

ANALYSIS OF GLACIAL STREAMS ON MOUNT RAINIER:
TEMPORAL AND SPATIAL TRENDS IN GLACIAL MELTWATER

by

Kristin Wilmes

A Thesis
Submitted in partial fulfillment
of the requirements for the degree
Master of Environmental Studies
The Evergreen State College
June 2017

© 2017 by Kristin Wilmes. All rights reserved.

This Thesis for the Master of Environmental Studies Degree

by

Kristin Wilmes

has been approved for

The Evergreen State College

by

{Erin Martin, Ph. D.}
Member of the Faculty

Date

ABSTRACT

Analysis of Glacial Streams on Mount Rainier: Temporal and Spatial Trends in Glacial Meltwater

Kristin Wilmes

Organic carbon (OC) is stored in glacial environments. During the melt season, some of this OC is exported to downstream aquatic ecosystems in the form of dissolved organic carbon (DOC). The labile quality of OC found in glacial environments can stimulate heterotrophic communities at the base of downstream food webs. The current temporal trends of DOC export in glacial meltwater in Washington are unknown, even though Washington is the second most glaciated state in the country. Here, data collected from glacial meltwater on Mount Rainier displays the highest DOC concentrations occurring early during spring snowmelt (1.5–4.9 mg L⁻¹), with levels decreasing after mid-June and staying consistently low for the rest of the melt season (0.5-1.3 mg L⁻¹). Simple linear regression analysis suggests that DOC concentrations are dependent upon snow depth and the amount of snowmelt, being generally significantly positively correlated ($p < 0.05$) with DOC concentrations. This indicates that snowmelt is likely a mobilizer of DOC from glacial environments during the spring when snow depths are high. This also likely indicates that snowmelt mobilizes any terrestrial DOC deposited on the snow surface. High concentrations of sulphate, reflecting the composition of underlying rocks and minerals, generally occur around the same time as high DOC concentrations suggest that some of the meltwater in the glacial streams originates beneath the glacier. Given the association with DOC concentrations, this may suggest DOC is also mobilized from the drainage system beneath the glacier. As such, the spring appears to be a time of high DOC export from glaciers. With projections of decreasing snow pack, earlier snowmelt and disappearing glacial ice, sources of glacially-derived DOC will decrease and may display peak concentrations at different times. These changes could result in changes to the structure of glacial streams on Mount Rainier.

Table of Contents

1. Introduction.....	1
2. Literature Review.....	5
2.1 Glacial Melt Season Drainage Dynamics.....	6
2.2 Dissolved Organic Carbon in Glacial Environments.....	9
2.3 Glaciers Local to the Pacific Northwest.....	15
2.4 Dissolved Organic Carbon in the Food Web.....	18
2.5 Using Major Ions to Understand Chemical Weathering Processes in the Subglacial Environment.....	20
3. Methods.....	27
3.1 Research Design.....	27
3.2 Sampling Locations.....	29
3.3 Geology of Mount Rainier.....	32
3.4 Field Methodology.....	33
3.5 Lab Methodology.....	35
3.6 Statistical Analysis Methods.....	38
4. Results.....	38
4.1 Dissolved Organic Carbon Analysis.....	38
4.2 Other Parameters: pH, alkalinity and pCO ₂	47
4.3 Major Ion Analysis.....	50
5. Discussion.....	62
5.1 Temporal and spatial patterns of DOC export.....	62
5.2 Chemical weathering patterns in the subglacial environment.....	67

5.3 The effects of glacial area on DOC and major ion export: The implications of continued glacial recession and climate change.....73

6. Conclusion.....76

List of Figures

Figure 1: Figure displaying the evolving subglacial drainage system for an alpine (temperate) glacier. A) Snow melt dominates early in the melt season. B) Snow melt retreats up the ice and the exposed ice develops crevasses and moulins rerouting meltwater to the base of the glacier. C) The continued retreat of the snow line affects the development of the drainage system beneath the ice. It transitions from a distributed system to a channelized system as the snow line retreats. (as cited in Brown, 2002).....	8
Figure 2: Glacier DOC concentrations. a–e, Average concentration of DOC in cryoconites (a), surface (b), englacial (c) and basal ice (d) and in glacier melt water (e) for the AIS, GIS and MGL. Red dots indicate the single values for each entity (Hood et al., 2015).....	10
Figure 3: Reconstruction of glaciers showing the glacial recession on Mount Rainier from 1896 to 1994 (Hekkers & Thorneycroft, 2011).....	16
Figure 4: Zoomed out view of the glaciers the feed the rivers where the sampling locations are located. Emmons Glacier is about 4.3 mi ² in area and the Inter Glacier situated next to Emmons Glacier is about 0.3 mi ² in area. The White River comes from the glacial melt off Emmons Glacier and the Inter Fork River comes from the melt waters of the Inter Glacier (Hekkers & Thorneycroft, 2011).....	30
Figure 5: Zoomed-in view of the field area and sites on Mount Rainier (adapted from USGS, 2016).....	31
Figure 6: DOC concentrations in the upper and lower White River sites over the glacial melt season.....	39
Figure 7: DOC concentrations at the upper and lower Inter Fork White River sites over the glacial melt season.....	40
Figure 8: DOC concentrations in the two non-glacial creek sites over the glacial melt season.....	40
Figure 9: Relationship between DOC (mg L ⁻¹) and snow depth (inches) at the upper Inter Fork White River site.....	43
Figure 10: Relationship between DOC (mg L ⁻¹) and snow depth (inches) at the lower Inter Fork White River site.....	43
Figure 11: Relationship between DOC (mg L ⁻¹) and total 7-day snowmelt (inches) at the lower White River site.....	44
Figure 12: Relationship between DOC (mg L ⁻¹) and total 7-day snowmelt (inches) at the	upper I

Figure 13: Relationship between DOC (mg L^{-1}) and snowmelt (inches) at the lower Inter Fork White River site.....	45
Figure 14: Relationship between DOC (mg L^{-1}) and velocity (m/sec) at the upper Inter Fork White River site.....	45
Figure 15: Relationship between DOC (mg L^{-1}) and velocity (m/sec) at the upper White River site.....	46
Figure 16: Relationship between DOC (mg L^{-1}) and daily precipitation (cm) at the upper White River site.....	47
Figure 17: Alkalinity values ($\mu\text{eq L}^{-1}$) for all glacial and non-glacial streams throughout the field season.....	50
Figure 18: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the upper White River.....	52
Figure 19: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the lower White River.....	52
Figure 20: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the upper Inter Fork White River.....	53
Figure 21: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the lower Inter Fork White River.....	53
Figure 22: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the non-glacial creek 1. Major ion concentrations were much higher initially in the non-glacial creek, so y-axis has a different scale than all the other graphs.....	54
Figure 23: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the non-glacial creek 2.....	54
Figure 24: HCO_3^- concentrations ($\mu\text{eq L}^{-1}$) in the glacial and non-glacial streams over the field season.....	55
Figure 25: Concentrations of SO_4^{2-} ($\mu\text{eq L}^{-1}$) for the glacial and non-glacial streams over the field season.....	56
Figure 26: Visual comparison of SO_4^{2-} ($\mu\text{eq L}^{-1}$) and DOC (mg L^{-1}) at both White River sites over the field season.....	57
Figure 27: Visual comparison of SO_4^{2-} ($\mu\text{eq L}^{-1}$) and DOC (mg L^{-1}) at both Inter Fork River sites over the field season.....	57
Figure 28: C-ratio values for the White River, the Inter Fork White River and the non-glacial creeks over the field season.....	59
Figure 29: The comparisons of HCO_3^- ($\mu\text{eq L}^{-1}$) and SO_4^{2-} ($\mu\text{eq L}^{-1}$) for the upper White River site.....	60

Figure 30: The comparisons of HCO_3^- ($\mu\text{eq L}^{-1}$) and SO_4^{2-} ($\mu\text{eq L}^{-1}$) for the lower White River site.....60

Figure 31: The comparisons of HCO_3^- ($\mu\text{eq L}^{-1}$) and SO_4^{2-} ($\mu\text{eq L}^{-1}$) for the upper Inter Fork White River site.....61

Figure 32: The comparisons of HCO_3^- ($\mu\text{eq L}^{-1}$) and SO_4^{2-} ($\mu\text{eq L}^{-1}$) for the lower Inter Fork White River site.....61

List of Tables

Table 1: Data for snow depth, snowmelt, precipitation and temperature (NOAA, 2016).....	41
Table 2: Correlation results of DOC concentration with multiple parameters. R-value based on correlation analysis using Spearman’s ρ due to the data being not normally distributed. Significant p values reported.....	42
Table 3: pCO ₂ values at the glacial and non-glacial stream sites over the field season...	48
Table 4: pH values for the glacial and non-glacial sites over the field season.....	48
Table 5: Alkalinity values ($\mu\text{eq/L}$) for the glacial and non-glacial streams over the field season.....	49
Table 6: Average major ion concentrations ($\mu\text{eq/L}$) for all glacial and non-glacial stream sites.....	51

Acknowledgements

I would like to thank my thesis advisor, Dr. Erin Martin, for providing me with encouragement and guidance through the thesis process. I would also like to thank the Science Support Center staff for providing me with equipment to complete this project. A special thanks to Jenna Nelson who was my Science Instruction Technician and helped me with many different aspects of my laboratory work, Sina Hill who helped me with laboratory equipment, and Kaile Adney who always made sure I had all the filters necessary for this project! Another big thank you to the Evergreen State College for the Student Foundation Activity Grant, as well as the Mazama's Club for providing me with a grant that helped me fund this project. One last huge thank you to my friends and family who supported me through this long project, especially my husband Tal, who helped me with all the field work!

1. Introduction

Worldwide, glaciers contribute a surprisingly large source of carbon to downstream environments, around 1.04 ± 0.18 teragrams (Tg) of dissolved organic carbon (DOC) per year to freshwater and marine ecosystems (Hood, Battin, Fellman, O'Neel & Spencer, 2015). Mountain glaciers contribute the largest amount of DOC to these aquatic environments (Hood et al., 2015). Since glaciers are sensitive to environmental changes, they are great indicators of climatic changes. Over the last century, the mountain glaciers in Washington have consistently receded. With Washington being the second most glaciated state in the country, these mountain glaciers are an important source of freshwater and DOC to local streams and rivers (Hekkers & Thorneycroft, 2011). Mount Rainier's glaciers alone contribute meltwater to six major rivers in the region (National Park Service [NPS], 2016).

Recent research has shown that the DOC from glacial environments is more labile in nature than other forms of carbon (Hood et al., 2009; Hood et al., 2015). The labile nature found in some of this glacially derived DOC is a product of microbial communities living on the glacial surface and beneath the glacier (Anesio, Hodson, Fritz, Psenner & Sattler, 2009; Bhatia et al., 2013; Sharp et al., 1999; Skidmore, Fought & Sharp, 2000; Wadham et al., 2004; Wadham et al., 2010). Microbial communities found in holes on the glacial surface perform photosynthesis resulting in the accumulation of organic carbon (OC) (Anesio et al., 2010; Anesio et al., 2009), while OC found beneath the glacial ice is from soils and vegetation that were overridden by the ice during the last ice age (Bhatia et al., 2013; Wadham et al., 2010). Microbial communities have been discovered living beneath glaciers that can mobilize and metabolize this source of ancient

OC. This can not only degrade the OC and make it more labile, but it can produce CO₂ beneath the ice that can drive chemical weathering processes (Barker, Sharp, Fitzsimons & Turner, 2006; Lawson et al., 2104). The more labile or bioavailable nature of glacially derived DOC stimulates heterotrophic communities in downstream ecosystems, which influences organisms in the rest of the aquatic food web (Hood & Scott, 2008; Hood et al., 2009; Hood et al., 2015; Fellman et al., 2015).

Warmer atmospheric temperatures caused by climate change are resulting in a decreasing snowpack during the winter months and earlier snowmelt in the spring (International Panel on Climate Change [IPCC], 2014). With projections of glacial recession continuing, the current temporal trends of DOC export will shift in time and quantity. This shift in timing and quantity of glacially derived DOC will likely affect the structure of the local aquatic food webs that rely on this flux of labile OC (Hood & Scott, 2008; Hood et al., 2009; Hood et al., 2015) and freshwater during the dry summer months when other mountainous ephemeral streams dry up and no longer provide any DOC to the larger river systems.

In Washington, there are numerous glaciers in the Cascade and Olympic Mountains. These glaciers feed many important rivers in the Pacific Northwest, but similar to other regions, almost all the glaciers have been receding for decades (NPS, 2016). These rivers are home to many important aquatic species, like salmon, which the Washington Department of Fish and Wildlife [WDFW] (2017) have listed as a federally threatened species. A study completed by Fellman et al. (2015) tracked glacially derived OC through different trophic levels in an Alaskan stream, from macroinvertebrates to fish. A shift in timing in the OC export through glacial meltwater would potentially have

effects on the local aquatic food web, including native fish species in Washington's rivers and streams.

