon-derived nutrients (SDN) during the early portions of the ascending limb of the hydrograph (Fellman et al., 2008). The glacial outflow in this study, like many glacial rivers, did not have riparian wetlands, organic soil layers, or a run of spawning salmon. The physical restrictions on organic matter pools available for export during storm events in glaciated watersheds can contribute less variation in concentration and yield of DOM during late summer storms. The difference in DOM pools between glaciated and forested watersheds is larger during this time of year because precipitation in

southeast Alaska is high, and many species of salmon are entering coastal streams to spawn. Flushing of salmon from the near-stream zone back into the channel during a storm has been shown to contribute to nutrient and DOM concentrations in streamwater in a nearby forested stream during a late summer storm (Fellman et al., 2008).

The isotopic signature of the runoff from the glacial surface suggests the source of the increased discharge was from a more depleted pool of water that fell as rain or snow at a higher elevation and at colder temperatures than the rainfall collected at sea level during the monitored storm event. Previous research in the study watersheds and in other glacial systems has consistently shown increasing isotopic depletion with increasing glacial meltwater contributions (Hood and Berner, 2009; Bhatia et al., 2011). A comparison of the isotopic signature in the forested and glacial discharge reveals opposite trends during the period of increased discharge (Figure 4.7). As discharge increased, the isotopic signature of the forested stream became less depleted and moved closer to the signature found in the event precipitation. Conversely, the isotopic signature in glacial outflow became more depleted and trended away from the precipitation signature.

The increase in isotopically depleted discharge from the glacier suggest water coming from the glacier terminus during the storm event contained more contributions from pre-event water, which likely fell as rain or snow further up the glacier or in the Juneau Icefield, and was not new water associated with the monitored storm. As summer melting occurs at locations higher than the glacier terminus, meltwater flows on the surface of the glacier in supra-glacial streams and enters into subsurface pools in ice. Because residence time in the sub-glacial system can impact the isotopic signature

and chemistry of glacial outflow (Hindshaw et al., 2011), it is expected meltwater slowly flowing through the glacier has a different composition from meltwater forced through due to increased water contributions on the glacial surface. The isotopic data, coupled with the results of continuous specific conductivity monitoring and DOC concentrations, suggest a sub-glacial source of meltwater is the primary contributor to increased discharge at the glacier outflow. The extended recession limb of the storm hydrograph on the glacier surface showed discharge becoming more isotopically depleted with decreasing DOC values and increasing specific conductivity. This combination of trends suggest increased contact with the rock-ice interface and decreased contributions from the glacier surface where it is hypothesized anthropogenic DOM is deposited (Stubbins et al., 2012).

The fluorescence index (FI) for the forested watershed was inversely proportional to discharge and DOC (Figure 4.3 A; Figure 4.5) during the storm event. This inverse relationship to DOC and concentrations lower than that of a nearby glacial source has been observed in study sites in other regions (Lafreniere and Sharp, 2004). The lack of a correlation between FI values and discharge in glacial outflow is consistent with the steady DOC and nutrient concentrations observed across the storm hydrograph from the glacier surface. The high FI values throughout the storm in the glacial outflow suggest the contribution of discharge from the glacial surface does not travel through new flow paths that interact with organic soil layers containing DOM pools with high aromaticity during storm flows. This is in contrast to the tightly coupled relationship seen in the forested stream, where more flow contributions from shallower organic soils result

in decreasing FI values indicating increased contributions from DOM pools with higher aromatic content.

Total DOM flux from the glaciated surface was greater than from the forested watershed because specific discharge in the glacial watershed was more than 6 times greater than from the forested watershed. When normalized to watershed area, however, the forested watershed yielded more DOC (34 kg km^{-2}) and TDN (3.4 kg km^{-2}) than the glacier (22 kg km^{-2} , 1.5 kg km^{-2}) (Table 4.1). This further suggests new, DOM-rich flow paths activated in a forested catchment are not present in any significant amount on a glaciated surface. The glacial surface had a higher area-weighted flux of PO_4^{3-} (0.24 kg km^{-2}) than the forested stream (0.12 kg km^{-2}). This also supports the notion that DOM export from glaciated watershed is not linked to storm driven discharge in the same way as export from non-glacial watersheds. PO_4^{3-} from the glacier likely comes from unweathered rock at the ice-rock interface and therefore has higher concentrations in glacial streams than forested streams during baseflow conditions.

The data collected during this meltseason storm event suggests glacial land cover does not export significantly different concentrations of DOM and nutrients during increased discharge driven by precipitation. Changes in PO_4^{3-} , NH_4^+ , and TDN in the glacier outflow were all within the limits of instrument precision. A small decrease in DOC during the storm event, coupled with increasing isotopic depletion further suggest runoff from glacial surfaces is not accessing unique, carbon-rich landscape pools during rain events in the same way as runoff in non-glacial watersheds. High FI values not correlated to discharge from the glacier also indicates the source of glacial runoff during meltseason storms is dominated by glacier meltwater, and not precipitation.

These findings are significant because approximately 75% of freshwater inputs to the GOA come from small coastal watersheds (Wang et al., 2004; Neal et al., 2010). During the summer melt season, storm flows account for a significant portion of the flow regimes in these watersheds. The carbon and nutrients transported from the landscape to the coastal zone, and the resulting mixing of fresh and saltwater regulates many ecosystem functions, including primary production, and influences the health of fish stocks (Gargett, 1997). Glacial contributions are of significant importance because the DOM exported from these landscapes characterized by high FI values indicative of high BDOC content. These inputs then impact a larger region as the Alaska Coastal Current transports most of the glacier meltwater and freshwater discharge along the Alaskan coast to the Bering Sea and Arctic Ocean (Weingartner et al., 2005). These findings will be beneficial to researchers modeling the impact of receding glaciers and changing meltwater inputs to the biogeochemistry of the coastal GOA and beyond.

Table 4.1: Area-weighted flux and area-weighted flux per specific discharge for a glacier and forested watershed during a meltseason storm event in southeast Alaska. Area weighted flux was calculated as total analyte export per watershed area over the duration of the monitored storm event. Area-weighted flux per specific discharge is area-weighted flux normalized to specific discharge over the monitored storm event.

	Area-Weighted Flux (kg km ⁻²)	
	Forest	Glacier
Volume (L)	7 x 10 ⁸	2 x 10 ¹⁰
DOC	34	22
TDN	3.4	1.5
NH ₄ ⁺	1.2	1.3
NO ₃ ⁻	1.3	n.a.
PO ₄ ³⁻	0.12	0.24

	Area-Weighted Flux per Specific Discharge (kg km ⁻² mm ⁻¹)	
	Forest	Glacier
Runoff Depth (mm)	20	137
DOC	1.6	0.16
TDN	0.17	0.011
NH ₄ ⁺	0.06	0.01
NO ₃ ⁻	0.063	n.a.
PO ₄ ³⁻	0.0057	0.0017

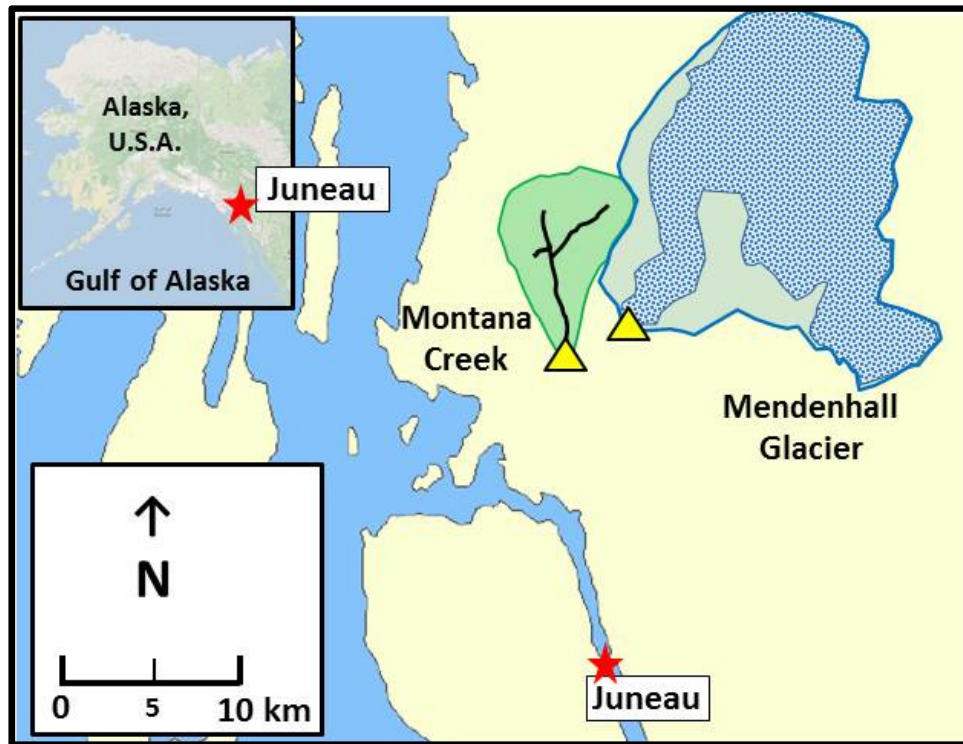


Figure 4.1: Watershed map showing contributing areas to sampling locations in the non-glacial Montana Creek and Mendenhall Glacier watersheds in coastal southeast Alaska. Location of sample and data collection at each stream denoted with triangle.

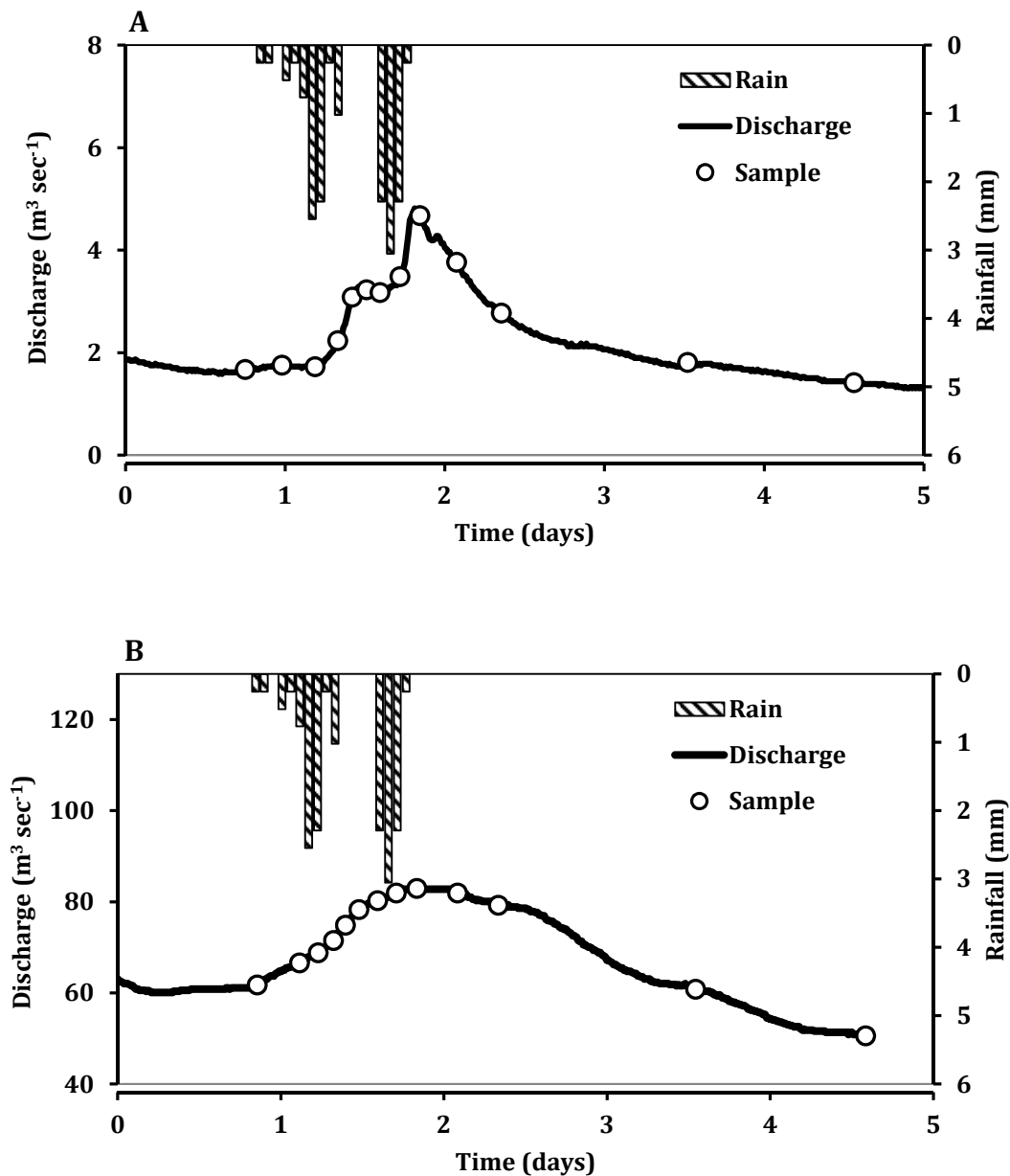


Figure 4.2: Discharge values from the USGS Montana Creek gaging station (15052800) (A) and modeled discharge from the Mendenhall Glacier (B) during a melt season storm event near Juneau, Alaska. Sampling points at each location are highlighted on the discharge record, and hourly precipitation totaling 19 mm is presented on the top of each graph.

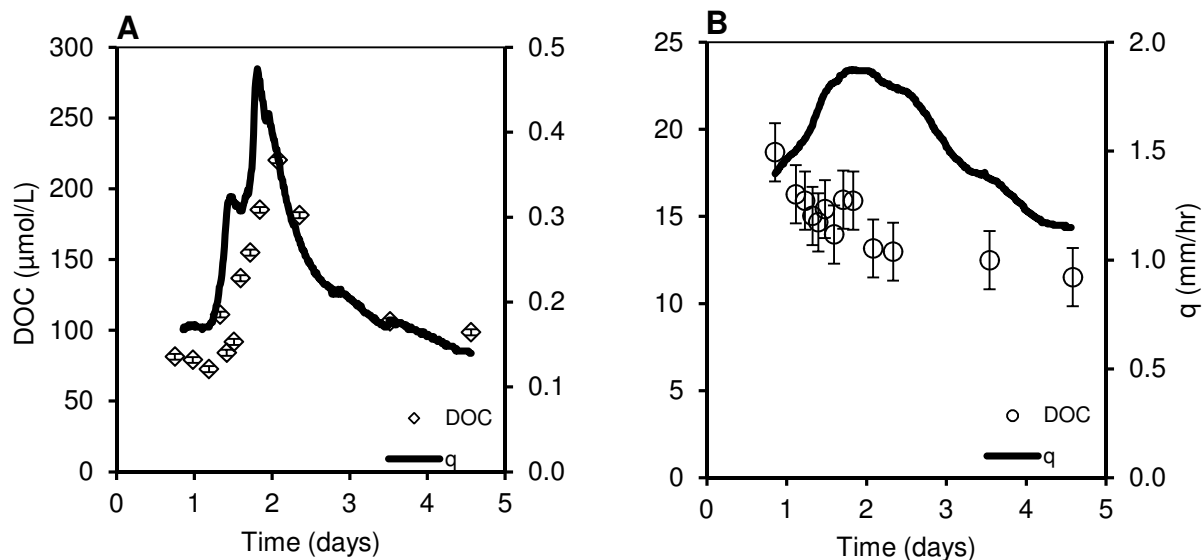


Figure 4.3: Measured dissolved organic carbon (DOC) concentrations with specific discharge recorded at the USGS Montana Creek (non-glacial) gaging station (15052800) (A) and estimated specific discharge from the Mendenhall Glacier (B) during a melt season storm event. Error bars indicate ± 1 S.E., $N = 3$.