As glaciers recede the amount of water being exported from the glacial environment changes. Studies have shown that initially there may be an increase in meltwater, but eventually glacial recession leads to a decrease in meltwater export as the glacier gets smaller (Fountain & Tangborne, 1985). This change in meltwater may affect the amount of DOC exported from glacial environments. Another consideration is that as glaciers recede terrestrial succession follows the retreating ice, so in the coming decades there will likely be a shift from glacially-derived DOC to terrestrial DOC sources (Fellman et al., 2014; Hood et al., 2008). To address the question of how glacial recession may affect DOC export from glacial environments, this study examined the DOC export from the meltwater of one of the largest glaciers on Mount Rainer, Emmons Glacier, and one of the smallest glaciers, Inter Glacier. By examining data from these two differing glaciers it may be possible to understand changes that could occur as glaciers in the region continue to recede.

Presently, there are multiple studies that have examined the temporal trends of OC export from larger ice sheets, like the Greenland Ice Sheet and the Antarctic Ice Sheet, and in mountainous glaciers in Alaska, the European Alps and the Himalayan Mountain range (Barker et al., 2006; Bhatia et al., 2013; Hood et al., 2008; Hood et al., 2009; Lawson et al., 2014; Spencer et al., 2014; Wadham et al., 2010).). There have been no such studies completed on the DOC export from glacial meltwater in the Pacific Northwest region. Data from these other glaciated regions cannot be extrapolated to the Pacific Northwest because they do not have the same climate and lithology which can

result in differing DOC trends. Without any data on the current temporal trends of DOC export to proglacial streams, there will be no way to understand how these trends will change with continued glacial recession or if it will affect local aquatic ecosystems.

The purpose of this study is to gather data on the current temporal and spatial trends in DOC and major ion export in glacial meltwater from Emmons Glacier and Inter Glacier on Mount Rainier. Major ion export is important because it can elucidate flow paths by which meltwater is leaving the glacier, and can therefore clarify pathways of carbon export within the glacier. This research will provide local natural resource managers and policy makers with information to use to help protect our natural resources as climate change continues to affect the environment and local ecosystems. This study examines how DOC and major ion concentrations in streams draining glaciers change over the summer meltwater period. To my knowledge this study provides a first estimate of the potential delivery of carbon to downstream environments that originate from glacial environments in the state of Washington. The study will also provide an understanding of how the glacial area at the streams' headwaters influences the DOC and major ion concentrations. By looking at streams with different glacial sizes at the headwaters, insight into how DOC and major ions concentrations may change as glaciers recede can be concluded. To answer these questions, this study examined DOC and major ion concentrations from two glacial streams on Mount Rainier, as well as two non-glacial streams for comparison

2. Literature Review

The purpose of this literature review is to provide background information as to why studying the export of dissolved organic carbon (DOC) and major ions from bulk glacial meltwater on Mount Rainier is crucial for local and global comprehension of how DOC influences food web structures in proglacial aquatic ecosystems. Previous studies have examined the export of glacial organic carbon (OC) from mountain glaciers in Alaska, India, Norway, Sweden and the European Alps, as well as on the Antarctic Ice Sheet (AIS) and the Greenland Ice Sheet (GIS) (Barker et al., 2006; Bhatia et al., 2013; Hood et al., 2008; Hood et al., 2009; Lawson et al., 2014; Spencer et al., 2014; Wadham et al., 2010). These studies all occur in regions displaying a variety of differing climates, latitudes and lithologies. The varying results from these studies presents evidence that DOC and major ion export from glacial environments can differ depending on the geology of the region, the climate of the region, the time in the glacial melt season, and the size of glacial coverage. Studies have shown how this glacially-derived OC is integrated through food webs in aquatic ecosystems (Fellman et al., 2015) and how it can affect these ecosystems (Slemmons, Saros and Simon, 2013). To my knowledge there have been no studies examining the export of DOC from bulk glacial meltwater in the Pacific Northwest. The research highlighted in this literature review gives an overview of the methods used to examine DOC export in glacial meltwater and the methods used to gain insight into the unique properties of this glacially derived OC. This literature review also covers the methods used to determine chemical weathering patterns and drainage system dynamics beneath the ice by utilizing the major ion concentrations.

This research project will add a new data set from a region previously unstudied to the larger pool of data on carbon export from glacial meltwater. The data gathered can be beneficial on a local level, giving natural resource managers an understanding of the current temporal and spatial trends of glacial DOC and major ion export. With this knowledge, hopefully they can properly protect our local natural resources as these export trends will likely shift with the projected changing snowpack, precipitation, temperature and ultimately the receding glaciers.

2.1 Glacial Melt Season Drainage Dynamics

Glaciers have different temperature regimes allocating them into three categories: 1) temperate (warm-based) glaciers, 2) subpolar (polythermal) glaciers and 3) polar (cold-based glaciers) (as cited in Brown, 2002, p.857-858). The glaciers found on Mount Rainier are temperate (warm-based) glaciers, so this section focuses on the melt season drainage dynamics of this specific type of glacier. The significance of warm-based glaciers is they have water between the glacial ice and the bedrock because the glacial ice is at the pressure melting point (Bennet & Glasser, 1996) compared with cold-based glaciers that are frozen to the bedrock because the glacial ice is below the melting point (Tranter et al., 1996).

As the melt season begins in Washington, typically early to late May depending on the year, snow melt dominates stream runoff in the alpine regions. At this stage in the melt season, most the water in the streams beyond the glacier comes from snow melt instead of glacial ice melt (see figure 1, part a) (Collins, 1979; Fountain & Walder, 1998). Before any ice is exposed, the snowmelt percolates through the snow and firn (granulated

snow that has not yet been compacted into glacial ice) until it reaches the ice below and where it is either stored in the firn until later in the melt season or it is exported down the ice to proglacial (beyond the ice) streams (Fountain & Walder, 1998) During this early stage of the melt season the drainage system beneath alpine glaciers is considered to be a distributed system, with low passages and cavities resulting in slower flowing water (Brown, 2002; Fountain & Walder, 1998).

As the snowline retreats up the glacial ice, snow and ice melt initially runoff the top of the glacial ice to proglacial streams. As more ice is exposed, moulins and crevasses begin to form in the glacier. Once these moulins and crevasses are established the melt water travels to the base of the glacier through these routes (see figure 1, part b) (Brown, 2002; Fountain & Walder, 1998). This influx of water from the surface of the glacier to the base of the glacier is generally a quick process which causes the drainage system to evolve into a more channelized system comprised of larger channels and faster flowing water (Brown, 2002; Fountain & Walder, 1998).

During the transition from the distributed system to the channelized system the drainage system is often closed to the atmosphere since the channels fill up quickly with water and become pressurized before larger channels are cut into the sediment and ice under the glacier (Fountain & Walder, 1998). The channelized drainage system continues to develop beneath the ice following the retreating snow line. As more glacial ice is exposed more crevasses and moulins form in the glacier. This allows more meltwater to travel to the drainage system beneath the ice (see figure 1, part c) (Brown, 2002; Fountain & Walder, 1998).

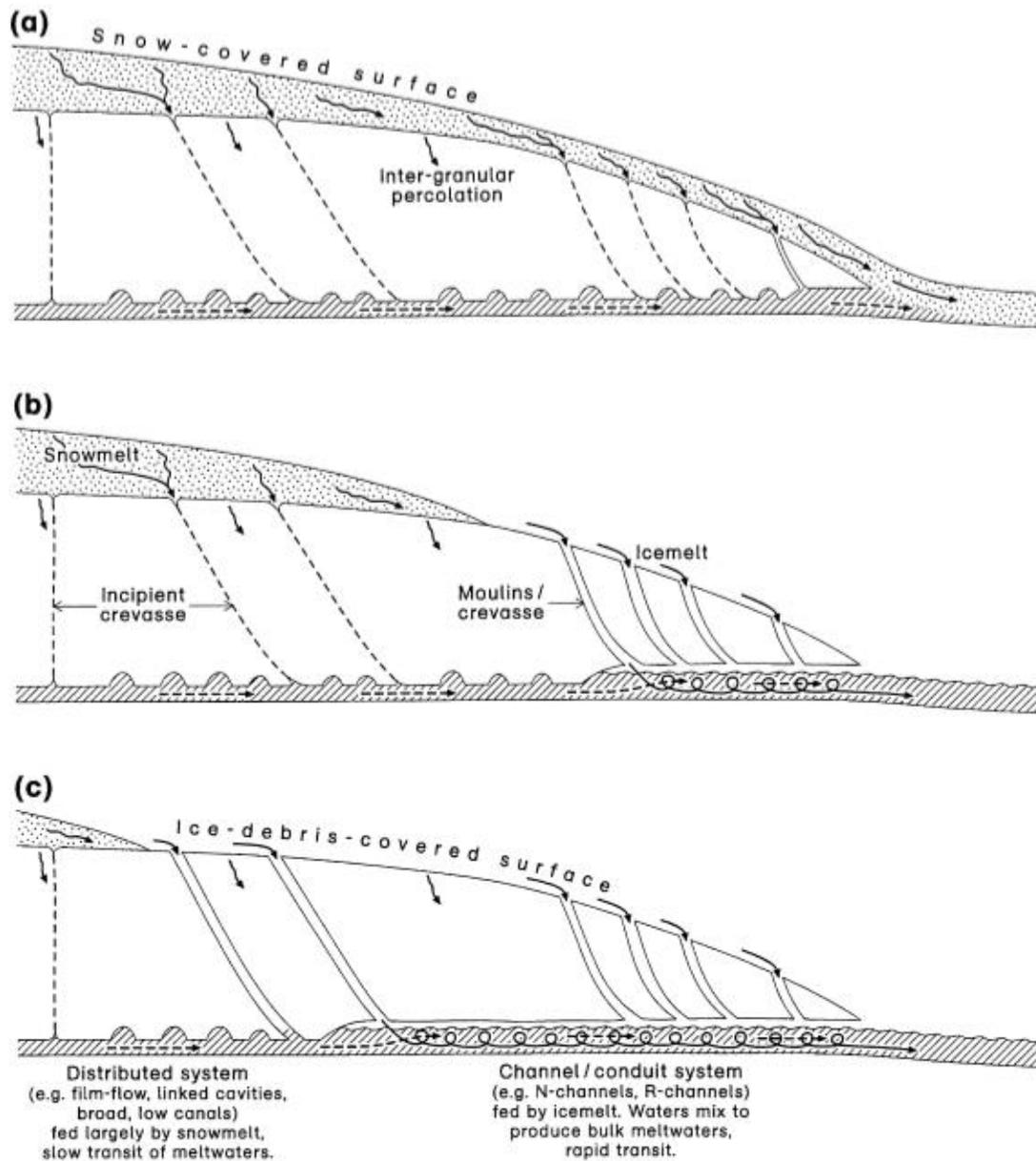


Figure 1: Figure displaying the evolving subglacial drainage system for an alpine (temperate) glacier. A) Snow melt dominates early in the melt season. B) Snow melt retreats up the ice and the exposed ice develops crevasses and moulins rerouting meltwater to the base of the glacier. C) The continued retreat of the snow line affects the development of the drainage system beneath the ice. It transitions from a distributed system to a channelized system as the snow line retreats. (as cited in Brown, 2002).

2.2 Dissolved Organic Carbon in Glacial Environments

Mountain glaciers and ice sheets play a significant role in the global carbon cycle. These frozen settings contain organic carbon (OC) in the supraglacial (the glacial surface), englacial (situated in the glacier) and subglacial (beneath the glacial ice) environments. The export of this OC to proglacial (anything immediately beyond the terminus of the mountain glacier) aquatic ecosystems occurs through snowmelt and glacial meltwater over the summer months (Lawson et al., 2014; Spencer et al., 2014). Mountain glaciers and ice sheets also export major ions to proglacial streams as chemical weathering occurs in the subglacial drainage system resulting in the ions accumulating in the meltwater (Brown, 2002).

Glaciers and ice sheets globally store around 70% of the Earth's freshwater. With climate change causing an increase in atmospheric temperatures, glaciers are receding at increased rates and supplying more freshwater to downstream environments (Hood et al., 2015, Slemmons et al., 2013). The recession of mountain glaciers is occurring at faster rates than the recession of larger ice sheets, so they provide important insight into how the timing and magnitude of OC export to proglacial stream environments will occur (Hood et al., 2015).