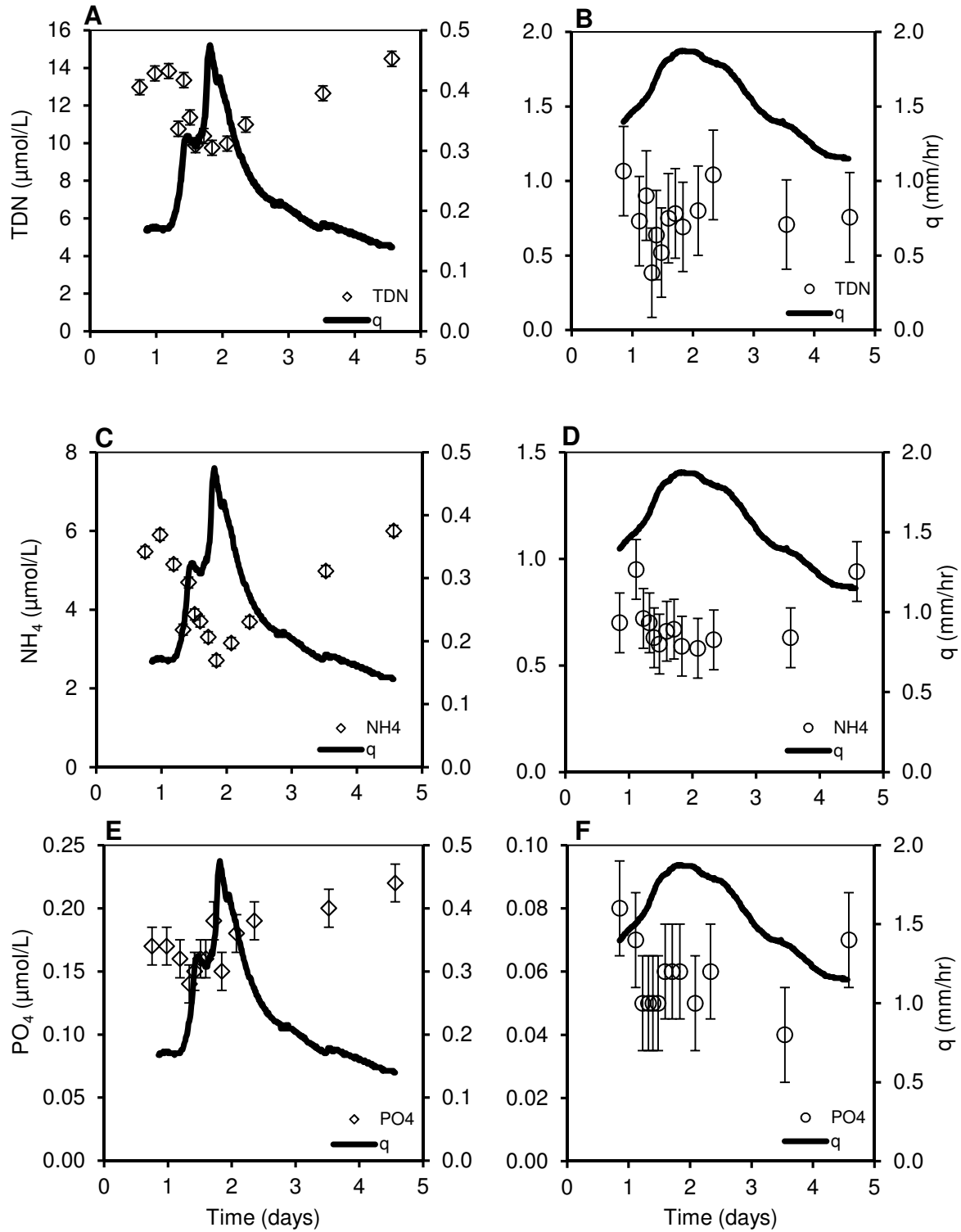


Figure 4.4: Measured total dissolved nitrogen (TDN) (A and B), ammonium (NH_4^+) (C and D), and phosphate (PO_4^{3-}) concentrations (E and F) with specific discharge recorded at the USGS Montana Creek (non-glacial) gaging station (15052800) (A, C, and E) and estimated specific discharge from the Mendenhall Glacier (B, D, and F) during a melt season storm event. TDN error bars indicate ± 1 S.E., $N = 3$; NH_4^+ and PO_4^{3-} error bars indicate instrument precision.

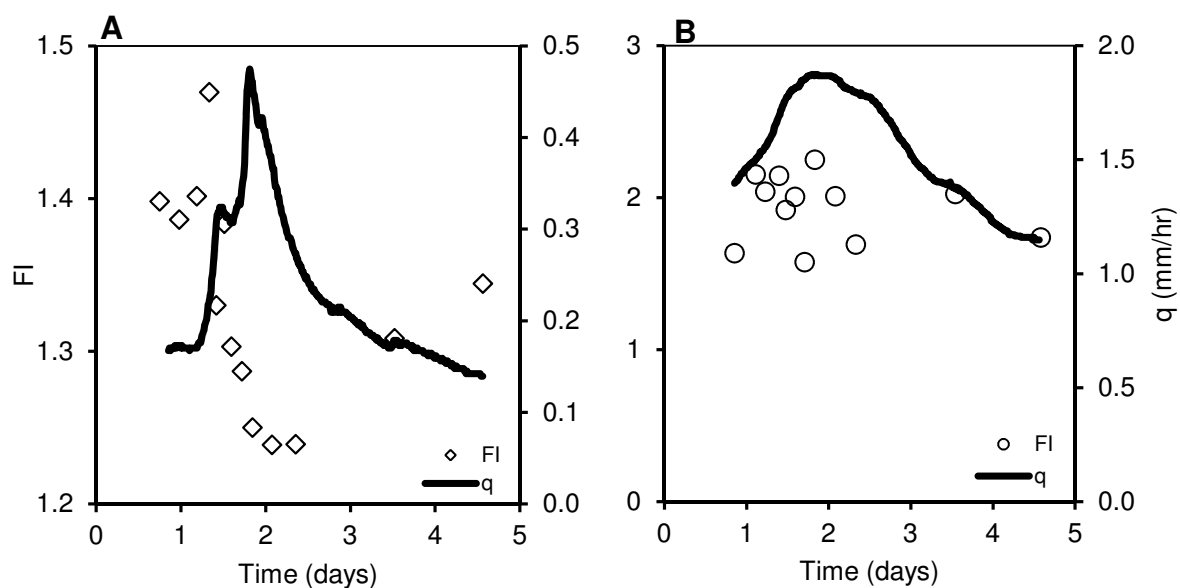


Figure 4.5: Calculated fluorescence index (FI) values with specific discharge recorded at the USGS Montana Creek gaging station (15052800) (A) and estimated discharge from the Mendenhall Glacier (B) during a melt season storm event. FI calculated as the ratio of emission intensity from 450 to 500 nm at an excitation of 370 nm.

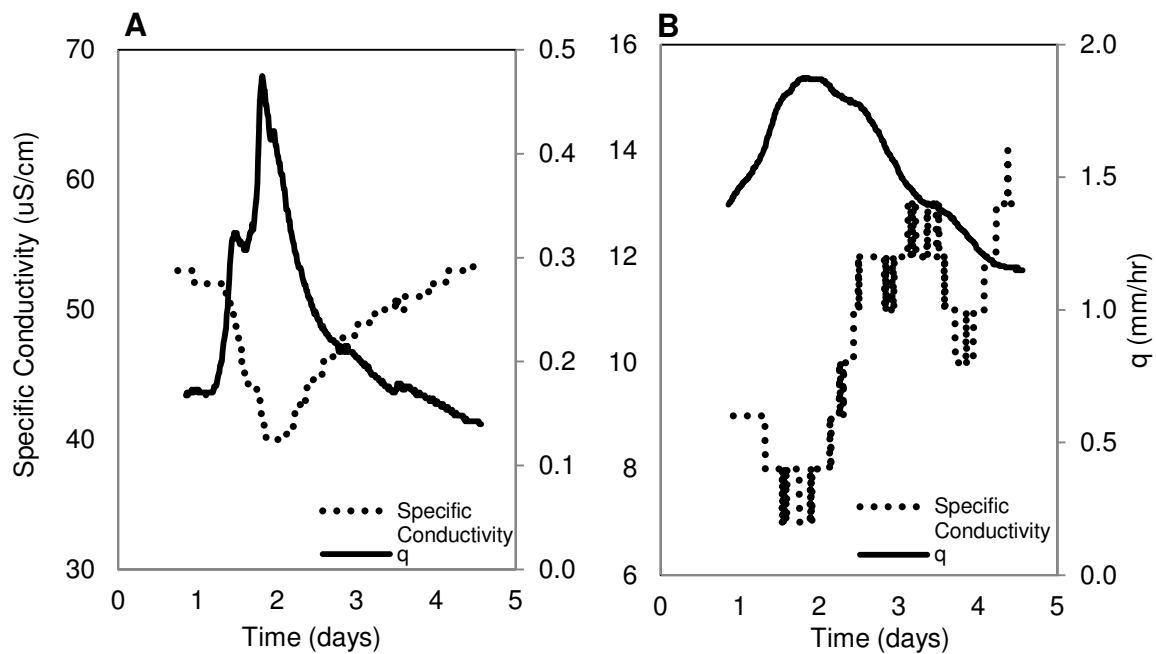


Figure 4.6: Specific conductivity values measured at 5 minute increments with a YSI multiparameter sonde and specific discharge recorded at the USGS Montana Creek gaging station (15052800) (A) and estimated discharge from the Mendenhall Glacier (B) during a melt season storm event.

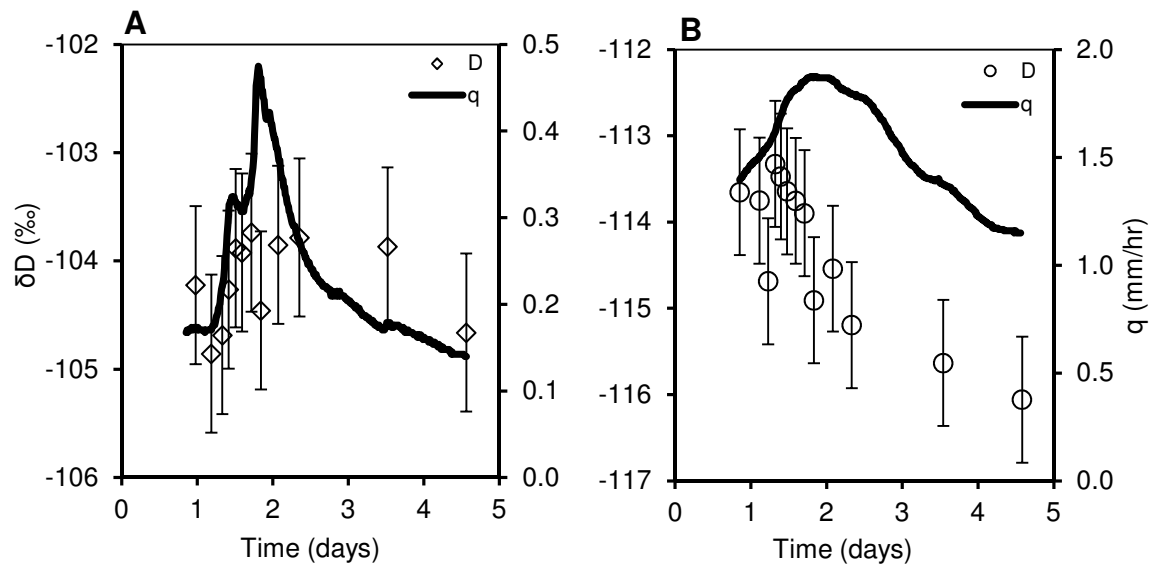


Figure 4.7: Stable hydrogen isotope (δD) values with specific discharge recorded at the USGS Montana Creek gaging station (15052800) (A) and estimated discharge from the Mendenhall Glacier (B) during a melt season storm event. Error bars indicate instrument precision.

4.6 References

- Bhatia, M. P., S. B. Das, E. B. Kujawinski, P. Henderson, A. Burke, and M. A. Charette. 2011. Seasonal evolution of water contributions to discharge from a Greenland outlet glacier; insight from a new isotope-mixing model. *Journal of Glaciology*
- Fellman, J., Hood, E., Edwards, R. and D. D'Amore. 2008a. Return of salmon-derived nutrients from the riparian zone to the stream during a storm in southeastern Alaska. *Ecosystems* doi: 10.1007/s10021-008-9139-y.
- Fellman, J, E. Hood, D. D'Amore, and R. Boone. 2008b. Fluorescence characteristics and biodegradability of DOM in forest and wetland soils from coastal temperate watersheds. *Biogeochemistry* doi: 10.1007/s10533-008-9203-x.
- Fellman, J. B., E. Hood, R. T. Edwards, and D. V. D'Amore. 2009. Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. *J. Geophys. Res.* 114, G01021, doi:10.1029/2008JG000790.
- Fellman, J. B., R. G. M. Spence, P. J. Hernes, R. T. Edwards, D. V. D'Amore, and E. Hood. 2010. The impact of glacier runoff on the biodegradability and biochemical composition of terrigenous dissolved organic matter in near-shore marine ecosystems. *Marine Chemistry* 121: 112-122.
- Findlay, S. E. G., and R. L. Sinsabaugh. 2003. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Burlington, Massachusetts: Elsevier Science.
- Gargett, A. E. 1997. The optimal stability "window": A mechanism underlying decadal fluctuations in North Pacific salmon stocks? *Fish. Oceanogr.* 6(2): 109-117.
- Hartmann, B., and G. Wendler. 2005. The significance of the 1976 Pacific climate shift in the climatology of Alaska. *Journal of Climate* 18: 4824.
- Hindshaw, R. S., E. T. Tipper, B. C. Reynolds, E. Lemarchand, J. G. Wiederhold, J. Magnusson, S. M. Bernasconi, and B. Bourdon. 2011. Hydrological control of stream water chemistry in a glacial catchment (Damma Glacier, Switzerland). *Chemical Geology* 285: 215-230.
- Hinton, M. J., S. L. Schiff, and M. C. English. 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. *Biogeochemistry* 36: 67-88.
- Hood, E., Gooseff, M. and S. Johnson. 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds. *J. Geophys. Res.* 111: G01007.

- Hood, E. and D. T. Scott. 2008. Riverine dissolved organic matter and nutrient yields in southeast Alaska affected by glacial coverage. *Nature Geoscience* 1: 583-587.
- Hood, E., and L. Berner. 2009. Effects of changing glacial coverage on the physical and biogeochemical properties of coastal streams in southeastern Alaska, *J. Geophys. Res.* 114, G03001, doi:10.1029/2009JG000971.
- Hood, E., J. Fellman, R. G. M. Spencer, P. J. Hernes, R. Edwards, D. D'Amore, and D. Scott. 2009. Glaciers as a source of ancient and labile organic matter to the marine environment. *Nature* 462: 1044-1047.
- Hunt, A. P., J. D. Parry, and J. Hamilton-Taylor. 2000. Further evidence of elemental composition as an indicator of bioavailability of substances to bacteria. *Limnol. Oceanogr.* 45(1): 237-241.
- Lafreniere, M. and M. J. Sharp. 2004. The concentration and spectrofluorometric properties of DOC from glacial and non-glacial catchments. *J. Arc. Ant. Alp. Res.* 36: 156–165.
- McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Anderson. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanogr.* 46(1): 38-48.
- Motyka, R. J., S. O'Neel, C. L. Conner, and K. A. Echelmeyer. 2002. Twentieth century thinning of Mendenhall Glacier, Alaska, and its relationship to climate, lake calving, and glacier run-off. *Global and Planetary Change* 35: 93-112.
- Neal, E. G., and R. H. Host. 1999. Hydrology, geomorphology and flood profiles of the Mendenhall River, Juneau, Alaska. *USGS WRI Report*: 99-4150.
- Neal, E. G., E. Hood, and K Smikrud. 2010. Contribution of glacier runoff to freshwater discharge into the Gulf of Alaska. *Geophysical Research Letters* 37: L06404.
- NOAA. 2013. Alaska Climate Database: Juneau Airport. National Weather Service. Available at: <http://pajk.arh.noaa.gov/cliMap/akClimate.php>. Accessed 5 March 2013.
- Stedmon, C., S. Markager, and R. Bro. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* 82: 239-254.
- Vermilyea et al., In press.

- Wang, J., M. Jin, D. L. Musgrave, and M. Ikeda. 2004. A hydrological digital elevation model for freshwater discharge into the Gulf of Alaska. *J. Geophys. Res.*, 109: doi:10.1029/2002JC001430.
- Weingartner, T. J., S. Danielson, and T. C. Royer. 2005. Freshwater variability and predictability in the Alaska Coastal Current, *Deep Sea Res., Part II* 52: 169–191.
- Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, and R. Fuji, and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *En. Sci. Tech.* 37: 4702-4708.
- Williams, M. W., E. H. Hood, G. Ostberg, B. Francou, and R. Galarraga. 2001. Synoptic survey of surface water isotopes and nutrient concentrations, Paramo high-elevation region, Antisana ecological Reserve, Ecuador. *Artic, Antarctic, and Alpine Research* 33(4): 397-403.

Chapter 5: Conclusions and Future Research

5.1. Conclusions

The objective of this research was to characterize the effect of glacial landcover and meltwater contributions on the in-stream processing of DOM and nutrients during downstream transport through watersheds undergoing glacial recession. Streams representing end-members across the glacial landcover gradient were compared to: 1) evaluate the impact of glacial landcover and meltwater contributions on the in-stream metabolism potential of proglacial streams; 2) characterize the impact of glacier landcover and meltwater contributions on longitudinal trends in the physical and chemical signature of streamwater through changing watershed landscapes; and 3) quantify changes in DOM composition and concentration in glacial runoff and total event flux of DOM and nutrients during precipitation-driven flushing of a glaciated landscape.

In-Stream Metabolism and Uptake Estimates

In-stream metabolism estimates suggest periods of abundant sunlight in open-canopied glacial streams result in net autotrophic systems when environmental conditions in the stream channel can support primary producers. This is in contrast to the heterotrophic conditions observed during cloudy days at the glacial site and consistently at the closed-canopied non-glacial stream. Calculations of $epCO_2$ and CO_2 flux indicated lower CO_2 concentrations in the glacial stream than in the non-glacial stream. This difference in streamwater dissolved CO_2 saturation is likely driven by a combination of decreased biological in-stream activity and decreased soil respiration in the contributing watershed of the glacial stream.

Based on the results of metabolism estimates, the following conclusions can be made regarding glacial meltwater contributions to streams: 1) glacial streams and contributing landscapes mineralize less DOM and release less CO₂ into the atmosphere than non-glacial systems; and 2) streams that receive glacial meltwater and have suitable environmental conditions for microbial communities to become established are net autotrophic systems when cloud cover is low.

Longitudinal Stream Analysis

Data from the longitudinal stream analysis suggest the glacial stream was influenced less by discharge contributions from non-glacial sources compared to the non-glacial stream. The uniformity of DOM and nutrient concentrations along the lower reaches of the proglacial stream suggest meltwater from glacial landcover dominates discharge in small coastal watersheds. Stream water from an adjacent, non-glacial watershed draining high-elevation snowfields showed increases of carbon, nutrients, and temperature along the entire length of the stream as it transitioned from a high-elevation unvegetated landscape to a low-elevation forested landscape.

Discharge in the proglacial stream during the meltseason was driven by meltwater contributions from glaciated landcover. The increased uniformity of DOM and nutrients in the proglacial stream are likely a result of glacial meltwater contributing over 60% of the stream discharge, even though glacial landcover makes up only 28% of the contributing area at the base of the watershed. This decreases the influence of non-glacial landcover on stream water chemistry in proglacial streams. These findings

indicate glacial meltwater is delivered from the terminus of coastal glaciers downstream to the GOA with little influence from low-elevation landscape controls.

Precipitation-Driven Landscape Flushing Analysis

The results from this study suggest rainfall on a glaciated surface flushed subsurface pools of meltwater and did not access unique DOM pools in the glaciated watershed. Results also showed subsurface attenuation of precipitation across the glacial surface and lower area-weighted specific flux of DOM and nutrients from the glacial surface than from a non-glacial landscape. The absence of a correlation between discharge and both concentration and composition of DOM and nutrients in the glacial stream is in contrast to the strong correlation between discharge and DOC, nitrogen, FI, and % protein content in the non-glacial stream. This relationship suggests flushing of organic soil layers in the non-glacial watershed, and connection to DOM pools such as wetlands and muskegs that are disconnected from the channel during baseflow conditions. Together, these results show the different responses observed in glaciated and forested streams are a result of the flow paths generated by storm runoff interacting with different landscape components in each watershed.

Effect of Glacial Landcover and Meltwater on In-Stream Processing of DOM

This study found glacial meltwater contributions to streams decreases the rate of biological in-stream processing of DOM and nutrients. This conclusion is supported by decreased estimates of DOM mineralization and CO₂ flux, as well as uniform water chemistry along the stream length. One caveat to this conclusion is the indication that

shallow reaches of glacial streams with low discharge have the potential for higher metabolism rates when sunlight is abundant and can increase water temperatures and drive photosynthesis. Glacial streams were also shown to have uniform water chemistry during storms and export DOM and nutrients based on discharge and not contributing landscape source pools. These findings contribute information on landscape controls and biological in-stream processing to the growing literature on glacial systems and the environmental changes caused by glacial recession.

5.2. Future Research

Future research of organic matter and nutrient dynamics in the changing landscape and coastal marine zone of southeast Alaska is important to understanding the impacts of glacial recession on both the regional ecosystem and the valuable commercial fishery. Additional research should focus on the impact of glacial recession on streams and marine waters during the spring when the glaciers “turn on” and fall when they “turn off”. These shoulder seasons are ecologically important because they coincide with the arrival and departure of migrating species and the spawning activities of salmon.

One of the interesting and unpublished results from this study was from metabolism estimates in a high-elevation stream in May when snowmelt drove stream discharge and before glacier meltwater contributed to discharge. This recently exposed stream was likely covered with snow since the previous fall and drained a small catchment containing a hanging glacier disconnected from the larger Juneau Icefield. Even though this stream was only exposed to sunlight a few days earlier, it had a small

diurnal signal of dissolved oxygen concentrations. This signal aligned with PAR measurements in a similar manner as the other sites, but the magnitude was very small compared to lower-elevation streams. As glacier recession continues, mountain glaciers connected to the Juneau Icefield may become isolated and the beginning and duration of their melt seasons may change. Information on stream metabolism when streams transition from winter to summer discharge regimes could provide insight into future stream biological processing potential.

Another area that is not well understood in glacial systems is the abundance and composition of microbial communities throughout proglacial streams during the year. These communities are highly specialized because of the harsh environmental conditions in which they exist, and because they likely only have a short window during the year to function. Because the aquatic environment in proglacial streams changes abruptly and dramatically during the year, the microbial communities that specialize in utilizing in-stream resources during each of these discharge periods likely changes as well. A better understanding of the functional characteristics of these changing communities can provide a better understanding of the ecosystem services they provide throughout the year under changing landscape and climate conditions.

Appendix A

Table A.1: Average hourly water depth at data collection point for NEM estimates in non-glacial Lake Creek and glacial Herbert River in Juneau Alaska. Data collected at 10-min intervals with an In-Situ level logger (In-Situ, Inc., Ft. Collins, Colorado, USA).

Time (24 hr)	Depth (cm)					
	Lake 7/21/2011	Lake 7/22/2011	Lake 7/23/2011	Herbert 7/13/2011	Herbert 7/14/2011	Herbert 7/15/2011
0:00	24.05	21.97	19.19	13.70	19.79	16.81
1:00	24.16	21.77	19.78	13.90	19.57	16.86
2:00	24.20	21.80	19.88	14.10	18.69	16.97
3:00	24.22	21.89	19.92	14.30	18.16	17.12
4:00	24.22	21.86	19.96	14.50	17.84	17.37
5:00	24.21	21.75	20.27	14.75	17.71	17.51
6:00	24.13	21.88	20.32	15.00	17.34	17.44
7:00	23.93	21.74	20.24	15.30	17.22	17.62
8:00	23.70	21.29	20.17	15.70	16.96	17.61
9:00	23.55	20.98	19.98	16.20	16.56	17.62
10:00	23.30	20.91	19.97	16.80	16.37	18.04
11:00	22.99	20.45	19.86	17.10	16.41	18.41
12:00	22.68	20.39	19.59	17.50	16.24	18.51
13:00	22.45	20.33	19.03	18.00	16.07	18.97
14:00	22.20	20.07	18.60	18.50	15.71	19.31
15:00	21.99	19.74	18.35	19.19	15.57	19.57
16:00	21.80	19.25	18.00	19.89	15.39	19.67
17:00	21.67	19.06	17.75	20.77	15.09	19.92
18:00	21.54	18.70	17.56	21.16	15.22	20.09
19:00	21.40	18.60	17.56	20.94	15.52	20.22
20:00	21.44	18.78	17.61	21.01	16.16	20.34
21:00	21.61	18.84	17.45	20.79	16.51	20.64
22:00	21.95	19.04	17.56	20.84	16.74	20.82
23:00	22.08	19.21	17.84	20.19	16.69	20.89

Table A.2: Average hourly water temperature values for non-glacial Lake Creek and glacial Herbert River in Juneau Alaska. Data collected at 10-min intervals with a YSI optical dissolved oxygen (ODO) probe (YSI, Inc., Yellow Springs, Ohio, USA).

Time (24 hr)	Water Temperature (°C)					
	Lake 7/21/2011	Lake 7/22/2011	Lake 7/23/2011	Herbert 7/13/2011	Herbert 7/14/2011	Herbert 7/15/2011
0:00	11.25	11.77	12.25	1.43	1.50	1.77
1:00	11.15	11.68	12.20	1.41	1.57	1.75
2:00	11.07	11.58	12.10	1.40	1.65	1.75
3:00	10.97	11.50	12.02	1.35	1.67	1.72
4:00	10.87	11.40	11.95	1.40	1.72	1.73
5:00	10.80	11.32	11.85	1.80	1.78	1.73
6:00	10.70	11.30	11.80	2.20	1.87	1.92
7:00	10.75	11.30	11.72	2.60	1.83	2.33
8:00	10.83	11.35	11.80	2.90	1.95	2.70
9:00	10.93	11.50	11.80	3.30	2.02	3.18
10:00	11.02	11.73	11.88	3.60	2.12	3.50
11:00	11.28	12.00	12.05	3.90	2.10	3.42
12:00	11.80	12.43	12.23	4.20	2.25	3.98
13:00	12.17	12.80	12.60	4.38	2.37	3.95
14:00	12.27	12.90	13.00	4.55	2.25	4.38
15:00	12.23	12.91	13.25	4.23	2.28	4.10
16:00	12.30	12.90	13.33	3.62	2.26	3.83
17:00	12.30	12.85	13.23	3.27	2.12	3.55
18:00	12.30	12.80	13.10	2.95	2.20	3.28
19:00	12.23	12.70	13.00	2.52	2.15	2.85
20:00	12.15	12.63	12.95	2.03	1.97	2.52
21:00	12.05	12.58	12.83	1.72	1.88	2.33
22:00	11.93	12.48	12.75	1.57	1.82	2.23
23:00	11.87	12.37	12.67	1.52	1.75	2.13

Table A.3: Photosynthetically active radiation (PAR) daily averages for non-glacial Lake Creek and glacial Herbert River in Juneau Alaska. Data collected at 10-min intervals with a Solar Light PMA1132 Quantum detector (Solar Light Company, Inc., Glenside, Pennsylvania, USA). Instantaneous PAR values were measured from a wavelength of 400 to 700 nm ($\mu\text{mol photons m}^{-2} \text{ sec}^{-1}$) in the field and later extrapolated across 10-min intervals to calculate daily totals ($\text{mol photons m}^{-2} \text{ day}^{-1}$) (A1).

Location	Date	PAR ($\text{mol m}^{-2} \text{ d}^{-1}$)
Lake Creek	7/21/2011	30
Lake Creek	7/22/2011	26
Lake Creek	7/23/2011	32
Herbert River	7/13/2011	44
Herbert River	7/14/2011	10
Herbert River	7/15/2011	39

$$\text{PAR}_D = \sum(\text{PAR}_i \times \Delta t) \div \beta \quad (\text{A1})$$

where: PAR_D = daily PAR value (as $\text{mol photons m}^{-2} \text{ day}^{-1}$)

PAR_i = instantaneous PAR reading ($\mu\text{mol photons m}^{-2} \text{ sec}^{-1}$)

Δt = sample interval (sec)

β = unit conversion term, here = 1×10^6 (μmol to mol)

Table A.4: Average hourly oxygen surplus / deficit values for non-glacial Lake Creek and glacial Herbert River in Juneau Alaska. Data collected at 10-min intervals with a YSI optical dissolved oxygen (ODO) probe (YSI, Inc., Yellow Springs, Ohio, USA). Values corrected for temperature to determine surplus / deficit saturation concentration.

Time (24 hr)	O ₂ Surplus / Deficit (mg L ⁻¹)					
	Lake 7/21/2011	Lake 7/22/2011	Lake 7/23/2011	Herbert 7/13/2011	Herbert 7/14/2011	Herbert 7/15/2011
0:00	-0.10	-0.15	-0.17	-0.24	-0.27	-0.37
1:00	-0.10	-0.16	-0.16	-0.25	-0.28	-0.38
2:00	-0.10	-0.16	-0.17	-0.26	-0.28	-0.39
3:00	-0.11	-0.16	-0.16	-0.27	-0.30	-0.40
4:00	-0.09	-0.17	-0.16	-0.28	-0.30	-0.39
5:00	-0.08	-0.15	-0.16	-0.24	-0.29	-0.35
6:00	-0.06	-0.12	-0.15	-0.09	-0.24	-0.20
7:00	-0.05	-0.09	-0.13	0.07	-0.22	0.00
8:00	-0.02	-0.07	-0.09	0.21	-0.16	0.12
9:00	0.00	-0.02	-0.05	0.34	-0.11	0.26
10:00	0.03	0.00	0.01	0.40	-0.06	0.32
11:00	0.04	0.02	0.06	0.47	-0.08	0.35
12:00	0.03	0.03	0.08	0.50	-0.02	0.46
13:00	0.04	0.02	0.10	0.52	0.00	0.47
14:00	0.03	0.02	0.10	0.49	-0.01	0.46
15:00	0.01	0.01	0.06	0.33	-0.03	0.34
16:00	-0.01	-0.01	0.04	0.27	-0.05	0.28
17:00	-0.03	-0.03	0.00	0.20	-0.13	0.25
18:00	-0.08	-0.04	-0.03	0.06	-0.10	0.19
19:00	-0.11	-0.06	-0.05	-0.07	-0.15	0.01
20:00	-0.13	-0.08	-0.08	-0.17	-0.26	-0.14
21:00	-0.15	-0.11	-0.10	-0.22	-0.30	-0.35
22:00	-0.15	-0.14	-0.12	-0.25	-0.34	-0.50
23:00	-0.15	-0.16	-0.16	-0.24	-0.35	-0.55

Table A.5: Average hourly oxygen-based reaeration corrected rate of change of oxygen per unit area for non-glacial Lake Creek and glacial Herbert River in Juneau Alaska. Data collected at 10-min intervals with a YSI optical dissolved oxygen (ODO) probe (YSI, Inc., Yellow Springs, Ohio, USA). Reaeration correction calculated using surface renewal model (SRM).

O ₂ -Based Reaeration Corrected Rate of Change per area (g m ² h ⁻¹)						
Time (24 hr)	Lake 7/21/2011	Lake 7/22/2011	Lake 7/23/2011	Herbert 7/13/2011	Herbert 7/14/2011	Herbert 7/15/2011
0:00	-0.029	-0.048	-0.054	-0.092	-0.095	-0.138
1:00	-0.030	-0.049	-0.054	-0.089	-0.106	-0.137
2:00	-0.029	-0.049	-0.054	-0.088	-0.109	-0.144
3:00	-0.030	-0.051	-0.051	-0.086	-0.109	-0.146
4:00	-0.032	-0.051	-0.050	-0.085	-0.113	-0.144
5:00	-0.030	-0.048	-0.051	-0.087	-0.111	-0.131
6:00	-0.024	-0.040	-0.049	-0.084	-0.095	-0.087
7:00	-0.023	-0.032	-0.042	-0.054	-0.080	-0.031
8:00	-0.019	-0.026	-0.035	-0.006	-0.067	0.021
9:00	-0.010	-0.014	-0.017	0.046	-0.046	0.068
10:00	-0.002	-0.008	-0.003	0.091	-0.028	0.102
11:00	0.002	-0.002	0.012	0.128	-0.027	0.115
12:00	-0.002	-0.004	0.021	0.155	-0.017	0.144
13:00	0.001	-0.004	0.021	0.175	-0.006	0.171
14:00	0.009	0.004	0.021	0.193	0.003	0.182
15:00	0.010	0.003	0.015	0.200	-0.012	0.163
16:00	0.003	-0.002	0.012	0.167	-0.018	0.126
17:00	-0.002	-0.008	0.006	0.125	-0.036	0.114
18:00	-0.009	-0.013	-0.005	0.096	-0.043	0.088
19:00	-0.022	-0.019	-0.015	0.053	-0.046	0.035
20:00	-0.032	-0.023	-0.025	0.005	-0.074	-0.029
21:00	-0.038	-0.035	-0.031	-0.039	-0.102	-0.116
22:00	-0.046	-0.044	-0.037	-0.071	-0.116	-0.175
23:00	-0.049	-0.050	-0.050	-0.087	-0.121	-0.184

Table A.6: Average hourly carbon dioxide-based reaeration corrected rate of change of oxygen per unit area for non-glacial Lake Creek and glacial Herbert River in Juneau Alaska. Data collected at 10-min intervals with a Vaisala *in situ* CO₂ probe (Vaisala, Helsinki, Finland). Prior to deployment, CO₂ probes were waterproofed using a gas-permeable polytetrafluoroethylene (PTFE) membrane. Reaeration correction calculated using surface renewal model (SRM).