A study done by Hood et al. (2015) calculated the amount of DOC currently stored and then released from mountain glaciers and ice sheets across the world (see figure 2). The study used data on the amount of DOC concentrated in englacial ice core samples from multiple mountain glacier (MGL) sites, as well as the Greenland Ice Sheet (GIS) and the Antarctic Ice Sheet (AIS) to calculate the global mass of DOC stored in glacial environments (Hood et al., 2015). The research team found that the global

estimate of dissolved organic carbon (DOC) in glaciers is 4.48 ± 2.79 petagrams of carbon (PgC) (Hood et al., 2015). This is in comparison to the northern arctic permafrost regions that store around 1672 PgC in the frozen soil (Tarnocai et al., 2009). Hood et al. (2015) went on to calculate the amount of DOC stored in different glacial regions, with 93% (4.19 ± 2.78 Pg C) of the glacial DOC stored in the AIS, 5% ($.22 \pm .06$ Pg C) stored in the GIS and 2% ($.07 \pm .01$ Pg C) stored in mountain glaciers. As glacier and ice sheets continue to melt this OC will be released to proglacial stream and marine environments.

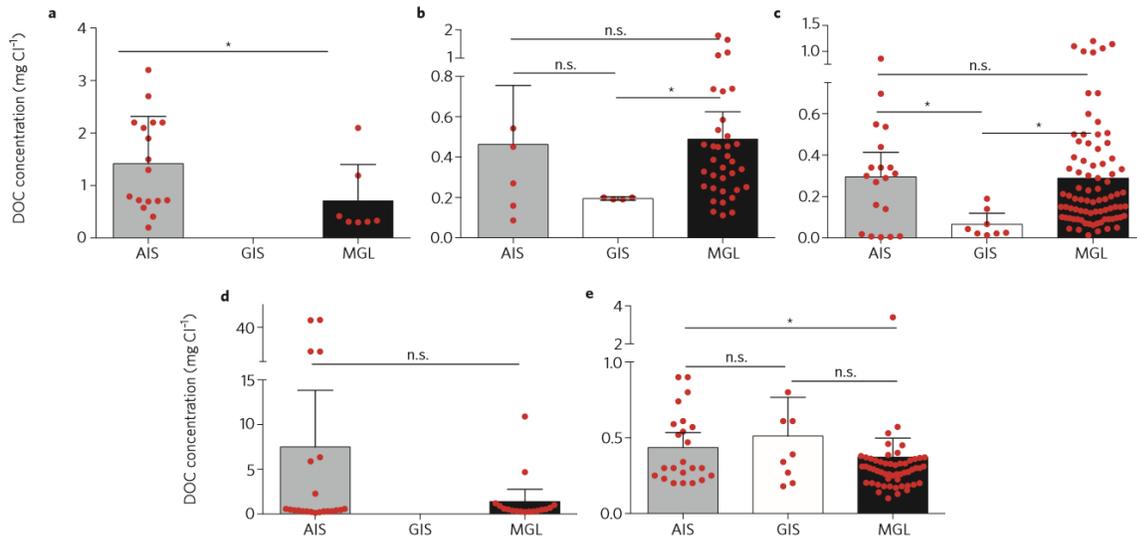


Figure 2: Glacier DOC concentrations. a–e, Average concentration of DOC in cryoconites (a), surface (b), englacial (c) and basal ice (d) and in glacier melt water (e) for the AIS, GIS and MGL. Red dots indicate the single values for each entity (Hood et al., 2015).

Although the AIS and GIS store significantly more DOC than mountain glaciers, the mountain glaciers are receding at faster rates than the large ice sheets, which results in them exporting a higher amount of DOC to proglacial ecosystems (see figure 2). Hood et al., (2015) estimated that globally the annual export of DOC from glacial meltwater is

around 1.04 ± 0.18 teragrams of carbon (TgC), which is less than the carbon that evades rivers, streams, lakes and reservoirs every year but it is still significant. According to Raymond et al., (2013) around $1.8 \pm .25$ PgC evades from streams and rivers every year, while $0.32 \pm .26$ to $.52$ PgC comes from lakes and reservoirs annually. When broken up into glacial region, MGL export 56% (0.58 ± 0.07 TgC) of the DOC to proglacial aquatic ecosystems annually, compared to the GIS that exports 0.22 ± 0.04 TgC yr^{-1} and the AIS that exports 0.24 ± 0.16 TgC yr^{-1} (Hood et al., 2015). Mountain glaciers across the world come from different regions with different geology and climates, so they may have varying concentrations of DOC exported through glacial meltwater.

Currently, mountain glaciers experience a higher glacial mass loss per year than larger ice sheets due to glacial recession occurring at quicker rates in the mountain glaciers (Hood et al., 2015). One study found that globally, around 0.14 TgC of the DOC exported every year to proglacial aquatic ecosystems was the result of glacial mass loss (Hood et al., 2015). Since the glacial mass loss occurring in mountain glaciers does not represent a steady flux over time, this means that as glaciers continue to recede, there will be a change in the amount of DOC exported to proglacial environments (Hood et al., 2015). The timing of glacial melt will also change as climate change continues to cause changes in weather patterns, snowmelt, and ultimately glacial recession. The amount of snowpack is likely to diminish with rising atmospheric temperatures, leading to earlier snowmelt or no snow, and a change in glacial melt discharge (Department of Ecology [DOE], 2007; Grandshaw & Fountain, 2006; NPS, 2016). This highlights the importance in understanding the role mountain glaciers play in the global carbon cycle, since they are currently contributing more DOC to aquatic environments than the larger ice sheets.

Over the last one hundred years, the air temperature in alpine regions has increased by an average of 0.3°C per decade resulting in continual glacial recession and making mountainous glaciers an important signifier of climate change (Slemmons et al., 2013). Studies have shown that glacial coverage is a factor influencing the timing, magnitude and source of OC and major ion export, so comparing mountain glaciers of different sizes may provide critical insight into how this export will change as glaciers continue to recede (Fellman, Hood, Spencer, Stubbins & Raymond, 2014; Hood and Scott, 2008). Results from studies comparing watersheds with differing glacial coverage showed that decreasing glacial coverage caused a decrease in the glacially derived DOC concentrations but an increase in terrestrial DOC concentrations (Fellman et al., 2014; Hood & Scott, 2008). This is because vegetative succession progresses as the ice retreats in alpine regions.

In non-glacial streams and rivers, OC typically comes from terrestrial sources, like plant or soil material, but many glacial streams begin above the tree line so the stream is receiving less terrestrial sources of OC (Fellman et al., 2015; Hood et al., 2009). Instead, these glacial stream ecosystems rely on the delivery of OC from the snow and glacial meltwater. Recent studies have shown that the OC from glacial environments is typically more labile, or bioavailable, to aquatic ecosystems in comparison to OC from terrestrial sources (Barker et al., 2006; Bhatia et al., 2013; Hood et al., 2009; Lawson et al., 2014; Spencer et al., 2014). A study done by Hood et al., (2009) found that watersheds with large glacial coverage displayed an increase in the bioavailability of the carbon. This means that the OC is readily available to heterotrophic communities that make up the base of the aquatic food web. Export of glacial DOC can stimulate the

heterotrophic communities, which then can fuel production in throughout the rest of the food web (Bhatia et al., 2013; Fellman et al., 2015; Hood et al., 2009; Hood et al., 2015).

OC on the surface of these glaciers and ice sheets comes from cryoconite holes, which harbor microbial communities (Anesio et al., 2009; Anesio et al., 2010; Porazinska, Fountain, Nylén, Tranter & Virginia, 2004). These cryoconite holes form due to the deposition of organic matter onto the glacial surface. The sun warms this organic matter, which is darker than the ice, causing it to melt into the ice. The organic matter deposited on the ice surface comes from terrestrial sources, such as dust and soil deposition, as well as from aerosol particles from anthropogenic combustion products (Anesio et al., 2009; Bhatia et al., 2013; Hood et al., 2009; Hood et al., 2015). The cryoconite holes fill up with water as the melt season begins, which can create an autotrophic system that is home to an extremely diverse microbial community (Anesio et al., 2009). These microbial communities consist of different assemblages of viruses, algae, and bacteria (Anesio et al., 2009; Anesio et al., 2010; Porazinska et al., 2004; Stibal & Tranter, 2007). The microbial communities photosynthesize and grow within the cryoconite holes. (Anesio et al., 2009; Stibal & Tranter, 2007). This in situ primary production results in organic carbon accumulating in these cryoconite holes faster than decomposition from respiration can occur (Anesio et al., 2009; Stibal & Tranter, 2007).

Organic carbon can be flushed from these cryoconite holes early in the melt season when snowmelt is the dominant source of the meltwater. A study by Anesio et al. (2009) used $\Delta^{14}\text{C}$ signatures to track the DOC fixed in cryoconite holes. The research team found that around 10% of this DOC from these holes is exported to proglacial environments early in the season as the snowmelt flushes out some of the carbon from

these autotrophic environments (Anesio et al., 2009). As the melt season continues and the melt regime shifts away from snowmelt, the DOC from the cryoconite holes or from atmospheric deposition can be delivered to the subglacial environment as ice melts on the glacial surface. This ice melt can release frozen DOC from the surface ice and can flush DOC from the cryoconite holes as the water travels across the ice and then to the subglacial environment through moulins and crevasses in the ice (Anesio et al., 2009; Bhatia et al., 2013; Brown, 2002; Fountain & Walder, 1998; Lawson et al., 2014).

The delivery of DOC to the subglacial environment from the surface through cracks and crevasses in the ice is not the only source of OC to the subglacial environment. During the last ice age, soils and vegetation were overridden by glaciers trapping it beneath the ice (Sharp et al., 1999; Skidmore et al., 2000). Recent studies have found evidence that there can be microbial communities in these rock-water-ice interfaces utilizing OC sources and affecting chemical weathering processes occurring beneath the ice and (Bhatia et al., 2013; Hood et al., 2009; Skidmore et al., 2000; Sharp et al., 1999; Wadham et al., 2010). Researchers have discovered that these microbial communities can fix inorganic carbon through the process of chemolithoautotrophy as well as metabolize the organic carbon found in the subglacial environment (Lawson et al., 2014; Skidmore et al., 2000). These microbial processes produce a more labile form of OC that is then exported in the glacial meltwater (Lawson et al., 2014). The carbon products of chemolithoautotrophy and primary production represent a younger source of carbon, while the carbon from soils and vegetation beneath the ice represent an older source of carbon (Lawson et al., 2014; Skidmore et al., 2000). By looking at the $\Delta^{14}\text{C}$ signatures of the DOC, the age of the carbon sources in glacial environments can be

determined. The export of this bioavailable OC occurs as meltwater drains to proglacial aquatic environments from the subglacial environment.

2.3 Glaciers Local to the Pacific Northwest

The Pacific Northwest has mountain glaciers throughout the Cascade Mountain range and in the Olympic Mountains, with ~ 449 km² of glaciers and perennial snow and ice in Washington (Hekkers & Thorneycroft, 2011). This makes Washington the second most glaciated state in the country and these glaciers feed many of the local streams and rivers (Hekkers & Thorneycroft, 2011; NPS, 2016). Mount Rainier has 27 glaciers, and it is the most ice-covered mountain outside of Alaska (NPS, 2016; U.S Geological Survey [USGS], 2014). The glaciers on Mount Rainier feed the headwaters for six major rivers in the region suggesting the potential importance of DOC export from glacial meltwater to food webs downstream (NPS, 2016).

On Mount Rainier, the glaciers have been receding for at least the last 70 years, with ~ 17% mass ice loss on the northern side of the mountain and ~ 26% mass ice loss on the southern side of the mountain (see figure 3) (Hekkers & Thorneycroft, 2011; Nylen, 2001). This mass ice loss from glaciers over large time scales initially causes an increase in meltwater discharge to proglacial environments, but as glaciers continue to get smaller over time the discharge eventually decreases. This changing discharge due to glacial recession demonstrates how shrinking glaciers will cause a change in the timing and magnitude of this meltwater. A study done by Granshaw & Fountain (2006) on glacial recession in the Northern Cascade Mountains found that glacial mass loss in the months of August through September resulted in a 0.1% to 6.0% increase in stream flow.