Time (24 hr)	O ₂ (g m ² h ⁻¹)					
	Lake 7/21/2011	Lake 7/22/2011	Lake 7/23/2011	Herbert 7/13/2011	Herbert 7/14/2011	Herbert 7/15/2011
0:00	-0.208	-0.264	-0.291	n.a.	-0.031	-0.042
1:00	-0.202	-0.260	-0.291	n.a.	-0.038	-0.037
2:00	-0.207	-0.260	-0.297	n.a.	-0.032	-0.041
3:00	-0.208	-0.258	-0.298	n.a.	-0.037	-0.039
4:00	-0.208	-0.258	-0.293	n.a.	-0.035	-0.033
5:00	-0.207	-0.257	-0.289	n.a.	-0.027	-0.019
6:00	-0.204	-0.250	-0.278	n.a.	-0.008	0.026
7:00	-0.205	-0.237	-0.270	n.a.	-0.010	0.065
8:00	-0.207	-0.238	-0.188	n.a.	0.006	0.079
9:00	-0.206	-0.236	-0.254	n.a.	0.019	0.084
10:00	-0.208	-0.234	-0.246	n.a.	0.031	0.089
11:00	-0.201	-0.226	-0.236	n.a.	0.029	0.073
12:00	-0.199	-0.226	-0.238	n.a.	0.042	0.090
13:00	-0.200	-0.236	-0.248	n.a.	0.033	0.078
14:00	-0.202	-0.239	-0.180	n.a.	0.034	0.073
15:00	-0.203	-0.244	-0.264	n.a.	0.035	0.066
16:00	-0.209	-0.250	-0.282	n.a.	0.022	0.064
17:00	-0.211	-0.253	-0.291	n.a.	0.009	0.066
18:00	-0.226	-0.263	-0.299	n.a.	0.016	0.042
19:00	-0.256	-0.279	-0.312	n.a.	0.000	0.015
20:00	-0.279	-0.289	-0.326	n.a.	-0.027	-0.013
21:00	-0.270	-0.303	-0.332	n.a.	-0.034	-0.034
22:00	-0.274	-0.287	-0.313	n.a.	-0.038	-0.044
23:00	-0.269	-0.287	-0.324	n.a.	-0.038	-0.045

Table A.7: Metabolism estimates from non-glacial Lake Creek and glacial Herbert River using in situ dissolved CO₂ concentrations. All values are calculated from single station, open water measurements and corrected for temperature and depth. Reaeration was estimated with the surface renewal model (SRM) adjusted for CO₂, and NEM was calculated as GPP – CR₂₄. All values are reported in g CO₂-O₂ m⁻² day⁻¹.

	Date	CR ₂₄	GPP	NEM
Non-Glacial	7/21/2011	5.48	0.90	-4.58
	7/22/2011	6.42	1.09	-5.33
	7/23/2011	7.20	1.46	-5.74
Glacial	7/14/2011	0.71	0.72	0.01
	7/15/2011	0.51	1.41	0.63

CR₂₄ = 24-hr community respiration

GPP = Gross primary production

NEM = Net ecosystem metabolism

Table A.8: Sediment mesocosm results for three replicates of non-glacial Lake Creek, glacial Herbert River, and a control containing only filtered water. All mesocosms incubated at 20°C for 24 hr using 0.20 μm glass fiber filtered water from Lake Creek. Results reported as an increase in column CO_2 generation ($\text{CO}_2 \mu\text{mol L}^{-1}$) and daily estimates of respiration ($\text{g CO}_2\text{-O}_2 \text{ m}^{-2} \text{ d}^{-1}$).

Location	Replicate 1	Replicate 2	Replicate 3
$\text{CO}_2 \mu\text{mol L}^{-1}$			
Lake Creek	11.00	6.00	7.00
Herbert River	4.00	2.00	4.00
Control	2.00	1.00	1.00
$\text{g CO}_2\text{-O}_2 \text{ m}^{-2} \text{ d}^{-1}$			
Lake Creek	0.154	0.090	0.119
Herbert River	0.056	0.030	0.068
Control	0.028	0.015	0.017

Table A.9: Bioavailable nitrogen (NH_4^+) concentrations in non-glacial Lake Creek and glacial Herbert River during in-stream uptake experiment. Distance is reported as meters downstream from injection site, with upstream (background) location reported as a negative number.

Distance (m)	Date	Location	NH_4^+ ($\mu\text{mol/L}$)
-5	7/13/2011	Herbert River A	0.62
60	7/13/2011	Herbert River B	2.45
100	7/13/2011	Herbert River C	2.49
140	7/13/2011	Herbert River D	2.48
170	7/13/2011	Herbert River E	2.55
-5	7/13/2011	Herbert River A	0.67
-5	7/20/2011	Lake Creek A	0.55
20	7/21/2011	Lake Creek B	5.31
58	7/22/2011	Lake Creek C	3.32
58	7/22/2011	Lake Creek C	3.34
70	7/22/2011	Lake Creek D	3.59
100	7/22/2011	Lake Creek E	3.33
100	7/22/2011	Lake Creek E	3.07
-5	7/22/2011	Lake Creek A	0.42

Table A.10: Bioavailable nitrogen (NH_4^+) in-stream uptake calculation results and equations for a 100 meter reach of non-glacial Lake Creek. Values calculated using equations (A2) – (A4). Conservative chloride concentrations plateaued at $176 \mu\text{mol L}^{-1}$ above background, and NH_4^+ concentrations plateaued at $36 \mu\text{mol/L}$ above background. Uptake was not observed in the 170 meter glacial study reach. Both uptake experiments occurred during the summer melt season on coastal streams near Juneau Alaska.

k_w	-0.0086	Longitudinal Uptake Rate	
S_w	116	Uptake Length (m)	
V_f	5.39E-05	Uptake Velocity (m sec^{-1})	Lake Creek
U	1.8	Areal Uptake ($\mu\text{mol m}^{-2} \text{min}^{-1}$)	Lake Creek

$$V_f = \frac{u \times z}{S_w} \quad (\text{A2})$$

where: V_f = uptake velocity (m min^{-1})

u = water velocity (m min^{-1})

z = water depth (m)

$$U = V_f \times C \quad (\text{A3})$$

where: U = areal uptake ($\mu\text{mol m}^{-2} \text{min}^{-1}$)

C = ambient nutrient concentration ($\mu\text{mol L}^{-1}$)

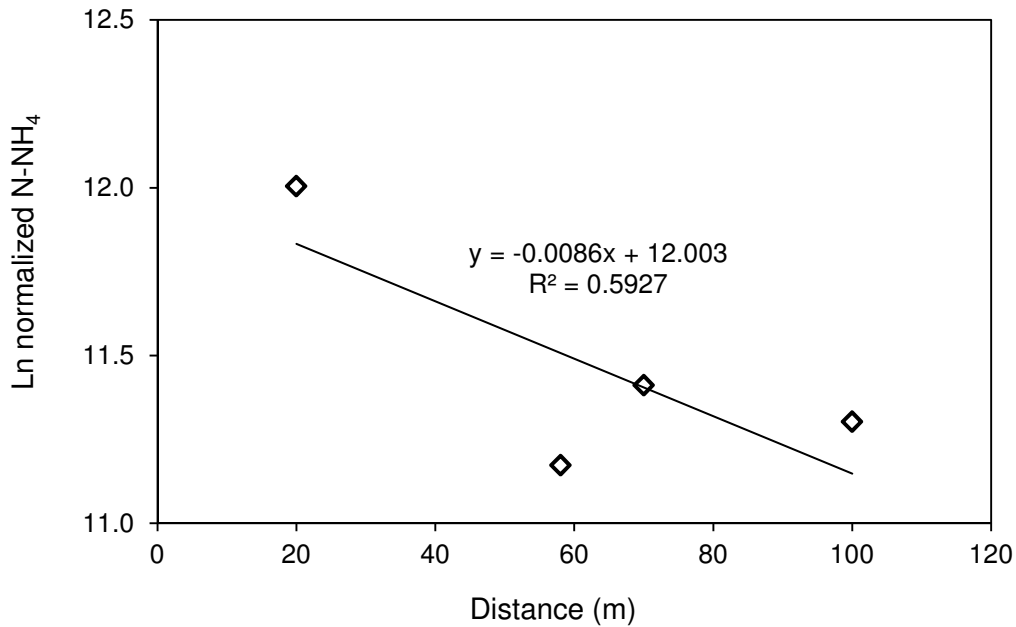


Figure A.1: Bioavailable nitrogen (NH_4^+) concentrations for a 100 meter reach of non-glacial Lake Creek. Conservative chloride concentrations plateaued at $176 \mu\text{mol/L}$ above background, and NH_4^+ concentrations plateaued at $36 \mu\text{mol/L}$ above background. Uptake experiment occurred during the summer melt season near Juneau Alaska. Nutrient uptake length (S_w) calculated using slope (A4). Raw data presented in Table A.9.

$$S_w = \frac{1}{k_w} \quad (\text{A4})$$

where: S_w = uptake length (m)

k_w = slope of normalized uptake rate vs. distance (min^{-1})

Appendix B

Table B.1: Landcover classification and descriptions. Alpine and sub-alpine were grouped in the same category, as were deciduous forests and muskegs. Landcover characteristics were applied on whole watershed scales and sub-watersheds (NLCD, 2011).

Value	LC Level 1	LC Level 2	POG Description	Classification
1	Forest	Conifer Forest (POG)	Large POG	Conifer Forest
2	Forest	Conifer Forest (POG)	Med POG	
3	Forest	Conifer Forest (POG)	Med POG	
4	Forest	Conifer Forest (POG)	Med POG	
5	Forest	Conifer Forest (POG)	Med POG	
7	Forest	Conifer Forest (POG)	Small POG	
8	Forest	Conifer Forest (POG)	Large POG	
9	Forest	Conifer Forest (POG)	Med POG	
10	Forest	Conifer Forest (POG)	Med POG	
11	Forest	Conifer Forest (POG)	Large POG	
12	Forest	Conifer Forest (POG)	Med POG	
13	Forest	Conifer Forest (POG)	Med POG	
31	Forest	Conifer Forest (other)	Sub-alpine forest	Sub-Alpine
32	Forest	Conifer Forest (other)	Sub-alpine forest (wet)	
33	Forest	Conifer Forest (other)	Conifer (YG)	
35	Forest	Conifer Forest (other)	Scrub forest (wet)	
41	Nonforest Veg	Tall Shrubland	Shrubland	Alpine
42	Nonforest Veg	Tall Shrubland	Slide zone	
43	Nonforest Veg	Dwarf Shrubland	Alpine tundra	
61	Unvegetated	Unvegetated	Ice & Snow	Glacier
62	Unvegetated	Unvegetated	Rock	Rock

POG = Productive Old Growth

YG = Young Growth

Table B.2: Longitudinal sampling data for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), dissolved inorganic carbon (DIC), ammonium nitrogen (NH_4^+), nitrate nitrogen (NO_3^-), and phosphate (PO_4^{3-}). All units are reported in micromolar per liter with average standard deviation of triplicate DOC and TDN of $\pm 4.5 \mu\text{mol/L}$ and $0.18 \mu\text{mol/L}$, respectively. Average instrument precision of duplicates of DIC, NH_4^+ , and PO_4^{3-} are $6.7 \mu\text{mol/L}$, $0.24 \mu\text{mol/L}$, $0.01 \mu\text{mol/L}$, respectively. Samples collected along non-glacial Montana Creek and glacial Lemon Creek near Juneau Alaska.

Non-Glacial ID	DOC ($\mu\text{mol/L}$)	TDN ($\mu\text{mol/L}$)	DIC ($\mu\text{mol/L}$)	NH_4^+ ($\mu\text{mol/L}$)	PO_4^{3-} ($\mu\text{mol/L}$)	NO_3^- ($\mu\text{mol/L}$)
MC-1	167	9.61	331	2	0.11	5.2
MC-2	145	8.57	365	1.86	0.09	5.1
MC-3	100	7.03	326	0.93	0.06	5.6
MC-4	89	6.82	334	0.84	0.06	5.4
MC-5	279	7.66	445	2.06	0.13	5.8
MC-7	285	7.28	405	0.72	0.03	5.7
MC-6	239	4.47	509	0.44	0.07	1.7
MC-8	51	6.05	307	0.72	0.04	n.a.
MC-9	30	5.73	300	1.25	0.09	n.a.
Glacial ID	DOC ($\mu\text{mol/L}$)	TDN ($\mu\text{mol/L}$)	DIC ($\mu\text{mol/L}$)	NH_4^+ ($\mu\text{mol/L}$)	PO_4^{3-} ($\mu\text{mol/L}$)	NO_3^- ($\mu\text{mol/L}$)
LC-1	28	4.07	266	0.93	0.04	3.0
LC-3	72	16.95	642	1.22	0.04	2.7
LC-4	22	2.85	263	0.74	0.03	2.4
LC-5	25	3.16	216	0.6	0.03	n.a.
LC-6	24	2.45	233	0.58	0.02	2.1
LC-7	37	4.96	388	0.43	0.02	1.9
LC-8	20	2.37	209	0.55	0.03	1.3
LC-9	23	2.17	201	0.67	0.03	n.a.
LC-10	39	3.75	331	0.69	0.03	n.a.
LC-11	18	1.48	160	0.43	0.04	n.a.
LC-12	13	0.42	133	0.68	0.05	17.6
LC-13	21	1.54	159	0.57	0.01	3.7
LC-14	23	0.40	200	0.61	0.04	3.2

Table B.3: Longitudinal sampling data for modeled % protein DOM fractions, water oxygen isotope ($\delta^{18}\text{O}$), fluorescence index (FI), temperature, turbidity, and specific conductivity along non-glacial Montana Creek and glacial Lemon Creek near Juneau Alaska.

Non-Glacial ID	Protein (%)	$\delta^{18}\text{O}$ (‰)	FI	Temperature (°C)	Turbidity (NTU)	Specific Conductivity ($\mu\text{S}/\text{cm}$)
MC-1	3	-13.961	1.3	8.5	5.7	47
MC-2	4	-13.934	1.3	8.2	5.7	46
MC-3	7	-13.896	1.3	7.8	2.5	45
MC-4	6	-13.832	1.3	7.3	3.2	44
MC-5	3	-13.098	1.3	9.5	3.0	50
MC-7	4	-13.321	1.3	9.5	1.6	47
MC-6	3	-12.729	1.3	8.6	1.9	54
MC-8	10	-13.837	1.3	7.0	2.9	42
MC-9	27	-14.114	1.4	7.0	2.2	42
Glacial ID	Protein (%)	$\delta^{18}\text{O}$ (‰)	FI	Temperature (°C)	Turbidity (NTU)	Specific Conductivity ($\mu\text{S}/\text{cm}$)
LC-1	30	-14.702	1.4	5.7	15.6	33
LC-3	9	NA	1.4	8.9	1.3	76
LC-4	25	-14.508	1.4	5.5	10.6	30
LC-5	24	-14.706	1.4	5.6	12.3	27
LC-6	38	-14.720	1.6	6	14.0	29
LC-7	25	-14.070	1.4	9.6	2.8	50
LC-8	15	-14.463	1.4	5.5	13.8	26
LC-9	25	-14.573	1.4	5.7	16.5	27
LC-10	23	-14.411	1.4	8.9	1.1	41
LC-11	45	-15.032	3.0	4.2	12.3	20
LC-12	39	-15.279	2.5	NA	37.7	7
LC-13	29	-14.816	2.5	NA	3.6	7
LC-14	33	-14.633	1.7	NA	5.5	7

Table B.4: Watershed land cover (%) for non-glacial Montana Creek and glacial Lemon Creek near Juneau Alaska.

Non-Glacial ID	Land Cover (%)					
	Glacier	Rock	Conifer Forest	Alpine/Sub Alpine	Muskeg/Deciduous	Other
MC-1	0	14	47	28	7	4
MC-2	0	16	47	31	6	0
MC-3	0	19	47	30	4	0
MC-4	0	20	45	32	3	0
MC-5	0	12	68	15	5	0
MC-6	0	0	100	0	0	0
MC-7	0	14	68	17	1	0
MC-8	0	25	32	38	2	3
MC-9	0	29	28	42	1	0
Glacial ID	Glacier	Rock	Conifer Forest	Alpine/Sub Alpine	Muskeg/Deciduous	Other
LC-1	28	23	15	34	0	0
LC-3	0	5	40	55	0	0
LC-4	31	25	12	32	0	0
LC-5	33	26	9	32	0	0
LC-6	35	27	6	32	0	0
LC-7	0	27	7	66	0	0
LC-8	39	27	5	29	0	0
LC-9	42	29	3	26	0	0
LC-10	0	48	8	44	0	0
LC-11	54	26	1	19	0	0
LC-12	89	11	0	0	0	0
LC-13	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
LC-14	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table B.5: Emission intensity from samples in non-glacial Montana Creek and glacial Lemon Creek in southeast Alaska. The fluorescence index (FI) was calculated as the ratio of emission intensity from 450 to 500 nm at an excitation of 370 nm.

Non-Glacial ID	Emission Intensity	
	370nm x 450nm	370nm x 500nm
MC-1	0.0502	0.0386
MC-2	0.0562	0.0444
MC-3	0.0758	0.0593
MC-4	0.0606	0.0470
MC-5	0.0614	0.0484
MC-6	0.0594	0.0471
MC-7	0.0575	0.0441
MC-8	0.0359	0.0277
MC-9	0.0198	0.0138
Glacial ID	Emission Intensity	
	370nm x 450nm	370nm x 500nm
LC-1	0.0163	0.0115
LC-2	n.a.	n.a.
LC-3	0.0638	0.0470
LC-4	0.0133	0.0094
LC-5	0.0127	0.0089
LC-6	0.0070	0.0043
LC-7	0.0147	0.0103
LC-8	0.0105	0.0073
LC-9	0.0142	0.0101
LC-10	0.0310	0.0218
LC-11	0.0083	0.0028
LC-12	0.0042	0.0017
LC-13	0.0113	0.0046
LC-14	0.0042	0.0024

Table B.6: Average monthly air temperature (°C) values recorded at Juneau airport for selected years between 1951 and 2012. (NOAA, 2013)

YEAR	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	AVG
1951	18.5	21.5	26	39	46.8	52.2	60.2	55.5	50.5	37.8	31.1	22.4	38.5
1952	14.4	30.6	31.3	37.5	44.6	52.3	55.5	54.0	48.7	44.9	38.4	33.3	40.5
1953	18.7	34.3	31.4	41	49.1	56.3	57.3	54.8	49.1	43.2	33	32.2	41.7
1954	20.7	23.6	30.8	33	46.2	53.8	54.3	56.1	49.2	42.6	38.4	28	39.8
1955	32	29.3	27.8	38	42.8	50.5	56.8	52.0	47	38.6	21.8	18.1	37.9
1956	19.7	21.8	27.9	38.7	45.2	50.0	56.3	53.9	48.2	37.5	38.4	23.5	38.5
1957	20.6	25.3	32.8	38.6	47.9	54.9	55.4	57.6	52.4	41.9	37.8	29.4	41.3
1958	32.7	27.1	32.9	42.5	48	56.5	57.3	54.5	47.4	41.1	33.9	30	42.1
1959	18	28.2	33.8	38.8	46	55.2	54.1	52.6	48.2	40.3	34.4	34.9	40.4
1960	27.7	33.3	31.9	40.9	49.5	51.1	54.4	53.3	49.2	43.5	34.3	33.9	41.9
1961	30.5	31.5	34.5	39.9	47.4	52.4	56.3	53.9	47.7	40.2	30.6	24.5	40.8
1962	26.6	25.6	29.4	39.5	44.5	49.9	56.7	54.8	48.5	43.9	37.8	28.2	40.5
1963	27.7	33.1	31.8	36.6	48.7	50.4	55.4	56.9	52.2	44.6	28.3	32.7	41.6
1964	29.3	35.9	28.7	38.6	45.1	53.6	54.3	53.6	49.7	45	32.1	16.6	40.2
1965	23.1	23.6	35	37.7	42.4	48.5	55.3	55.1	50.2	43.7	29.9	26.6	39.4
1966	8.5	25.8	30.2	38	43.2	52.9	56.2	52.4	49.2	38.6	25.1	26.5	37.3
1967	23.1	30.4	24.1	37.3	45.6	54.8	53.8	55.0	50	43.1	32.3	27.3	39.8
1968	18.7	28.8	33.1	37.9	48.4	52.2	56.8	55.7	47.6	38.9	34.1	19.4	39.3
1969	6.8	21.2	30.7	40.6	49.8	57.8	53.7	50.3	47.4	41.4	32.2	35.1	39
1970	21.9	35.1	36.5	39.1	45.3	50.7	52.3	51.7	46.3	39.5	27.8	21.5	39
1971	13	28	28.9	38.6	43.5	53.2	57.5	55.4	48	38.5	31.4	20.9	38.1
1972	15.8	19.5	26.5	34.6	44.8	50.4	58.0	55.4	47	38.6	34.5	23.5	37.4
1973	18.9	24.5	32.9	39.6	45.9	51.2	53.7	51.7	48	41.2	23	28	38.3
1983	30.1	31.8	34.8	42.6	49.6	55.6	57.1	54.5	48	42.1	31.7	18.8	41.4
1984	32	35.8	39.6	43.1	49.1	53.5	55.5	55.3	50	40.4	31.5	24.2	42.5
1985	36.4	27.1	35.3	38.3	45.7	51.4	55.9	53.6	48.9	39.6	20.9	32.5	40.6
1986	34.3	28.7	35.3	37.3	46.5	54.3	56.7	54.4	50.7	45.8	30.5	36	42.6
2002	30.5	30.8	28.2	36.3	47	54.8	54.5	54.4	49.6	44.3	40	31.9	41.9
2003	31.5	31.7	30.5	41.7	46.8	53.7	58.0	54.9	48.8	43.3	30.5	31.8	42
2004	25.2	35.3	34.7	41	51.7	58.0	59.5	59.4	48.8	41.2	36.8	32.1	43.7
2005	25	30.7	37.4	44	52.7	56.1	56.2	57.2	51.1	41.5	35.5	33.7	43.5
2006	29.4	28.5	27.7	39	47.6	54.5	56.3	53.0	50	42.2	19.4	34.1	40.2
2007	31	25.1	28.4	38.6	46.7	54.4	56.6	56.5	49.7	42	35	27.4	41
2008	26	27.9	35.1	38.3	48	50.9	53.2	53.8	49.5	41.2	35.3	22.2	40.2
2009	25.8	27.1	28.5	39.2	48.1	54.9	59.9	55.8	49.8	42.6	35	27.9	41.3
2010	29.6	36.3	36.6	41.9	50.7	53.9	54.9	56.8	50.9	42.7	34.7	23.1	42.7
2011	28.2	25.2	28.8	39.1	48.2	53.9	55.9	53.0	48.8	42.2	29.7	33.7	40.7
2012	26.9	33.7	33	41.8	44.7	51.7	54.9	54.6	49.6	38.5	29.7	23.5	40.2

Table B7: Total monthly precipitation recorded at Juneau airport for selected years between 1951 and 2012. (NOAA, 2013)

YEAR	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	AVG
1951	0.07	0.08	0.12	0.12	0.07	0.14	0.09	0.09	0.13	0.12	0.16	0.07	0.1
1952	0.11	0.1	0.11	0.12	0.2	0.08	0.12	0.19	0.36	0.43	0.24	0.09	0.18
1953	0.05	0.22	0.12	0.1	0.08	0.1	0.1	0.18	0.21	0.4	0.09	0.16	0.15
1954	0.06	0.15	0.05	0.07	0.1	0.05	0.11	0.04	0.17	0.2	0.19	0.17	0.11
1955	0.13	0.12	0.15	0.08	0.16	0.07	0.08	0.21	0.18	0.24	0.09	0.09	0.13
1956	0.09	0.14	0.15	0.1	0.16	0.11	0.1	0.32	0.15	0.21	0.37	0.32	0.19
1957	0.03	0.14	0.04	0.12	0.08	0.05	0.09	0.05	0.19	0.13	0.29	0.12	0.11
1958	0.16	0.07	0.04	0.07	0.13	0.09	0.14	0.14	0.17	0.3	0.14	0.24	0.14
1959	0.04	0.15	0.15	0.11	0.12	0.05	0.24	0.17	0.18	0.19	0.23	0.19	0.15
1960	0.12	0.07	0.16	0.1	0.05	0.12	0.13	0.15	0.28	0.29	0.17	0.24	0.16
1961	0.12	0.15	0.09	0.13	0.15	0.11	0.19	0.4	0.23	0.33	0.2	0.13	0.19
1962	0.23	0.03	0.16	0.07	0.09	0.16	0.15	0.17	0.33	0.24	0.13	0.26	0.17
1963	0.21	0.22	0.12	0.13	0.07	0.15	0.17	0.04	0.27	0.25	0.13	0.15	0.16
1964	0.1	0.29	0.14	0.13	0.14	0.11	0.22	0.11	0.09	0.24	0.16	0.17	0.16
1965	0.25	0.18	0.05	0.11	0.14	0.1	0.07	0.13	0.08	0.26	0.05	0.14	0.13
1966	0.14	0.11	0.21	0.07	0.2	0.06	0.13	0.21	0.27	0.22	0.15	0.14	0.16
1967	0.13	0.17	0.04	0.04	0.09	0.1	0.14	0.18	0.28	0.18	0.19	0.1	0.14
1968	0.1	0.18	0.12	0.11	0.05	0.07	0.15	0.08	0.34	0.15	0.18	0.06	0.13
1969	0.03	0.02	0.13	0.06	0.11	0.08	0.25	0.24	0.18	0.12	0.29	0.14	0.14
1970	0.08	0.12	0.13	0.12	0.13	0.1	0.16	0.24	0.33	0.19	0.07	0.08	0.15
1971	0.18	0.14	0.11	0.08	0.14	0.06	0.05	0.22	0.18	0.19	0.15	0.1	0.13
1972	0.12	0.09	0.14	0.12	0.13	0.13	0.04	0.28	0.21	0.27	0.11	0.11	0.15
1973	0.14	0.14	0.1	0.08	0.13	0.09	0.12	0.21	0.17	0.2	0.05	0.07	0.13
1983	0.13	0.06	0.02	0.08	0.17	0.09	0.10	0.31	0.20	0.14	0.04	0.02	0.11
1984	0.20	0.19	0.12	0.07	0.06	0.14	0.22	0.20	0.12	0.22	0.20	0.16	0.16
1985	0.33	0.25	0.15	0.13	0.13	0.14	0.11	0.11	0.17	0.16	0.05	0.27	0.17
1986	0.23	0.12	0.20	0.10	0.08	0.09	0.08	0.22	0.08	0.40	0.20	0.21	0.17
2002	0.11	0.2	0.04	0.02	0.08	0.11	0.15	0.34	0.2	0.34	0.27	0.19	0.17
2003	0.18	0.05	0.11	0.03	0.09	0.12	0.11	0.15	0.38	0.14	0.21	0.19	0.15
2004	0.19	0.2	0.18	0.15	0.03	0.04	0.11	0.08	0.31	0.23	0.28	0.34	0.18
2005	0.19	0.22	0.13	0.1	0.03	0.1	0.17	0.21	0.33	0.29	0.46	0.22	0.2
2006	0.09	0.07	0.05	0.14	0.15	0.2	0.14	0.36	0.43	0.38	0.11	0.3	0.2
2007	0.2	0.11	0.18	0.1	0.14	0.06	0.22	0.08	0.3	0.38	0.11	0.12	0.17
2008	0.16	0.17	0.13	0.16	0.12	0.06	0.27	0.17	0.36	0.49	0.2	0.13	0.2
2009	0.3	0.14	0.1	0.07	0.09	0.09	0.08	0.24	0.3	0.18	0.25	0.13	0.16
2010	0.15	0.05	0.2	0.1	0.04	0.14	0.12	0.14	0.21	0.29	0.26	0.06	0.15
2011	0.17	0.2	0.04	0.06	0.09	0.14	0.11	0.35	0.29	0.24	0.26	0.24	0.18
2012	0.21	0.11	0.09	0.06	0.18	0.22	0.17	0.24	0.37	0.11	0.15	0.16	0.17

Table B.8: Average monthly discharge (cfs) in Lemon Creek near Juneau Alaska from 1951 to 2012. Values from USGS gaging stations in Lemon Creek. (USGS, 2013)

YEAR	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Site
1951	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	407	369	101	19	5	Upper Gauge
1952	2	1	2	7	47	158	310	383	429	350	67	10	
1953	3	2	2	12	115	310	446	515	358	200	28	n.a.	
1954	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	346	324	338	79	78	30	
1955	6	3	2	5	44	180	391	447	290	51	22	6	
1956	3	2	2	6	93	186	406	602	291	51	70	42	
1957	14	5	3	10	108	293	367	421	544	169	101	10	
1958	12	5	4	21	102	371	480	461	228	130	28	7	
1959	5	4	4	10	86	292	518	429	224	155	39	14	
1960	6	5	5	21	103	233	490	437	483	179	54	33	
1961	11	9	9	21	102	375	557	718	320	176	21	5	
1962	10	6	3	9	60	247	398	446	407	142	120	67	
1963	11	8	10	12	189	220	420	417	526	210	18	14	
1964	10	6	4	13	66	304	438	375	205	209	43	26	
1965	26	7	6	18	51	181	385	381	377	203	32	12	
1966	3	2	8	15	53	225	382	475	376	132	30	10	
1967	8	6	5	11	73	321	370	515	504	96	55	14	
1968	8	14	24	13	116	264	433	351	406	58	18	6	
1969	3	3	7	23	108	382	472	349	310	160	129	33	
1970	6	12	11	12	61	264	393	448	373	160	60	6	
1971	10	5	2	8	43	242	424	522	307	75	16	7	
1972	5	5	6	7	97	228	429	595	352	151	35	13	
1973	9	8	7	17	78	206	347	454	240	n.a.	n.a.	n.a.	
1983	42	24	23	65	138	284	319	722	411	170	60	25	Lower Gauge
1984	37	54	100	100	241	360	519	512	256	246	52	36	
1985	119	41	30	44	153	382	600	476	443	222	52	156	
1986	71	59	69	51	137	403	541	625	299	n.a.	n.a.	n.a.	
2002	n.a.	n.a.	n.a.	n.a.	111	345	442	669	290	429	86	69	Upper Gauge
2003	34	14	7	47	99	285	405	474	506	201	29	21	
2004	29	21	9	22	165	351	474	416	402	219	36	46	
2005	14	12	26	86	249	329	470	523	529	105	240	35	
2006	12	8	7	15	97	354	451	559	564	214	12	15	
2007	12	5	4	33	96	296	533	313	502	96	18	5	
2008	6	4	5	14	150	213	507	523	512	190	27	12	
2009	16	7	5	15	99	300	485	580	420	121	24	13	
2010	11	11	15	30	147	313	427	431	308	149	46	8	
2011	12	10	7	15	115	291	419	589	400	77	20	18	
2012	11	9	7	30	79	351	403	495	534	n.a.	n.a.	n.a.	