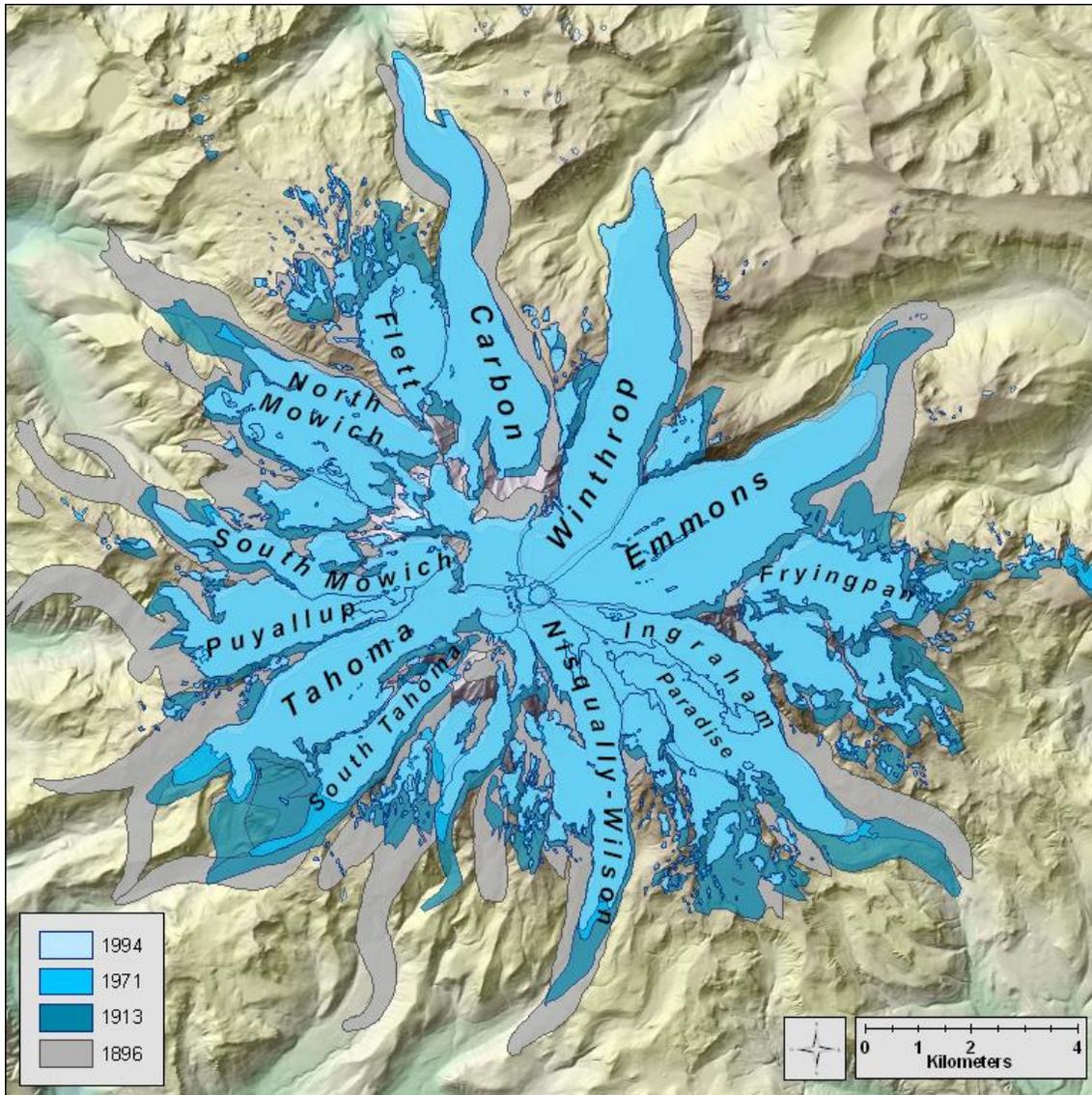


Figure 3: Reconstruction of glaciers showing the glacial recession on Mount Rainier from 1896 to 1994 (Hekkers & Thorneycroft, 2011).

According to the Department of Ecology [DOE] (2007), snowpack in about 73% of the Northern Cascades has decreased and the snowmelt is occurring at earlier times of the year, resulting in stream flows peaking at earlier times in the spring. The reduction of this snowpack is contributing to the increase in stream flow later in the summer months because it is causing the glacial ice surface to be exposed to solar radiation for longer

time-periods. The increase in the late summer months does not result in a huge discharge peak like the spring snowmelt peak, but it still represents an important change since it affects DOC export. In the summer of 2015, Mount Rainier's glacial melt was higher than ever previously observed in the early summer months (NPS, 2016).

Increases in meltwater will ultimately decrease and eventually disappear if trends in mountain glacial recession continue. As of 2007, at least 53 of the glaciers in the North Cascades have disappeared (DOE, 2007) and 82 glaciers have disappeared from the Olympic Mountains since 1980 (Riedel & Larrabee, 2015). As these alpine environments lose glacial coverage, there will be a shift in the DOC introduced to the aquatic ecosystems from glacial sources to terrestrial sources. This occurs as the bare ground left after the glaciers retreat is succeeded by vegetation. Since the DOC exported from glacial environments has been shown to be more labile in nature than DOC from terrestrial sources, this shift in OC sources could have an impact on primary production at the base of the food web (Hood et al., 2009; Hood et al., 2015; Hood & Scott, 2008; Slemmons et al., 2013). This change in primary production could ultimately cause a shift in food webs downstream (Bhatia et al., 2014; Fellman et al., 2015; Hood et al., 2009; Hood et al., 2015). This highlights the importance in gathering a data set for the current spatial and temporal trends in DOC export from meltwater on Mount Rainier. The shift in DOC sources may lead to shifts in our local aquatic food webs, which boast important local species like salmon. Examining data from glaciers with different glacial area may give an insight into the changes that could occur with glacial recession.

2.4 Dissolved Organic Carbon in the Food Web

Hood et al. (2009) conducted a study to understand the labile nature of DOC from glacial meltwater and what this indicates for proglacial aquatic ecosystems. This is possible because glacially derived DOC has a unique isotopic signature in comparison to DOC from non-glacial streams, where it is $\delta^{13}\text{C}$ enriched and $\Delta^{14}\text{C}$ depleted (Fellman et al. 2015; Hood et al., 2009). $\delta^{13}\text{C}$ is useful for understanding the source of carbon, because different carbon sources can have differing $\delta^{13}\text{C}$ values. $\Delta^{14}\text{C}$ is used to understand the age of the carbon. New evidence has revealed that microbial communities in the subglacial environment can survive on the ancient carbon stored beneath the ice and the alteration of the DOC gives the carbon the enriched $\delta^{13}\text{C}$ signature (Hood et al., 2009; Skidmore et al., 2000). This enriched $\delta^{13}\text{C}$ signature signifies the carbon is from autochthonous material found in aquatic ecosystems, meaning the carbon is produced from within the glacial environment (microbial processes) rather than being input from a terrestrial source (Hood et al., 2009). In the study by Hood et al. (2009) the researchers used $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotopes to calculate the percentage of bioavailable carbon in watersheds with differing glacial coverage. The study found that in the Gulf of Alaska, the watersheds with a higher glacial coverage had more labile matter in the meltwater and the glacially-derived C was responsible for the older $\Delta^{14}\text{C}$ age (Hood et al., 2009). This once again highlights the importance of comparing DOC export data between watershed with varying glacial coverage.

A study by Fellman et al. (2015) went further in understanding the role of this glacial DOC in food webs. Using $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$ and $\delta^{15}\text{N}$ (stable nitrogen isotope used to track food sources through food webs) values, the research team tracked the isotopic

signatures of sources (biofilm, particulate organic matter, leaf litter) and consumers (macroinvertebrates, Fish: Coho Salmon and Dolly Vardon). The study found that in a glacial stream in Juneau, Alaska ~ 51% of the carbon in consumers diets was from glacial OC sources in the upper part of the river, while downstream ~ 34% of the carbon in consumers diets was from glacial OC sources (Fellman et al., 2015). These glacial OC sources for consumers are in the form of biofilm that integrates this labile glacial OC into its structure giving it a ^{13}C enriched and ^{14}C depleted signature (Fellman et al., 2015).

The results showing that different fish species in Alaska rely on food sources that assimilate this glacial DOC into their structure demonstrates the importance of OC export from glacial meltwater to proglacial aquatic environments. In Washington, salmon are an important species for multiple reasons and for different groups of people. There are currently 624 populations of salmon in Washington's streams and rivers (WDFW, 2016). These salmon not only rely on the structure of the current food web which may be influenced by glacial DOC export in summer months, but they also rely on consistent cooler stream temperatures, high stream flows and high dissolved oxygen needed for spawning that the glacial melt provides (Slemmons et al., 2013). Glacial recession will affect all these properties, as well as shifting the timing and magnitude of glacial melt in coming years which will have negative impacts on salmon species. Salmon populations in Washington have already been declining over the past century due to loss or destruction of habitat, land use, dams, overfishing and hatcheries, yet salmon are still a very important part of Washington's past and present. According to Washington's Department of Fish and Wildlife (2008), "the non-treaty commercial fishery in Washington waters also contributes an estimated \$38 million in net economic values (net

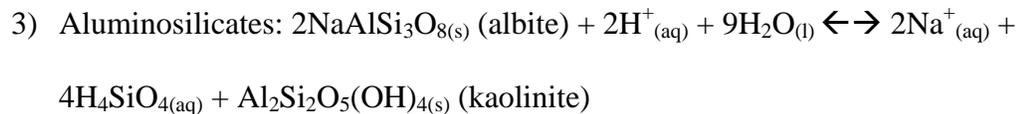
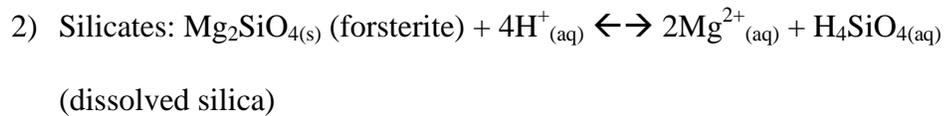
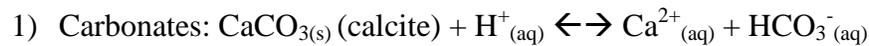
income or profits) and recreational fisheries generate an estimated \$424 million in net economic values.” Salmon are important to local Native American communities who have historically relied on these fish for sustainability and spiritual reasons.

A change in river food web structures could be damaging to multiple fish populations who are already struggling with population decline due to these other issues. By gathering data to form a better understanding of the local DOC export to these proglacial ecosystems, wildlife managers can make informed decisions about how to protect different species in these rivers, like salmon, steelhead and trout.

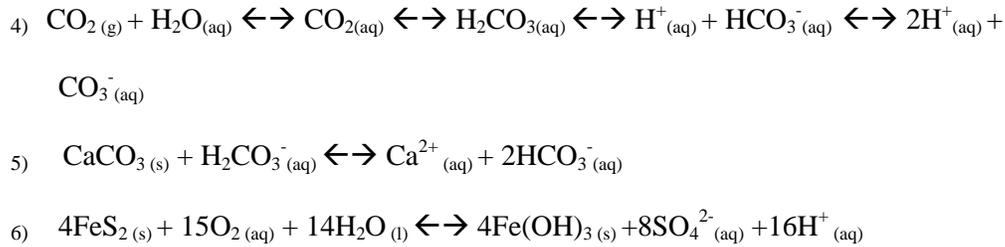
2.5 Using Major Ions to Understand Chemical Weathering Processes in the Subglacial Environment

To gather a general understanding of the chemical weathering occurring in the subglacial environment, this thesis project gathered data on major ion export over the summer months. If microbial communities are present in the subglacial environment and they are oxidizing organic carbon for energy, this could affect the chemical weathering processes and the major ions being assimilated into the meltwater (Bhatia et al., 2013; Wadham et al., 2010). The major ions of interest used here to understand the general chemical weathering patterns beneath the glacial ice are Na^+ , Mg^{2+} , Ca^{2+} , K^+ , HCO_3^- and SO_4^{2-} (Bhatia et al., 2013; Brown, 2002; Raiswell, 1984; Wadham et al., 2010). These ions are important to look at because Ca^{2+} and Mg^{2+} are the generally the first cations weathered into glacial meltwaters, followed by Na^+ and K^+ , while HCO_3^- and SO_4^{2-} are the principal anions (Brown, 2002; Raiswell, 1984).

By looking at the associations between different ions in glacial meltwater, a more detailed comprehension of the chemical weathering processes occurring can be understood. This information can then be compared between the streams with differing glacial coverage to assess whether chemical weathering and major ion export may change as glaciers recede. According to Raiswell, (1984) acid hydrolysis, which is the most important process in weathering rock minerals, is driven by free protons (H^+) in the subglacial environment. This process can be understood by looking at the chemical weathering processes of three minerals commonly found in bedrock beneath glaciers, carbonates, silicates and aluminosilicates (Raiswell, 1984).