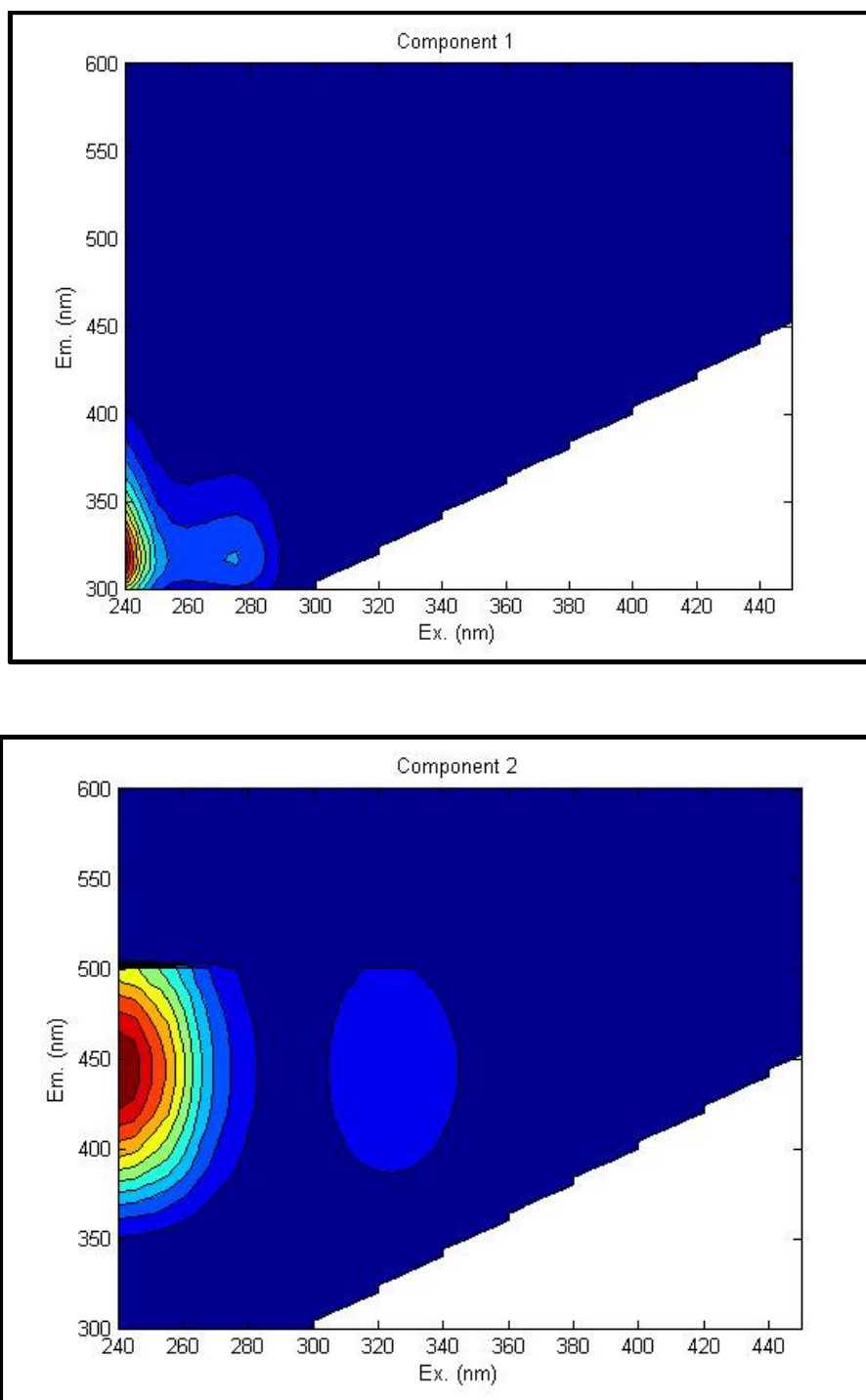


Figure B.1: Component excitation-emission matrices (EEMs) modeled using parallel factor analysis (PARAFAC) in MATLAB using the n-way toolbox. Samples were analyzed on a FluoroMax spectrofluorometer between excitation values of 240 and 450 nm and an emission range of 300 and 600 nm. Samples were corrected for background interference and normalized using a water Raman peak at an excitation of 350 nm.

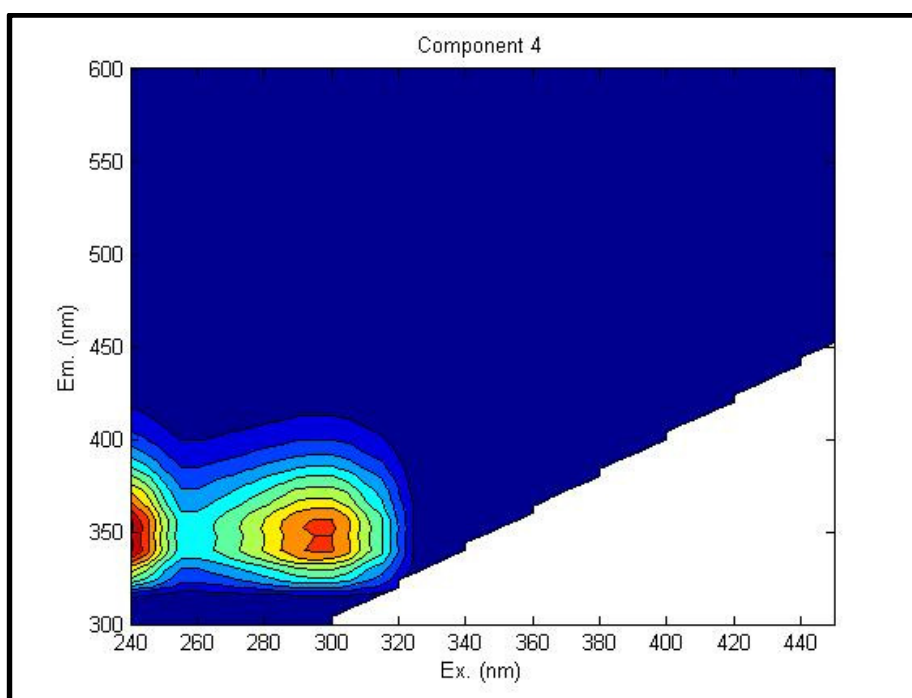
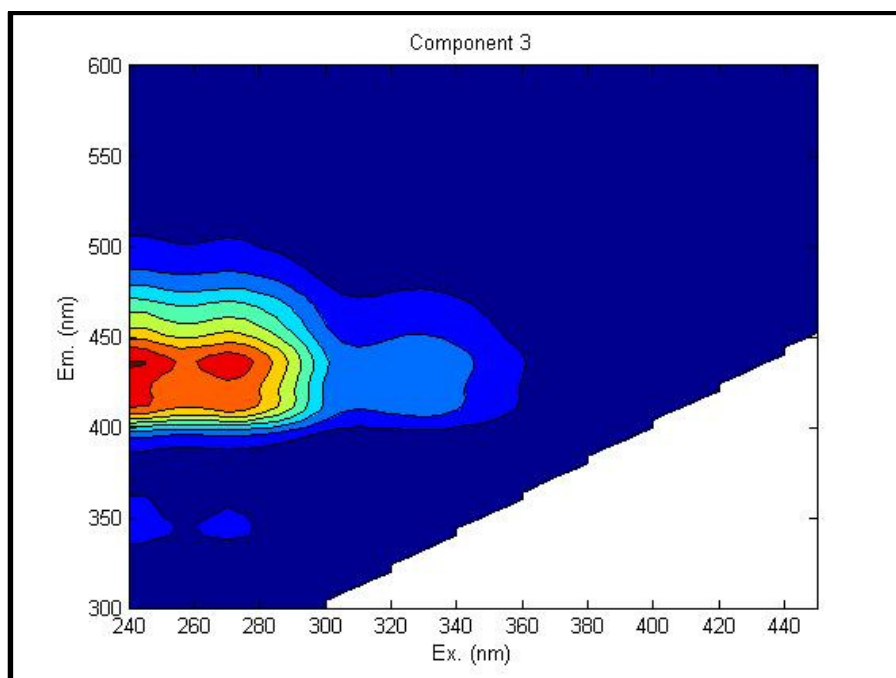


Figure B.1 (continued): Component excitation-emission matrices (EEMs) modeled using parallel factor analysis (PARAFAC) in MATLAB using the n-way toolbox. Samples were analyzed on a FluoroMax spectrofluorometer between excitation values of 240 and 450 nm and an emission range of 300 and 600 nm. Samples were corrected for background interference and normalized using a water Raman peak at an excitation of 350 nm.

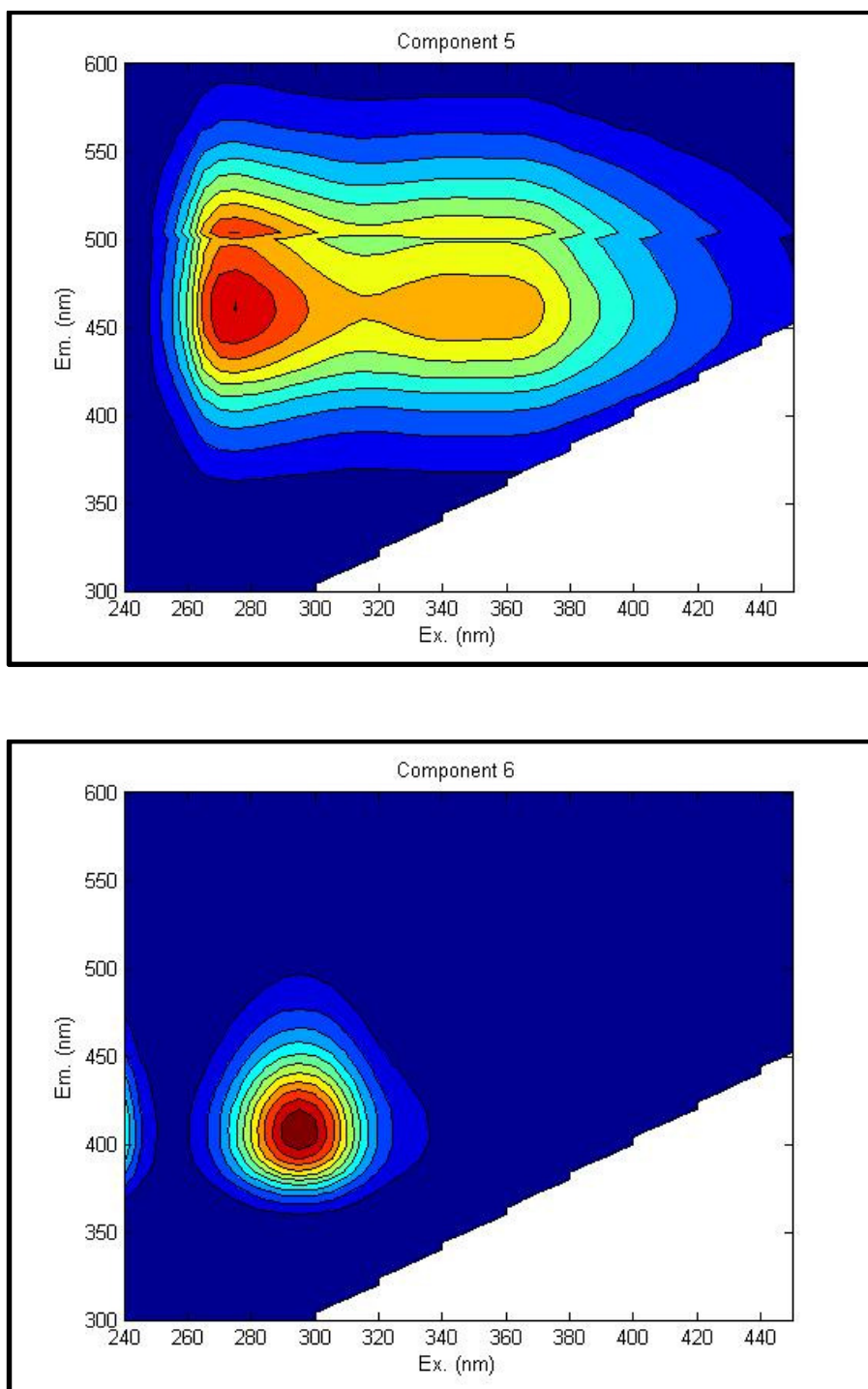


Figure B.1 (continued): Component excitation-emission matrices (EEMs) modeled using parallel factor analysis (PARAFAC) in MATLAB using the n-way toolbox. Samples were analyzed on a FluoroMax spectrofluorometer between excitation values of 240 and 450 nm and an emission range of 300 and 600 nm. Samples were corrected for background interference and normalized using a water Raman peak at an excitation of 350 nm.

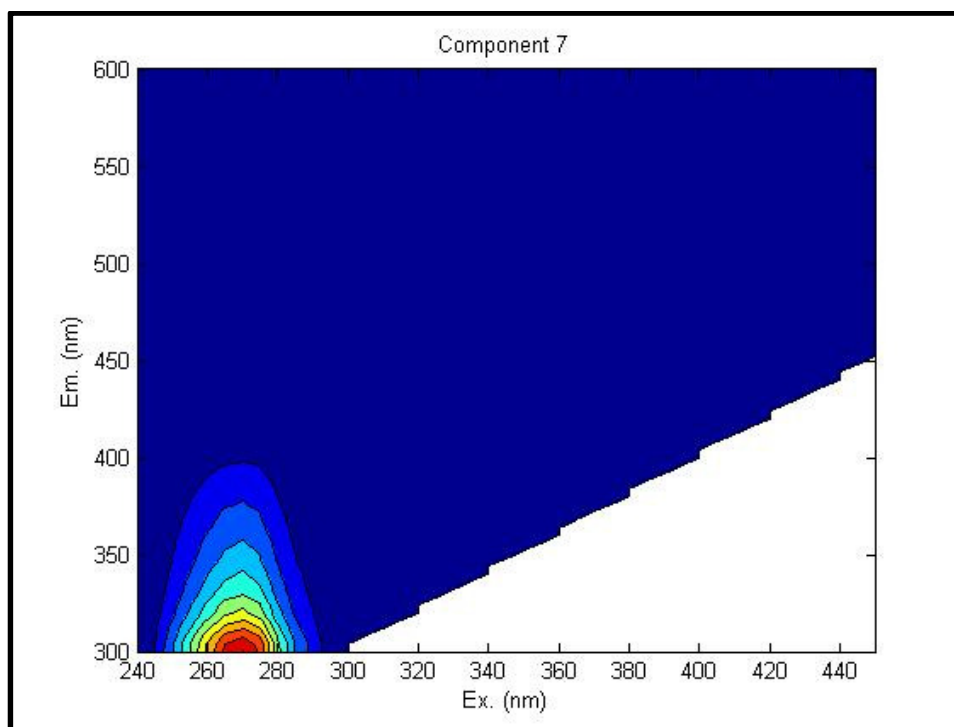


Figure B.1 (continued): Component excitation-emission matrices (EEMs) modeled using parallel factor analysis (PARAFAC) in MATLAB using the n-way toolbox. Samples were analyzed on a FluoroMax spectrofluorometer between excitation values of 240 and 450 nm and an emission range of 300 and 600 nm. Samples were corrected for background interference and normalized using a water Raman peak at an excitation of 350 nm.

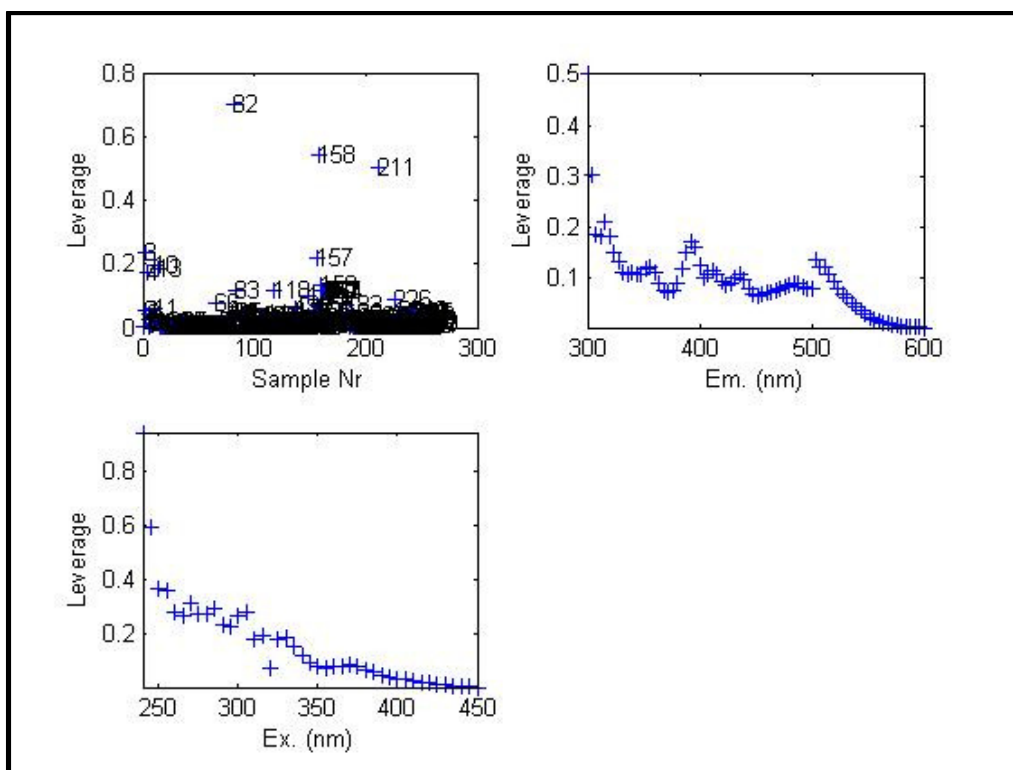


Figure B.2: Sample leverage of modeled excitation-emission matrices (EEMs) modeled using parallel factor analysis (PARAFAC) in MATLAB using the n-way toolbox. Sample leverage aides in the identification of samples disproportionately effecting PARAFAC component results.

Appendix C

Table C.1: Storm sample date, time, discharge, and specific discharge for samples collected in non-glacial Montana Creek and the Mendenhall Glacier near Juneau Alaska. Discharge in Montana Creek were collected at the USGS gaging station, and discharge for the Mendenhall Glacier was estimated using USGS gages in the Mendenhall River, Montana Creek, Salmon Creek and Nugget Creek.

Non-Glacial ID	Date	Time (24-hr)	Discharge (m ³ sec ⁻¹)	Spec. Discharge (mm hr ⁻¹)
MC-1	8/3/2011	18:00	1.7	0.1676
MC-2	8/3/2011	23:00	1.8	0.1732
MC-3	8/4/2011	16:30	1.7	0.1704
MC-4	8/4/2011	10:00	3.1	0.3044
MC-5	8/4/2011	12:15	3.2	0.3184
MC-6	8/4/2011	8:00	2.2	0.2206
MC-7	8/4/2011	14:15	3.2	0.3128
MC-8	8/4/2011	17:10	3.5	0.3435
MC-9	8/4/2011	20:15	4.7	0.4608
MC-10	8/5/2011	1:45	3.8	0.3715
MC-11	8/5/2011	8:30	2.8	0.2737
MC-12	8/6/2011	12:30	1.8	0.1787
MC-13	8/7/2011	13:30	1.4	0.1396
Glacial ID	Date	Time (24-hr)	Discharge (m ³ sec ⁻¹)	Spec. Discharge (mm hr ⁻¹)
GL-1	8/3/2011	20:30	62	1.3962
GL-2	8/4/2011	2:40	67	1.5062
GL-3	8/4/2011	5:30	69	1.5556
GL-4	8/4/2011	7:40	72	1.6161
GL-5	8/4/2011	9:30	75	1.6931
GL-6	8/4/2011	11:30	78	1.7700
GL-7	8/4/2011	2:20	80	1.8140
GL-8	8/4/2011	17:00	82	1.8525
GL-9	8/4/2011	20:00	83	1.8745
GL-10	8/5/2011	2:00	82	1.8525
GL-11	8/5/2011	8:00	79	1.7920
GL-12	8/6/2011	13:00	61	1.3742
GL-13	8/7/2011	14:00	51	1.1489

Table C.2: Storm sampling data for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), phosphate (PO_4^{3-}), ammonium nitrogen (NH_4^+), nitrate nitrogen (NO_3^-), and dissolved inorganic carbon (DIC). Samples collected from non-glacial Montana Creek and the Mendenhall Glacier near Juneau Alaska. Samples in Montana Creek were collected at the USGS gaging station, and samples from Mendenhall Glacier were collected from outflow of the glacier terminus above Lake Mendenhall.

	DOC	TDN	NH_4^+	NO_3^-	PO_4^{3-}	DIC
Non-Glacial ID	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)
MC-1	81	13	5.5	6.0	0.17	399
MC-2	79	14	5.9	5.7	0.17	410
MC-3	73	14	5.2	4.4	0.16	411
MC-4	92	11	3.9	5.5	0.16	382
MC-5	111	11	3.5	4.4	0.14	366
MC-6	84	13	4.7	6.1	0.15	383
MC-7	137	10	3.7	4.6	0.16	356
MC-8	155	10	3.3	4.0	0.19	307
MC-9	185	10	2.7	n.a.	0.15	317
MC-10	220	10	3.2	3.2	0.18	315
MC-11	181	11	3.7	4.1	0.19	340
MC-12	106	13	5.0	5.6	0.20	377
MC-13	99	14	6.0	6.5	0.22	398
	DOC	TDN	NH_4^+	NO_3^-	PO_4^{3-}	DIC
Glacial ID	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)	($\mu\text{mol/L}$)
GL-1	18.7	1.07	0.7	n.a.	0.08	84
GL-2	16.3	0.73	0.95	n.a.	0.07	73
GL-3	15.9	0.90	0.72	n.a.	0.05	75
GL-4	15.0	0.38	0.7	n.a.	0.05	72
GL-5	14.7	0.64	0.63	n.a.	0.05	75
GL-6	15.4	0.52	0.6	n.a.	0.05	74
GL-7	14.0	0.75	0.66	n.a.	0.06	69
GL-8	16.0	0.78	0.67	n.a.	0.06	53
GL-9	15.9	0.69	0.59	n.a.	0.06	67
GL-10	13.2	0.80	0.58	n.a.	0.05	69
GL-11	13.0	1.04	0.62	n.a.	0.06	82
GL-12	12.5	0.71	0.63	n.a.	0.04	81
GL-13	11.5	0.76	0.94	n.a.	0.07	75

Table C.3: Storm sampling data for oxygen-18 ($\delta^{18}\text{O}$), deuterium (δD), dissolved fluorescence index (FI), temperature, specific conductivity (Sp. Cond.), and turbidity. Samples collected from non-glacial Montana Creek and the Mendenhall Glacier near Juneau Alaska. Samples in Montana Creek were collected at the USGS gaging station, and samples from Mendenhall Glacier were collected from outflow of the glacier terminus above Lake Mendenhall.

Non-Glacial ID	$\delta^{18}\text{O}$ (‰)	δD (‰)	FI	Temp. (°C)	Sp. Cond. ($\mu\text{S}/\text{cm}$)	Turbidity (NTU)
MC-1	n.a.	n.a.	1.40	10.27	0.053	6.7
MC-2	-14.391	-104.222	1.39	9.61	0.052	8.4
MC-3	-14.196	-104.857	1.40	8.71	0.052	9.6
MC-4	-14.379	-104.264	1.33	8.4	0.05	15.7
MC-5	-14.369	-103.882	1.38	8.58	0.048	11.5
MC-6	-14.325	-104.685	1.47	8.38	0.052	10.3
MC-7	-14.083	-103.922	1.30	8.82	0.046	10
MC-8	-14.210	-103.737	1.29	9.11	0.044	9.8
MC-9	-13.967	-104.458	1.25	9.09	0.041	16.2
MC-10	-14.112	-103.852	1.24	8.48	0.04	10
MC-11	-14.346	-103.783	1.24	8.09	0.043	8.4
MC-12	-14.338	-103.867	1.31	8.37	0.051	6.6
MC-13	-14.546	-104.662	1.34	9.21	0.054	6.3
Glacial ID	$\delta^{18}\text{O}$ (‰)	δD (‰)	FI	Temp. (°C)	Sp. Cond. ($\mu\text{S}/\text{cm}$)	Turbidity (NTU)
GL-1	-15.637	-113.654	1.64	-0.01	0.009	75
GL-2	-15.511	-113.752	2.15	-0.01	0.009	68
GL-3	-15.756	-114.687	2.04	0	0.009	52
GL-4	-15.880	-113.326	4.35	0.01	0.008	67
GL-5	-15.686	-113.472	2.15	0	0.008	71
GL-6	-15.670	-113.644	1.92	0.01	0.008	92
GL-7	-15.661	-113.754	2.00	0.01	0.007	75
GL-8	-15.845	-113.898	1.58	0.02	0.008	99
GL-9	-15.847	-114.906	2.25	0.03	0.007	81
GL-10	-15.824	-114.541	2.01	0.01	0.008	101
GL-11	-15.652	-115.195	1.69	0	0.01	84
GL-12	-15.908	-115.633	2.02	-0.03	0.012	81
GL-13	-16.038	-116.059	1.74	0.01	0.013	67

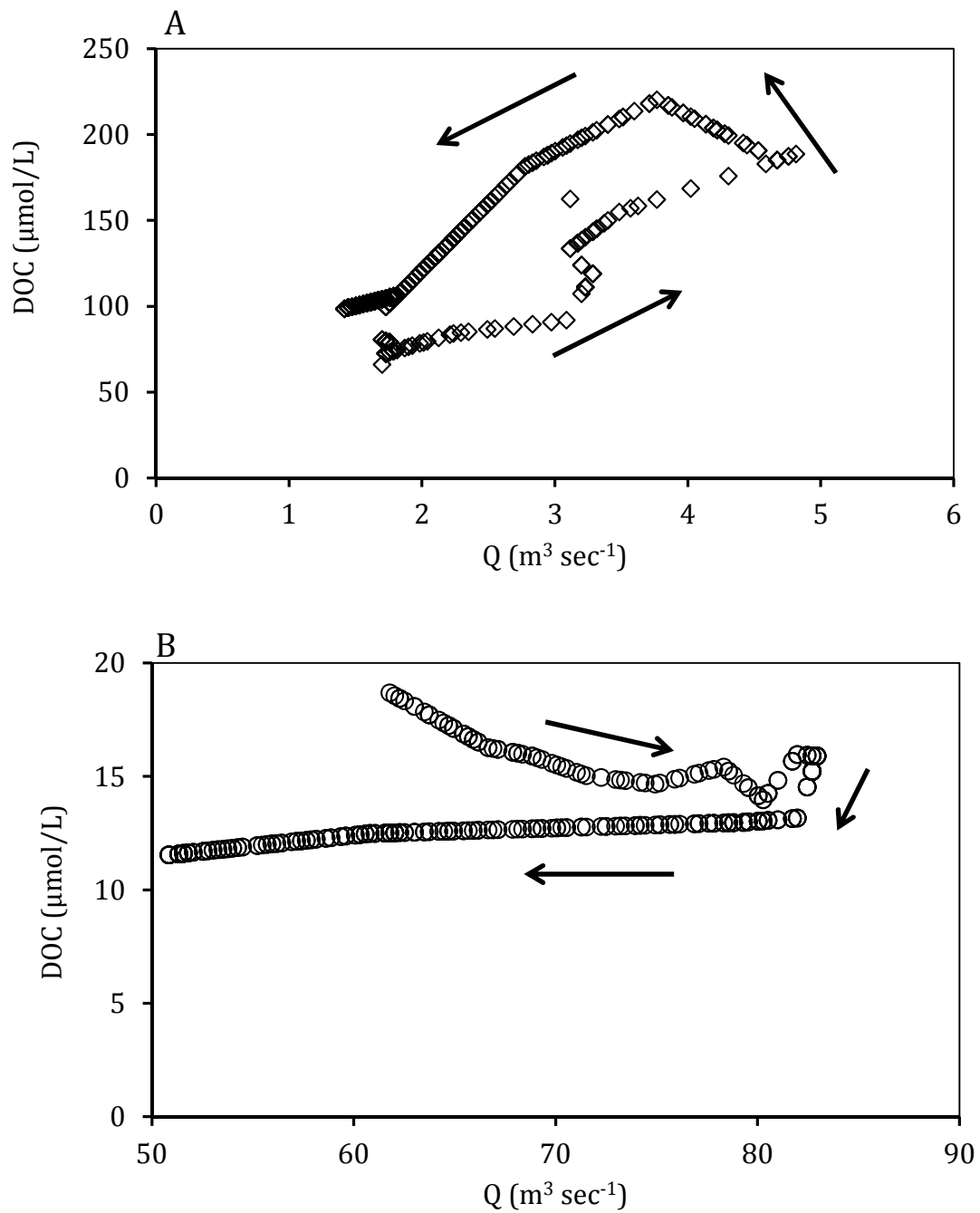


Figure C.1: Estimated dissolved organic carbon (DOC) concentrations vs. discharge recorded at the USGS Montana Creek gaging station (15052800) (A) and estimated discharge from the Mendenhall Glacier (B) during a melt season storm event.

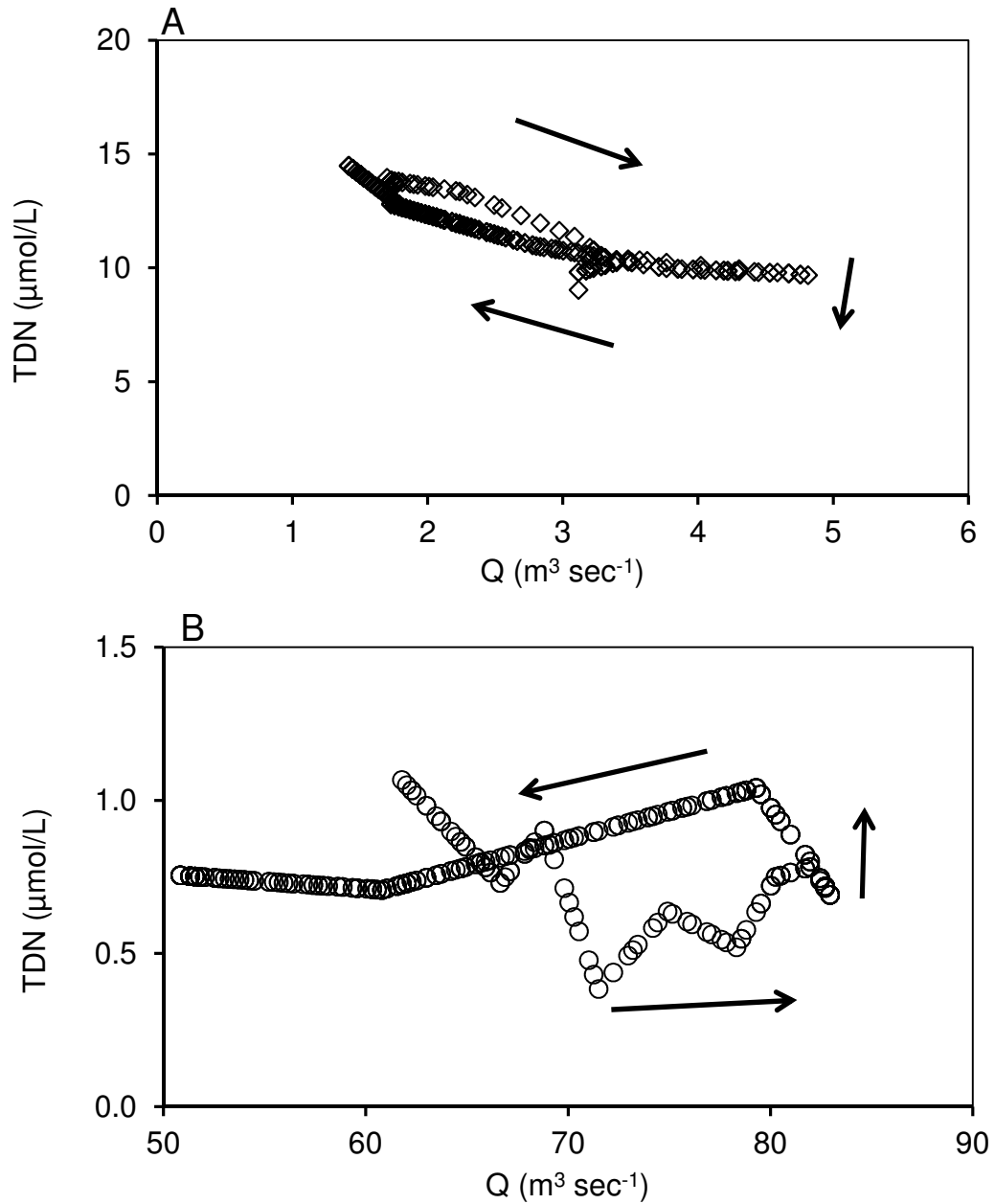


Figure C.2: Estimated total dissolved nitrogen (TDN) concentrations vs. discharge recorded at the USGS Montana Creek gaging station (15052800) (A) and estimated discharge from the Mendenhall Glacier (B) during a melt season storm event.