The availability of the protons beneath the ice controls the rate of ion dissolution into the subglacial waters. The weathering processes in equations 1, 2, and 3 show the general weathering processes of protons (H^+) on these common minerals, but there are two separate processes that provide these protons (H^+) that drive chemical weathering. The two main processes are carbonate dissolution and sulfide oxidation (Bhatia et al., 2013; Brown, 2002; Raiswell, 1984). The chemical equations for these two processes that result in free protons (H^+) are the dissolution and dissociation of atmospheric CO_2 which involves carbonate reactions (carbonate dissolution) (equation 4 and 5) and sulfide oxidation (equation 6) (Brown et al., 2002; Raiswell, 1984).



As the equations above indicate, O₂ and CO₂ are needed for carbonate dissolution to occur beneath the ice. This process is common not only in glacial environments, but also in non-glacial streams and rivers because carbonates are easily weathered into water by carbonic acid (H₂CO₃) attack (see equation 5) (Berner & Berner, 2012). Some constraints on ion dissolution into meltwater include the residence time of the water in subglacial environment, access the subglacial water has to weathered sediment (rock flour), the supply of O₂ and CO₂ in the drainage system, and the lithology of bedrock. The supply of O₂ and CO₂ in the subglacial environment is often limited by access of the meltwaters to the atmosphere. The drainage system can be closed to the atmosphere under certain conditions, like when the drainage tunnels are filled completely with meltwater. In a closed-system the only supply of O₂ or CO₂ is from gas bubbles in the ice, englacial voids or microbial activity that oxidizes OC (Brown, 2002).

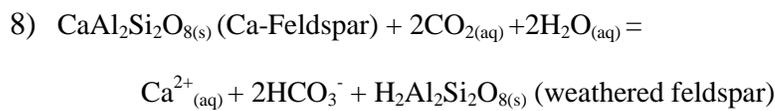
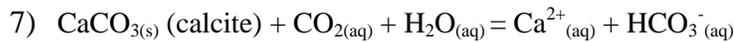
Sulfide oxidation is not as common as carbonate dissolution in non-glacial streams. In glacial environments, the glacier moves over the rocks grinding it into rock flour. This rock flour commonly contains pyrite minerals (FeS₂) and since the rock has been ground up it has fresh pyrite surfaces present (Brown, 2002; Raiswell, 1984). The fresh pyrite surfaces are reactive with water, resulting in the quick assimilation of sulphate (SO₄²⁻) into meltwater (see equation 6) (Brown, 2002; Bhatia et al., 2013; Raiswell, 1984; Wadham et al., 2010). In oxygen-rich waters at 0 °C, sulphate

concentrations can quickly reach concentrations as high as $\sim 400 \mu\text{eq L}^{-1}$ from sulfide reactions (Bhatia et al., 2013; Sharp et al., 1999). Non-glacial streams do not have rock flour present allowing for the quick production of sulphate, so they commonly have lower concentrations of sulphate. Studies have also indicated that snowmelt has little sulphate present, so sulphate in glacial meltwater is mostly due to pyrite weathering beneath the glacier (Brown, 2002, Mitchell et al., 2013). Because of this, sulphate is a metric that can be used as a tracer indicating meltwater in glacial streams likely came from the subglacial drainage system.

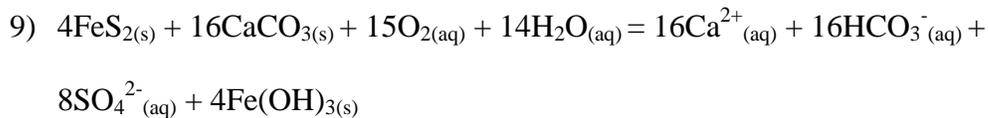
Microbial communities in the subglacial environment have also been shown to mediate sulfide oxidation, which is the reduction of sulfur compounds and this can result in additional sulphate in glacial meltwater (Bhatia et al., 2013; Mitchell et al., 2013; Wadham et al., 2010). Since sulphate concentrations should not get over $\sim 400 \mu\text{eq L}^{-1}$ from sulfide reactions involving pyrite in oxygen-rich waters at 0°C , sulphate concentrations over this amount may imply that microbial communities could be performing sulfide oxidation producing these high sulphate concentrations (as cited in Bhatia et al., 2013 p.340).

By comparing the proportions of HCO_3^- and SO_4^{2-} in the meltwater a general understanding of processes occurring in the subglacial drainage system can be concluded. Data on HCO_3^- and SO_4^{2-} can help distinguish the source of the protons (H^+) that drive the acid hydrolysis reactions (Bhatia et al., 2013; Brown, 2002; Hasnain, 1999a; Raiswell, 1984; Wadham et al., 2010). The C-ratio [$\text{HCO}_3^- / (\text{HCO}_3^- + \text{SO}_4^{2-})$] or the S-ratio [$\text{SO}_4^{2-} / (\text{SO}_4^{2-} + \text{HCO}_3^-)$] provide an understanding of the chemical weathering occurring beneath this ice (Brown, 2002; Hasnain, 1999a; Singh et al., 2014). For this project, the C-ratio

was utilized to understand the general chemical weathering processes. If the C-ratio produces a ratio ~ 1 then carbonate reactions dominate in the subglacial environment (Brown, 2002; Hasnain, 1999a). This means the dissolution and dissociation of CO_2 produces the protons needed for chemical weathering. The equations for these reactions are (Brown, 2002):



A C-ratio of 1 indicates that the drainage system is open to the atmosphere, because the atmospheric CO_2 is needed to produce protons, although CO_2 can also come from bubbles in the ice or from the oxidation of carbon by microbial communities beneath the ice (Bhatia et al., 2013; Brown, 2002; Wadham et al., 2010). If the C-ratio is ~ 0.5 then coupled sulfide oxidation and carbonate dissolution are the predominant hydrolysis processes occurring and pyrite oxidation produces some of the protons for chemical weathering (Brown, 2002; Hasnain, 1999a; Singh et al., 2014). The equation for this coupled reaction is (Brown, 2002):



The S-ratio $[\text{SO}_4^{2-} / (\text{SO}_4^{2-} + \text{HCO}_3^{-})]$ is an alternative ratio that researchers have used to give similar insight into the which reactions are occurring beneath the glaciers (Brown, 2002). An S-ratio of 0.5 signifies there is the coupled sulfide oxidation and

carbonate dissolution, where an S-ratio of 0.0 suggests the weathering is just from carbonate reactions (Brown, 2002).

Alternately data on HCO_3^- and SO_4^{2-} can be compared to gain insight into the possible presence of microbial communities beneath the ice. When meltwater flows through subglacial flour in the subglacial drainage system, carbonate hydrolysis occurs quickly due to the high reactivity of the minerals in the rock flour (Bhatia et al., 2013; Wadham et al., 2010). The carbonate hydrolysis reaction results in the production of HCO_3^- apart from SO_4^{2-} (Bhatia et al., 2013; Tranter et al., 2002; Wadham et al., 2010). By utilizing the theoretical solubility of calcite in meltwater at 0°C , this reaction should result in $\sim 220 \mu\text{eq L}^{-1}$ of HCO_3^- . Plots comparing HCO_3^- versus SO_4^{2-} with y-intercepts greater than $220 \mu\text{eq L}^{-1}$ indicates there must be an additional source of CO_2 to account for the additional HCO_3^- in the meltwaters (Bhatia et al., 2013; Brown, 2002; Wadham et al., 2010).

This CO_2 source could be from contact with the atmosphere if it is an open drainage system. If the drainage system is closed and there is no contact with atmospheric CO_2 , studies have recently shown it can be a result of the oxidation and fermentation of OC by microbial communities beneath the ice (Bhatia et al., 2013; Brown, 2002; Wadham et al., 2010). These ratios and ion comparisons can change over a glacial melt season reflecting the evolution from snowmelt to meltwater from the subglacial drainage system. These ratios allowed Wadham et al. (2010) to determine that microbial communities were present beneath the glacial ice in Antarctica, Greenland, Norway, Switzerland and Svalbard. The research team found high intercepts of HCO_3^- in borehole

samples of meltwater from glaciers in Norway and Switzerland, indicating microbes were oxidizing subglacial OC and creating CO₂ (Wadham et al., 2010).

A study by Brown (2002) discusses using pCO₂ values, along with the major ion data to get an understanding into if the glacial drainage system is open or closed to atmospheric gases. A drainage system open to the atmosphere would display pCO₂ values equal to atmospheric values, while a low or high pCO₂ value would indicate that the system is closed to the atmosphere (Brown, 2002; Hasnain, 1999a; Raiswell, 1984). Low pCO₂ values occur when carbonate reactions cause a more rapid use of protons in the subglacial environment than can be resupplied by CO₂ diffusion in these water-ice-rock interfaces (Brown, 2002). This often occurs when there is a large amount of new rock flour present and a large volume of meltwater (as cited in Brown, 2002 p.865). High pCO₂ values occur when hydrolysis provides more protons than there are protons being consumed in the subglacial environment (Brown, 2002; Hasnain, 1999a). This can happen when protons are provided to meltwater through sulphide oxidation or additional snowmelt input (Brown, 2002; Hasnain, 1999a). The neutralizing of acidity by carbonates or the freezing of the meltwater can also contribute to the high pCO₂ values. It is common for meltwater to transition from open to closed drainage systems or from high to low pCO₂ conditions throughout the summer as the drainage system evolves (Brown, 2002; Hasnain, 1999a). By combining pCO₂ data with the major ion data this study can gain more insight into the processes occurring beneath the ice and the main source rocks contributing to weathering.

This literature review has discussed the studies previously done on DOC and major ion export from glacial meltwater. It has discussed many methods used to

understand the properties of this glacial DOC and its importance to aquatic ecosystems downstream. It has also highlighted the need for similar research in the Pacific Northwest for two main reasons. To add to the larger body of knowledge on glaciers role in the global carbon cycle and so local wildlife and natural resource managers can properly protect our resources as glaciers continue to recede and ultimately disappear. My research project will give local insight into the temporal and spatial patterns of DOC and major ion export. This project looked at glacial meltwater from Emmons Glacier, which has the largest area on Mount Rainier (11.1 km²), and meltwater from the Inter Fork Glacier, which is one of the smallest glaciers on the mountain (0.8 km²) (NPS, 2016; USGS, 2016). Data from two non-glacial streams was also gathered, so a comparison with these should provide interesting insight into how DOC and major ion export varies depending on glacial size at the headwaters. This project presents an opportunity to study current temporal and spatial trends in local DOC export and study how the timing and concentration of DOC could change as glacial recession continues over time (NPS, 2016).

3. Methods

3.1 Research Design

This research project aimed to perform an analysis of multiple water parameters on glacial headwater streams on Mt. Rainier. The water parameters measured on sight from these streams included temperature, dissolved oxygen, conductivity, velocity, pH, and pCO₂. Stream samples were collected to analyze back in the lab for alkalinity, major ions (SO₄²⁻, HCO₃⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺) and dissolved organic carbon (DOC). The

samples were gathered throughout the months of May to September in 2016 in order to observe any changes that may occur to the water parameters over the glacial melting season.

The glacial rivers come from two significantly different sized glaciers. The White River comes from the Emmons Glacier, which is the largest glaciers on Mount Rainier with an area of 11.1 km² (NPS, 2016). The Inter Fork White River comes from the glacial melt waters of the Inter Glacier, which has an area of about 0.8 km² (USGS, 2016). The two non-glacial streams used for reference came from precipitation events and the waters of nearby lakes. Since the non-glacial streams come from the drainage waters of lakes rather than being dominantly precipitation driven, they do not represent perfect reference streams but do provide interesting references since they are in previously glaciated regions. Often as glaciers melt, they leave behind chunks of ice that can melt into lakes, so although not ideal reference streams they can still give some insight into how an evolving glacial landscape can alter stream parameters.

The first non-glacial stream comes from the waters of Shadow Lake, but this stream dried up by the end of June so another non-glacial stream nearby was used for continued sample collection. The second non-glacial stream came from the waters of Frozen Lake. The difference in glacial area at the headwaters will provide for comparison between glacial and non-glacial streams and provide understanding in how this glacial coverage may influence the water parameters. On the glacially fed streams, there were two sampling locations, one upstream and one downstream. A comparison of these two locations should provide insight into how distance from the glacier may affect the water parameters as well as any influence from merging streams.