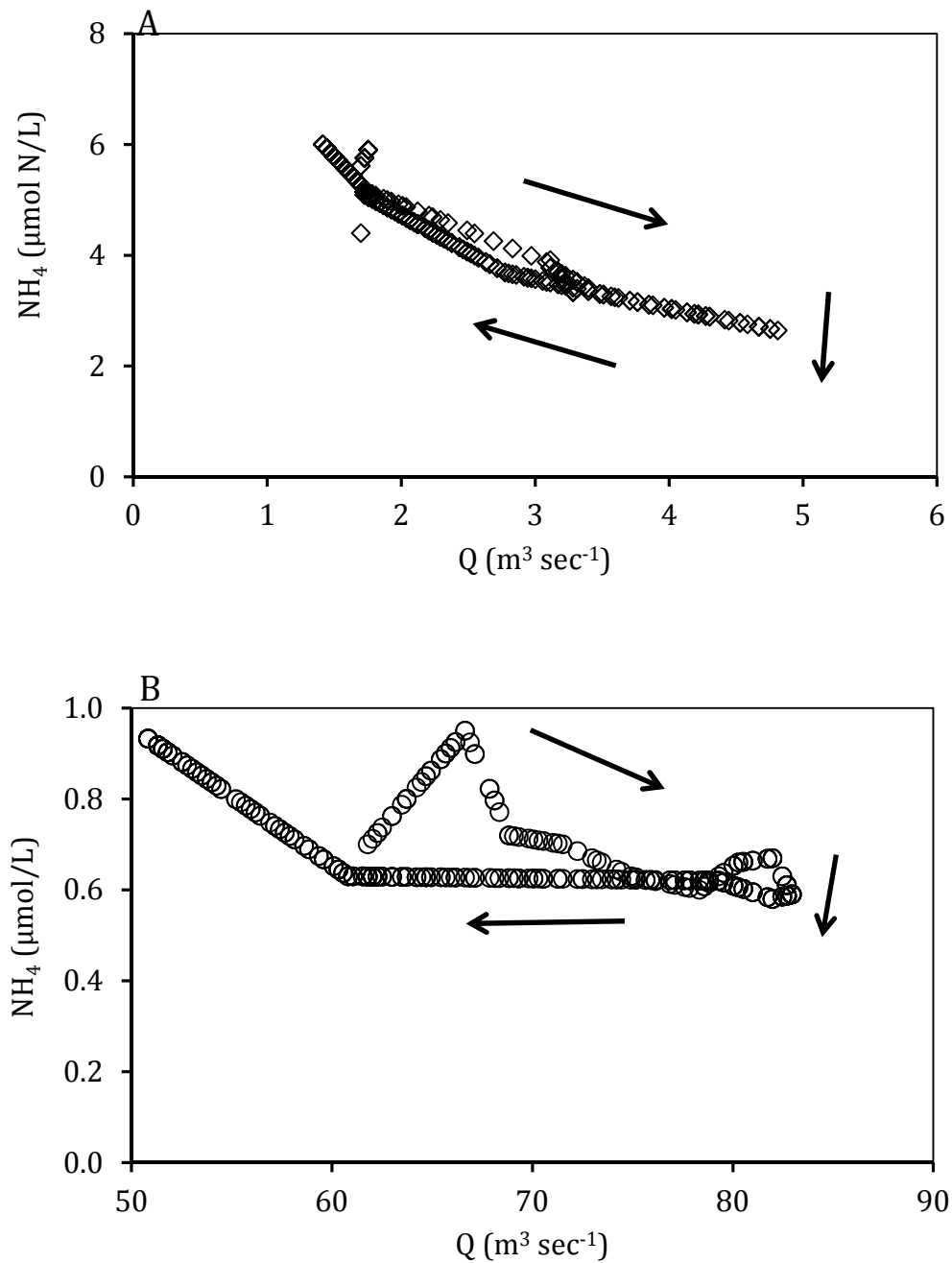


Figure C.3: Estimated ammonium (NH_4^+) concentrations vs. discharge recorded at the USGS Montana Creek gaging station (15052800) (A) and estimated discharge from the Mendenhall Glacier (B) during a melt season storm event.

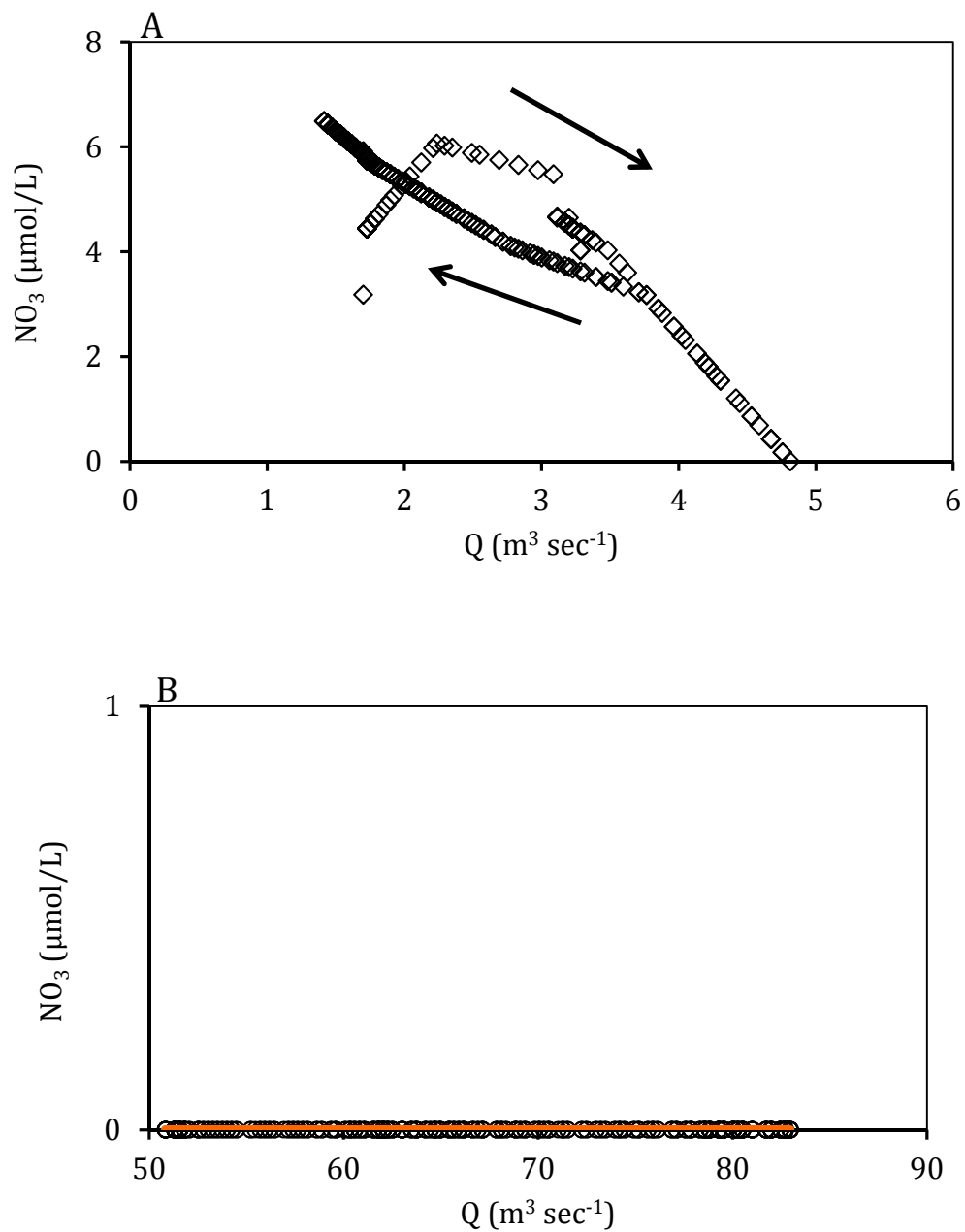


Figure C.4: Estimated nitrate (NO_3^-) concentrations vs. discharge recorded at the USGS Montana Creek gaging station (15052800) (A) and estimated discharge from the Mendenhall Glacier (B) during a melt season storm event.

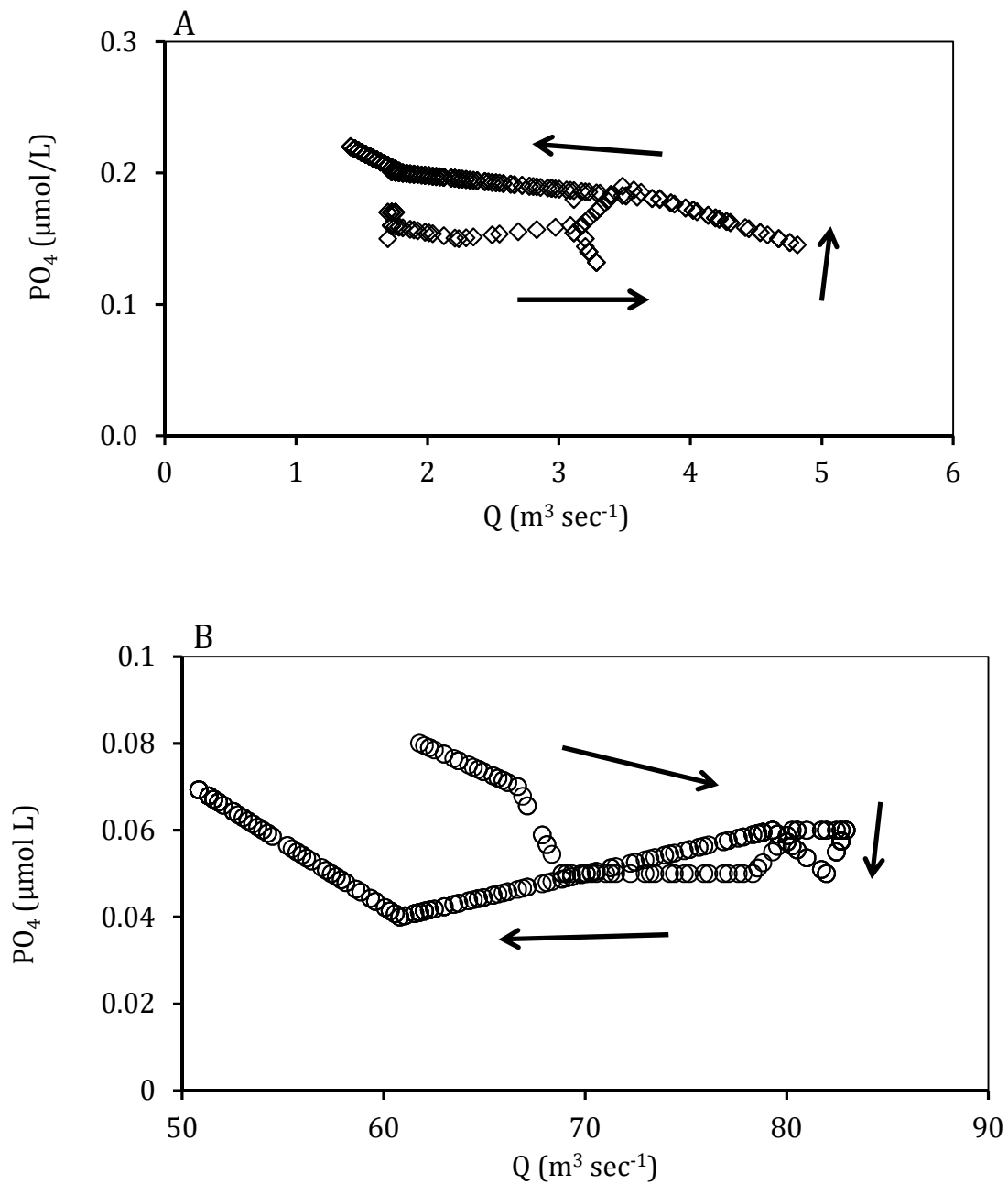


Figure C.5: Estimated phosphate (PO_4^{3-}) concentrations vs. discharge recorded at the USGS Montana Creek gaging station (15052800) (A) and estimated discharge from the Mendenhall Glacier (B) during a melt season storm event.

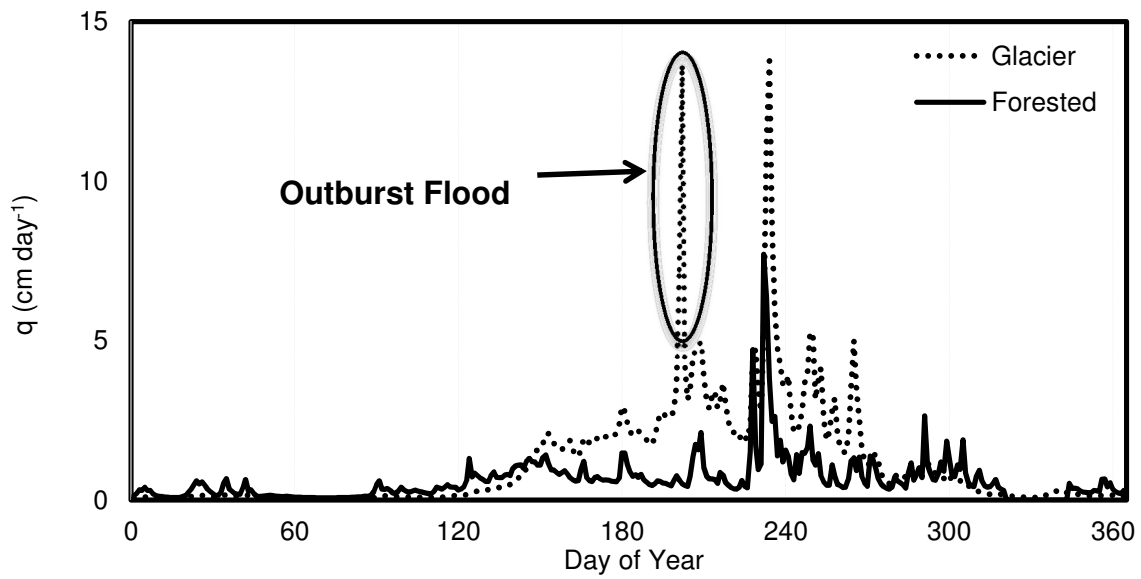


Figure C.6: Comparison of daily specific discharge (q , cm day⁻¹) values in forested Montana Creek and glacial Mendenhall River during 2011. Outburst flood in Suicide Basin of the Mendenhall Glacier highlighted.

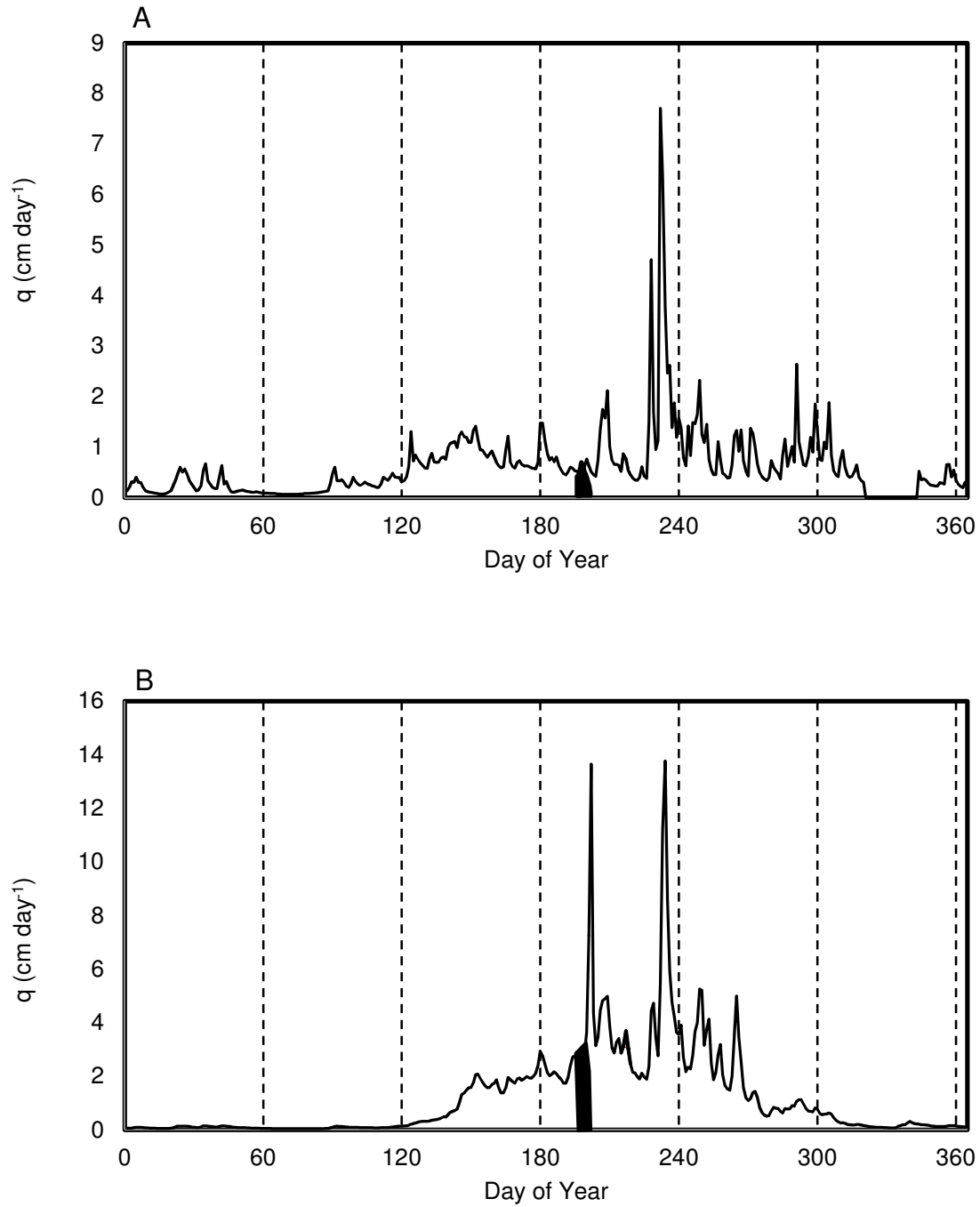


Figure C.7: Specific daily discharge values at the USGS Montana Creek gaging station (15052800) (A) and the Mendenhall River gaging station (15052500) (B) for 2011. Specific discharge was calculated as discharge per watershed area. The monitored period in this study from August 3rd to August 7th is highlighted in red on each graph.