3.2 Sampling Locations

All the glacial stream sites and non-glacial stream sites are located on the Eastern side of Mount Rainier in Washington State (see figure 4 and 5). These sites were chosen due to accessibility and the feasibility of collecting samples from multiple locations. There are two separate sampling sites on the glacially-derived streams, the White River and the Inter Fork White River, which eventually merge into one river. There is one sampling site on the two non-glacial streams nearby for reference, and these streams eventually merge into the Inter Fork River. On the White River, one sampling site (Upper White River) is located close to the terminus of Emmons glacier. The other White River site is located downstream (Lower White River), which is situated in an area past the merging of the Inter Fork White River with the White River. On the Inter Fork White River, one sampling site (Upper Inter Fork) is located upstream near the terminus of the Inter Glacier. The second sampling site on the Inter Fork White River (Lower Inter Fork) is located downstream from the merging of the non-glacial creek with the Inter Fork White River. Both non-glacial streams are located on the northern side of the Inter Fork White River and they both eventually merge into this stream. All the stream sampling locations are located between 4,000 and 4,500 feet in elevation (NPS, 2016).

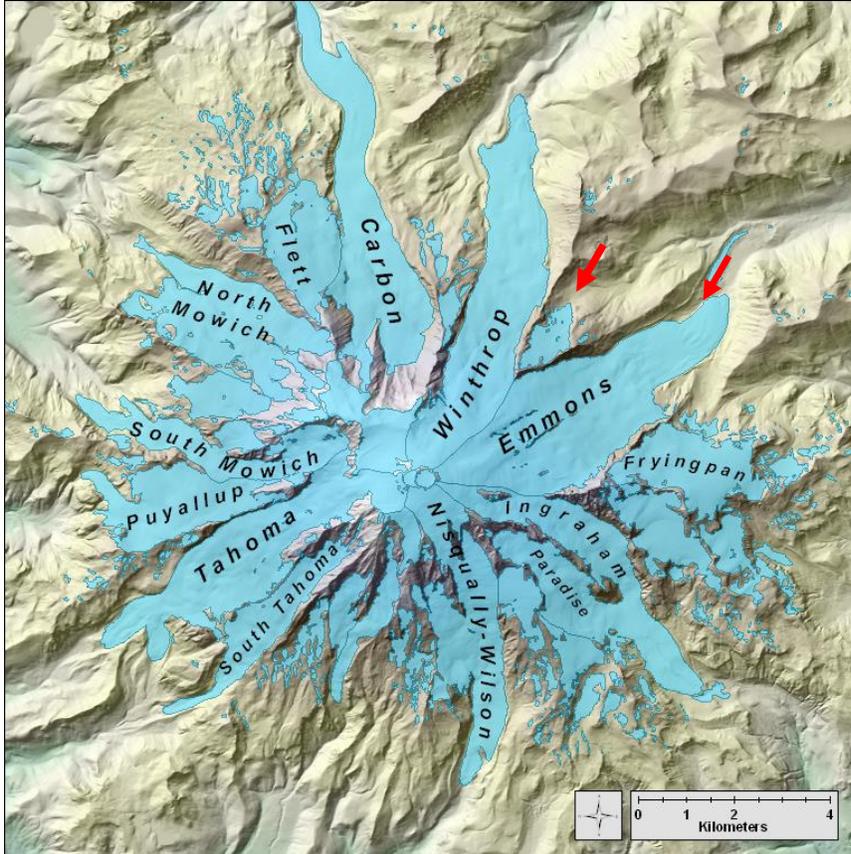


Figure 4: Zoomed out view of the glaciers the feed the rivers where the sampling locations are located. Emmons Glacier is about 4.3 mi^2 in area and the Inter Glacier situated next to Emmons Glacier is about 0.3 mi^2 in area. The White River comes from the glacial melt off Emmons Glacier and the Inter Fork River comes from the melt waters of the Inter Glacier (Hekkers & Thorneycroft, 2011).

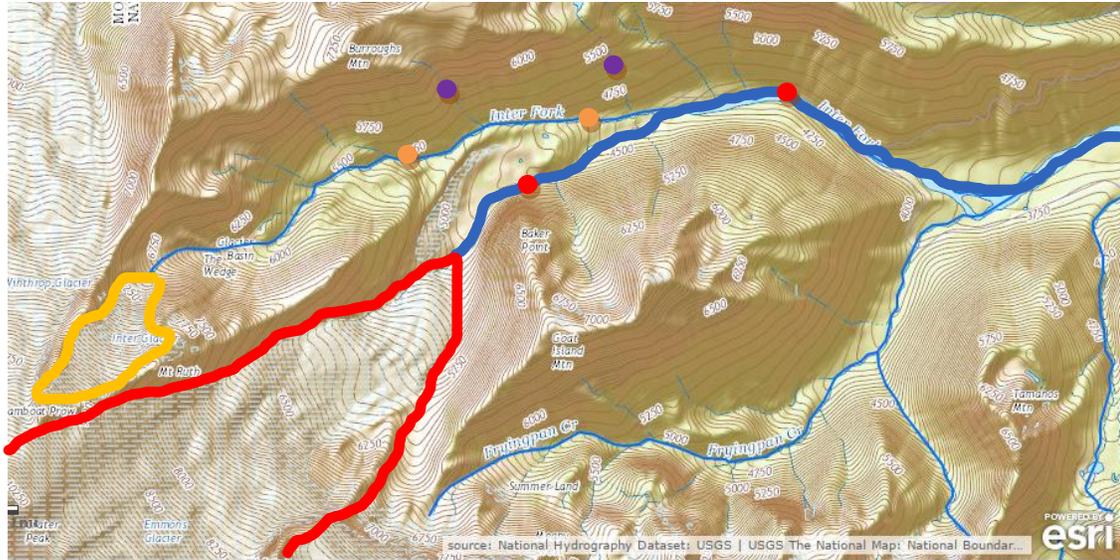


Figure 5: Zoomed-in view of the field area and sites on Mount Rainier (adapted from USGS, 2016).

- = Field sites along the White River, which comes from the Emmons glacier that has the largest glacial coverage
- = Field sites along the Inter Fork River, which comes from that Inter Fork glacier that has the smaller glacial coverage
- = Field sites on the non-glacial streams that receive no glacial melt (0% glacial coverage)

The forested areas in the White River region on Mount Rainier consist mostly of subalpine fir (*Abies lasiocarpa*), mountain hemlock (*Tsuga mertensiana*), Alaskan yellow cedar (*Cupressus nootkatensis*), whitebark pine (*Pinus albicaulis*), and Engelmann spruce (*Picea engelmannii*) (NPS, 2007). The White River area has a rich understory common for wet mountainous environments, including a variety of species of mushroom, ferns, mosses and wildflowers. (NPS, 2016). The White River begins near the tree line at the terminus of the Emmons Glacier and travels into the tree line. The sampling locations for this project were located near or slightly within the tree line. There was 0% canopy cover present in the White River sampling locations, which minimizes sources of possible

terrestrial carbon to the river system. The Inter Fork River begins at a much higher elevation at the terminus of the Inter Glacier, but its headwaters are still near the tree line. This is due to glacial recession from the Inter glacier leading to terrestrial succession at these higher latitudes. The Inter Fork River is mostly in the forest with both sampling locations along the river having ~ 30% to 40% canopy cover. The two non-glacial creeks were both located at lower elevations in the forest, and they ~ 70% tree canopy cover or more.

3.3 Geology of Mount Rainier

Mount Rainier is the tallest stratovolcano in the Cascade Mountain Range reaching 14,410 feet (NPS, 2005). This impressive height is one of the reasons that Mount Rainier has so many glaciers. With so much ice present, the mountain is the largest single peak glacial system in the country (NPS, 2005). The mountain began forming 500,000 years ago through successive lava and pyroclastic flows that left behind mainly andesitic and basaltic rocks (USGS, 2014). Erosion of these rocks by the glaciers leaves behind moraines and glacial till. Mudflows and debris flows have occurred in the past moving around vast amounts of material, while glacial outbursts move large amounts of water and sediments into the valleys below. In 1963, there were multiple rockslides from Little Tahoma Peak onto Emmons Glacier, which resulted in rock debris covering the lower part of the glacier. The rock cover on the ice creates insulation keeping the glacier cooler than the other glaciers on Mount Rainier. This has resulted in less recession occurring at the Emmons Glacier in comparison to the other glaciers, but it has still been receding since the late 1800's (Hekkers & Thorneycroft, 2011; NPS, 2005). The last volcanic activity at Mount Rainier occurred between 1820 and 1850 based on tephra

deposits (USGS, 2015). Currently, the volcanic status of Mount Rainier is active (USGS, 2014). Emmons Glacier is located on andesite flows that are around 180-280,000 years old and the Inter Glacier sit on top of andesite lava flows that are around 450-500,000 years old (USGS, 2014). Research has indicated the presence of pyrite minerals in hydrothermal alterations in the rocks on Mount Rainier (John, Sisson, Breit, Rye & Vallance, (2008).

3.4 Field Methodology

In the field, the glacial and non-glacial streams were measured for multiple water parameters. The pH was recorded on site using an Oakton pH probe. At least five measurements of pH were taken over a ten-minute period.

A YSI Pro 2030 meter, which was calibrated for freshwater, was used to measure dissolved oxygen, conductivity and temperature of the streams. At least three measurements each of dissolved oxygen, conductivity and temperature were recorded.

An Eosense GPsensor for measuring pCO₂ was used in the streams. The pCO₂ probe was turned on for 30 minutes before use. The pCO₂ probe was not always available in the field due to poor weather conditions so some pCO₂ rates were calculated using the temperature and alkalinity data gathered. The equation used to calculate pCO₂ is (Wanninkhof, 1992; Weiss, 1974):

$$pCO_2 = [H_2CO_3]/K_H$$

$$\text{Where } K_H = e^{(-58.0931+90.5069(100/T)+22.294\ln(T/100))}$$

The alkalinity data was used to determine the concentration of carbonic acid [H₂CO₃] in the water. This is because the equation for alkalinity is:

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2*[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Carbonic acid was calculated from the temperature-dependent equilibrium constant equation for the dissociation of carbonic acid to bicarbonate [HCO₃⁻] (USGS, 2012):

$$\text{H}_2\text{CO}_3 = ([\text{H}^+][\text{HCO}_3^-])/K_1$$

$$\text{Where } K_1 = ([\text{HCO}_3^-][\text{H}^+])/[\text{H}_2\text{CO}_3]$$

$$K_2 = ([\text{CO}_3^{2-}][\text{H}^+])/[\text{HCO}_3^-]$$

$$\text{pH} = -\log[\text{H}^+] \leftrightarrow [\text{H}^+] = 10^{-\text{pH}}$$

A Model 2100 Series Current Velocity “Swoffer” Meter was utilized to gather velocity data for the Inter Fork River and the non-glacial streams. Discharge of the White River was too high to safely use the swoffer meter or gather depth measurements. Due to this, it was not possible to get accurate velocity measurements, so the float method was used to gather data on the velocity of the White River. The float method uses an object that floats in the water to determine how fast the water is moving. For this project, an orange was floated down a 50 foot stretch of the White River and the time it traveled in the water was recorded. The float method was repeated three times. Then the equation $V = Q/A$ was used to calculate velocity where V = velocity (travel distance/travel time), Q = discharge (velocity * area) and A = cross sectional area (width * average depth).

Field observations were recorded at each site, including weather, canopy cover, substrate, and if there was the presence or absence of primary production or

macroinvertebrates in the streams. Data on precipitation, temperature and snow depth were gathered from NOAA's NOWData sets (2016) from the Paradise weather station on Mount Rainier. There is no weather station near the White River where the sampling locations were but the Paradise weather station is nearby and located at a similar elevation. This data was extrapolated to all the sampling locations since they are in close proximity to one another. Snowmelt data was calculated from snow depth data by subtracting snow depths. This study used the total snowmelt that occurred over 7 days prior to the date of field work to see if DOC concentrations were dependent on the snowmelt over the prior week.

3.5 Lab Methodology

Filtration and Preservation

Water samples for laboratory analysis (dissolved organic carbon, major ions, alkalinity) were gathered in one liter acid washed (10% or 1.2 molar HCl for 12 hours) polypropylene bottles in the field. These samples were kept on ice until they arrived back at the laboratory for filtration and analysis or storage. All water samples brought back from the field were immediately filtered in the laboratory at The Evergreen State College.

Dissolved Organic Carbon (DOC) Analysis

Water samples analyzed for DOC were filtered through 0.07 μm glass fiber filters that had been combusted at 450°C for 4.5 hours. The water samples were then stored in 25 mL glass vials that had been combusted at 500°C for 4.5 hours. These glass

vials were frozen until analysis (~28 days). The organic carbon analysis was completed by the Analytical Service Center at the University of Washington using the TOC/TN analyzer. DOC methods were gathered from the U.S.G.S methods (2002). Analytical error was less than 10% based on replicate samples.

Alkalinity Methods

Alkalinity samples were filtered through 0.45 μm cellulose acetate filters and stored in 250 mL acid washed polypropylene bottles and kept around 4°C for preservation until analysis (within 24 hours) (USGS, 2012). To analyze the water samples for alkalinity, a sulfuric acid titrant solution of 0.2 N, along with a standard solution of 0.01639 N Na_2CO_3 were created. To determine the normality of the sulfuric acid solution, 100 mL of the Na_2CO_3 solution was titrated with the sulfuric acid solution using a 0.2 mL Gilmont micrometer burette following methods described in the USGS protocols (2012). Titrations were repeated three times for accuracy.

Once the normality of the sulfuric acid solution was calculated, the sulfuric acid was then used to titrate the water samples from the field using 100 mL water samples following the USGS (2012) protocol for alkalinity. An Orion pH electrode was used for pH measurements. Each water sample was titrated three times for accuracy. The Gran method was used for calculating the alkalinity of the water samples

Dionex IC25 Methods

Water samples to be analyzed for major anions were run on the Dionex Ion Chromatograph 25. They were filtered through 0.45 μm cellulose acetate filters and stored in 250 mL acid washed polypropylene bottles and kept around 4°C for

preservation until analysis (within 1 month) (U.S EPA, 1993). Sulfate standards were created by drying K_2SO_4 at $105^\circ C$ for 30 minutes and then cooling it in a desiccator. Standards of 1 ppm, 5 ppm and 10 ppm and a quality control of 7 ppm were created to run on the IC25. The quality control was prepared from a different stock of K_2SO_4 to insure accuracy. Concentrations for the standards were determined based off previous studies findings of SO_4^{2-} in glacial melt water. The standards, quality control, blanks and stream water samples were all filtered through $0.2 \mu m$ filters on the IC25. The standard curve was always 0.9998 or greater and the quality control was $\pm 15\%$ of what the quality control concentration should be based on calculations. The major anion (SO_4^{2-}) was determined by ion chromatography on the Dionex IC 25 using an anion trap column (ACT-3, 4mm), a guard column (AG17, 4 mm) and an analytical column (AS17, 4 mm). The injected water samples were 25 mL and each sample ran for 14 minutes through the Dionex IC 25 with a flow rate of 1 mL/sec. The eluent was helium gas set at a concentration of 10 mM. Analytical error was less than 10% based on replicate samples.

PerkinElmer Elan DRC-e ICP-MS Methods

Water samples to be analyzed for major cations were run on the PerkinElmer Elan DRC-e ICP-MS. They were filtered through $0.45 \mu m$ cellulose acetate filters into 250 mL acid washed polypropylene bottles, acidified using nitric acid (HNO_3) and kept around $4^\circ C$ for preservation until analysis (within 6 month) (U.S EPA, 1994). Calibration standards of 100 ppb, 500 ppb, 1,000 ppb, 1,500 ppb and 2,500 ppb were created using Mg^{2+} , K^+ , Na^+ and Ca^{2+} . A quality control of 700 ppb was made using a different stock of the analytes and an internal standard of Scandium (Sc) was created. Each standard, the quality control and the blank were prepared in 50 mL acid washed tubes with a 1% HNO_3

matrix and 1 ppm of the internal standard. When ran, the standards had a R^2 value of 0.9998 or greater and the quality control was $\pm 10\%$ of what the quality control concentration should be based on prior calculations. The samples were prepared in 15 mL acid washed tubes with a 1% HNO_3 matrix and 1 ppm of the internal standard. The samples were run after the standards and quality control were ran to insure accuracy. The major cations (Mg^{2+} , K^+ , Na^+ , Ca^{2+}) were determined by inductively coupled plasma-mass spectrometry (ICP-MS) on the PerkinElmer using Elan instrument software. A quantitative summary analysis was performed with the machine in dual detector mode using an auto-analyzer. The ICP-MS was in peak processing mode and DRC mode throughout the analysis. Analytical error is generally less than 10% based on replicate samples.

3.6 Statistical Analysis Methods

The data analysis was completed using excel and JMP Pro12. Excel was used to plot the temporal data gathered on DOC and major ions throughout the melt season. Excel and JMP Pro12 were also used to perform simple linear regression analysis on the data. JMP Pro12 was used to perform correlation analysis on DOC concentrations against multiple parameters. Spearman's ρ was used because some of the data did not have a normal distribution.

4. Results

4.1 Dissolved Organic Carbon Analysis

Dissolved organic carbon concentrations had peak values in early to mid-June and then decreased over time for all sites (see Figure 6 & 7). Concentrations in the upper

White River (UWR) site ranged from 0.1 to 1.5 mg L⁻¹, while the lower White River (LWR) site had values that ranged from 0.7 to 4.9 mg L⁻¹. The upper Inter Fork White River (UIF) site had DOC concentrations ranging from 0.7 to 3.3 mg L⁻¹ and the lower Inter Fork White River (LIF) site had DOC concentrations of 0.8 to 3.4 mg L⁻¹. The first non-glacial creek (NGC1) had DOC concentrations of 1.5 to 7.0 mg L⁻¹. The DOC concentrations in the NGC1 showed a different pattern compared with the glacial streams displaying two high peaks between late May and mid-July. After mid-July, this non-glacial creek dried up, so there is no data past this date for that creek. The second non-glacial creek (NGC2) had DOC concentrations ranging from 2.0 to 4.0 mg L⁻¹.

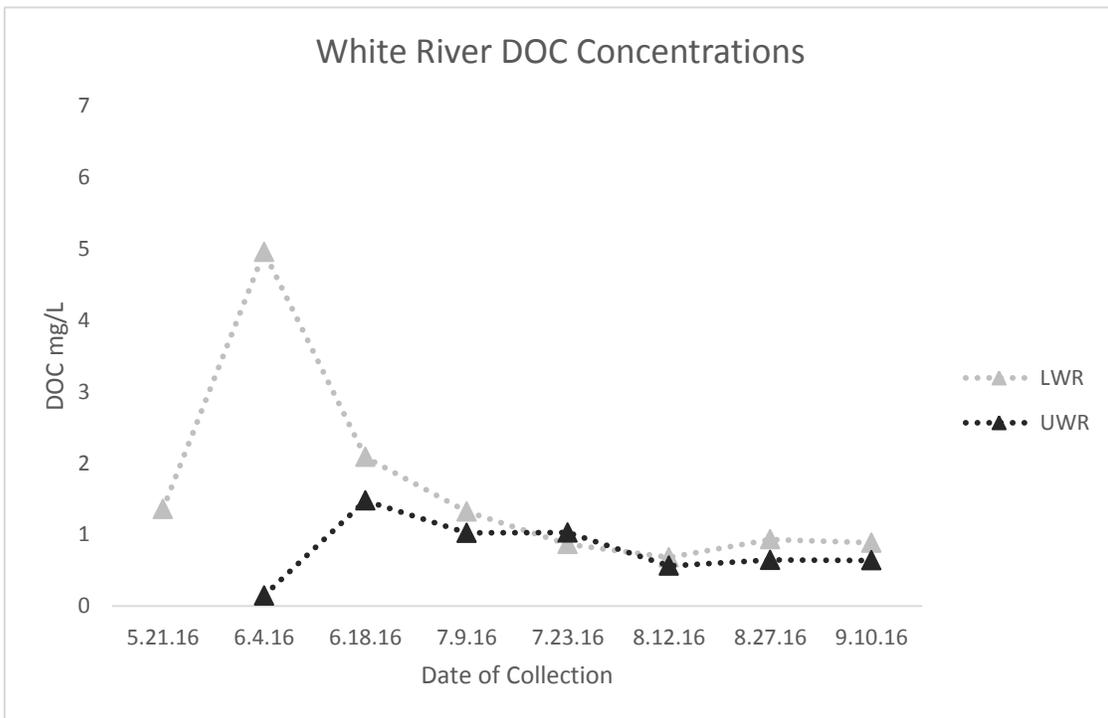


Figure 6: DOC concentrations in the upper and lower White River sites over the glacial melt season.

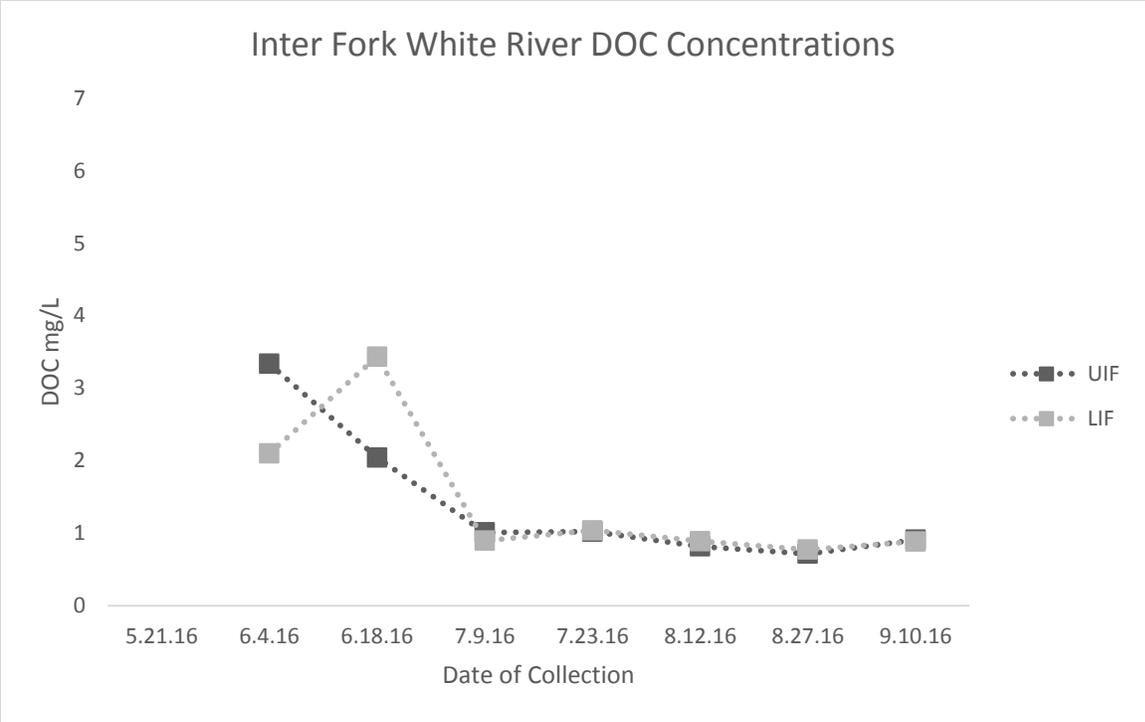


Figure 7: DOC concentrations at the upper and lower Inter Fork White River sites over the glacial melt season.

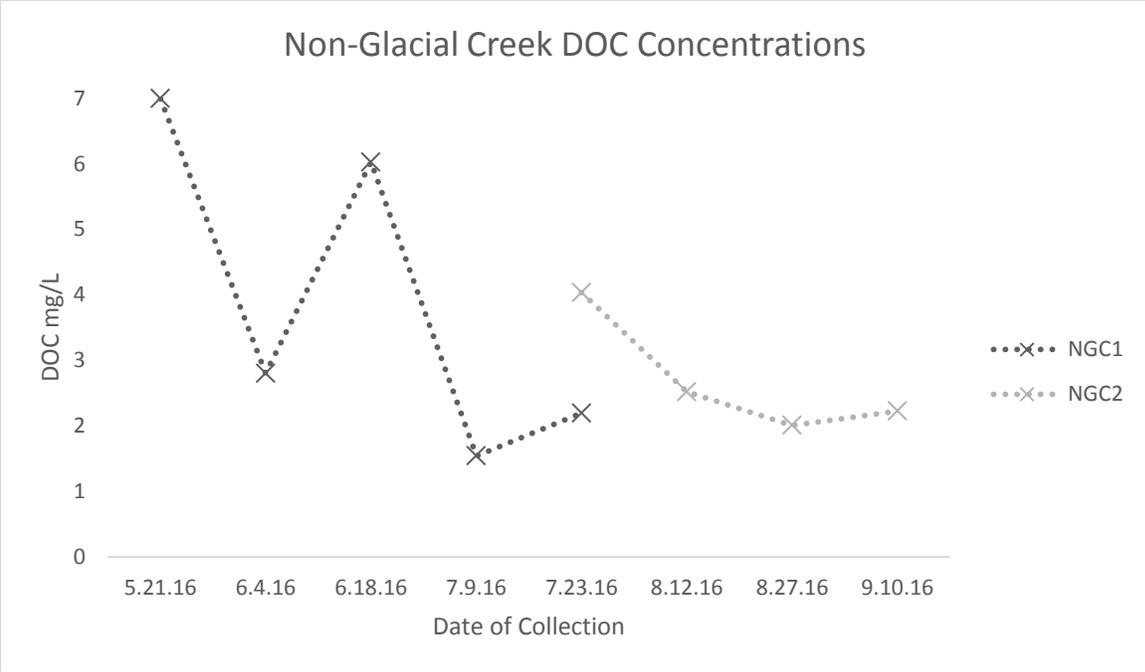


Figure 8: DOC concentrations in the two non-glacial creek sites over the glacial melt season.

To gain insight to what parameters may be controlling DOC export, DOC concentrations were plotted against data on temperature, precipitation, snow depth, snowmelt, and velocity (see table 1). Simple linear regression was used to understand if DOC was dependent on any specific parameter. A correlation analysis was also performed to understand positive and negative relationships between the data (see table 2). The data used for temperature, precipitation and snow depth all came from NOAA'S NOWData sets (2016), and this data is displayed in Table 1 for the timepoints that were sampled. Velocity data came from measurements made in the field using the swoffer meter or the float method. Snow depth, snow melt and velocity displayed significant results for some sites when plotted against DOC concentrations, while temperature and precipitation did not display significant results (see table 2).

Climatological Data from Paradise Rainier, WA								
	5.21.16	6.4.16	6.18.16	7.9.16	7.23.16	8.13.16	8.27.16	9.10.16
High Temperature (°C)	5	18.9	8.9	10	10	23.3	21.1	16.1
Low Temperature (°C)	0.6	3.3	1.1	2.8	4.4	13.9	10.6	8.9
Average Temperature (°C)	2.8	11.1	5	6.4	7.2	18.6	15.8	12.5
Precipitation (cm)	0.58	0	1.3	1.4	0	0	0	0
Snow Depth (inches)	100	70	42	0	0	0	0	0
Total 7-Day Snowmelt (inches)	10	25	20	10	0	0	0	0

Table 1: Data for snow depth, snowmelt, precipitation and temperature (NOAA, 2016).

R Values from Correlation Analysis				
	Upper White River	Lower White River	Upper Inter Fork	Lower Inter Fork
Velocity	-0.79 (p = 0.04)	-0.33	-0.68	-0.43
Snow Depth	-0.02	0.79 (p = 0.02)	0.08 (p = 0.03)	0.76 (p = 0.05)
Snowmelt	-0.13	0.76	0.81 (p = 0.03)	0.77 (p = 0.04)
1 Day Precipitation	0.78 (p=0.04)	0.33	0.37	0.51
7-Day Precipitation	0.47	0.003	0.02	0.34
1 Day Temperature	0.5	0.01	0.09	0.3
7-Day Temperature	0.16	0.1	0.26	0.55

Table 2: Correlation results of DOC concentration with multiple parameters. R-value based on correlation analysis using Spearman's ρ due to the data not being normally distributed.

Snow depths throughout the field season ranged from 0 to 100 inches (NOAA, 2016). The deepest snow level during the data collection period occurred in mid-May and then the snow depth decreased over time until July. After July, the snow depth stayed at 0 inches for the remaining part of the field season. Based on simple linear regression, the relationships between snow depth and DOC concentration were significant at the UIF with a $p = < 0.001$, $R^2 = 0.97$, followed by the LIF with a $p = 0.0427$, $R^2 = 0.59$. (see figures 9 & 10). Significant relationships between snowmelt and DOC were found at the UIF with a $p = 0.0031$, $R^2 = 0.85$, followed by the LWR with a $p = 0.0047$, $R^2 = 0.76$, and the LIF with a $p = 0.0298$, $R^2 = 0.64$ (see figures 11, 12, & 13).

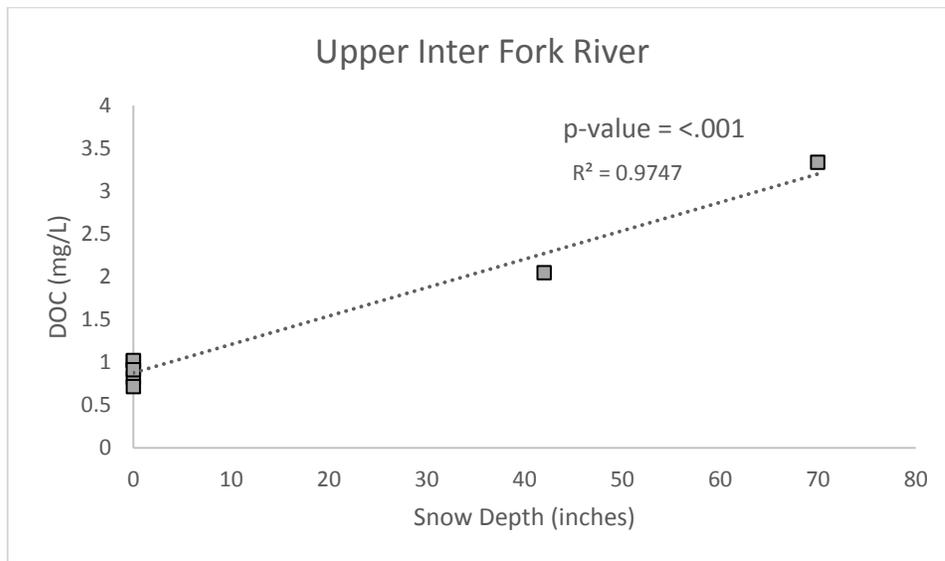


Figure 9: Relationship between DOC (mg L^{-1}) and snow depth (inches) at the upper Inter Fork White River site.

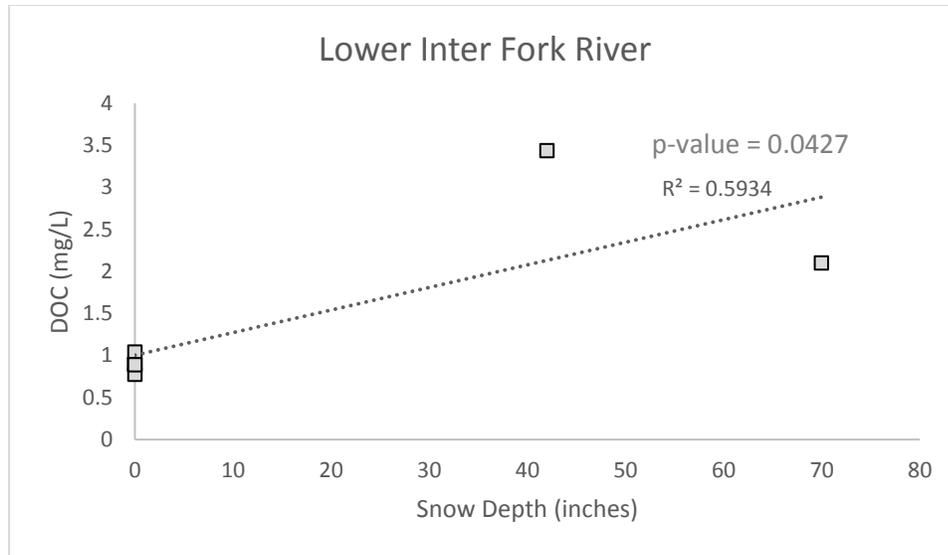


Figure 10: Relationship between DOC (mg L^{-1}) and snow depth (inches) at the lower Inter Fork White River site.

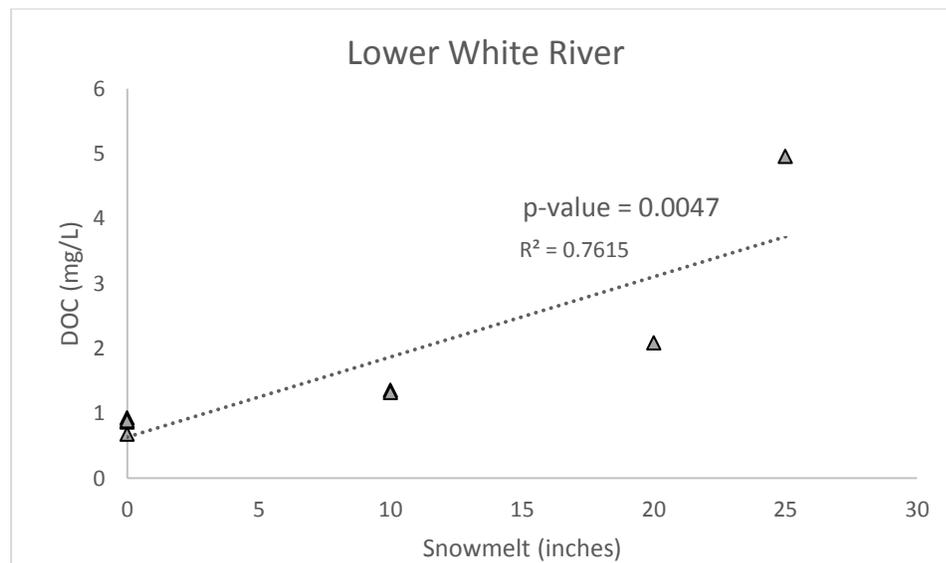


Figure 11: Relationship between DOC (mg L^{-1}) and total 7-day snowmelt (inches) at the lower White River site.

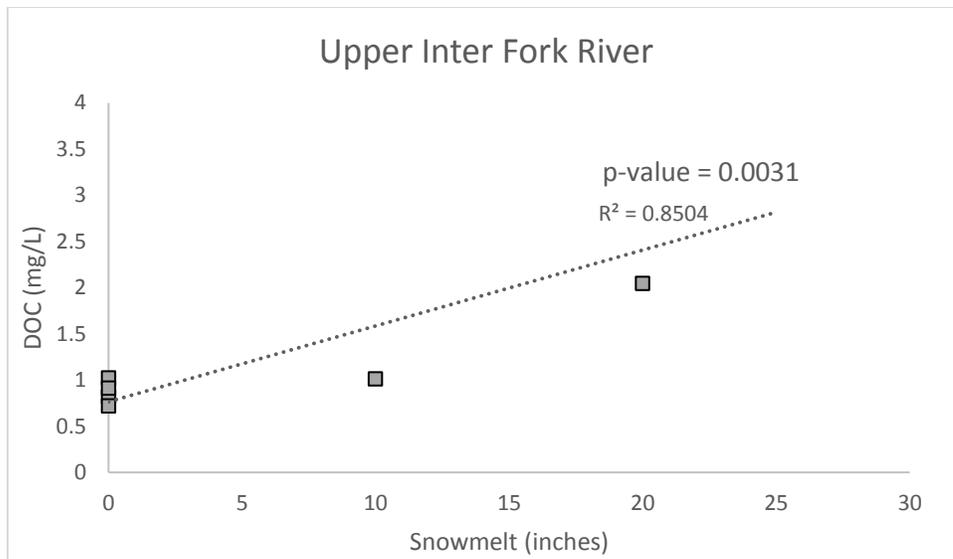


Figure 12: Relationship between DOC (mg L^{-1}) and total 7-day snowmelt (inches) at the upper Inter Fork White River site.

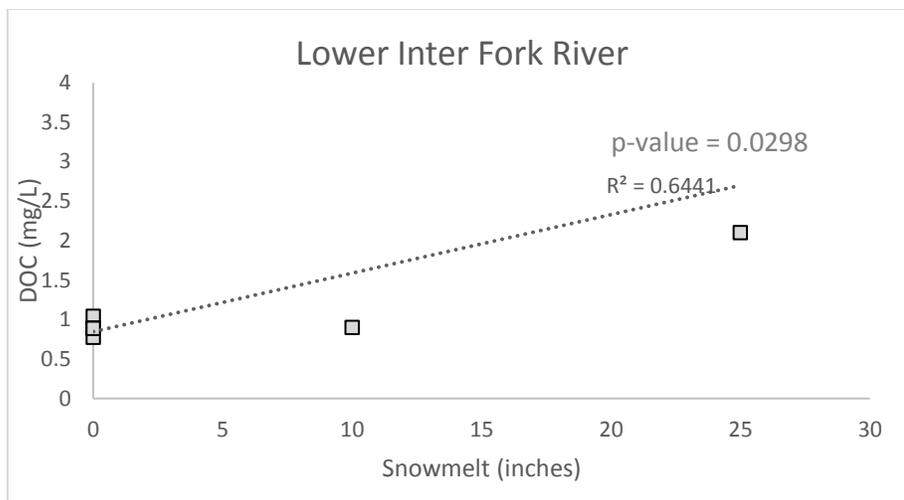


Figure 13: Relationship between DOC (mg L^{-1}) and snowmelt (inches) at the lower Inter Fork White River site.

Velocity values for the White River ranged from 0.4 to 0.7 m/sec while the Inter Fork White River had velocity values ranging from 0.4 to 1.2 m/sec. The non-glacial creeks had velocities ranging from 0 to 0.1 m/sec. Based on simple linear regressions of velocity against DOC, the UIF site displayed significant results with a $p = 0.0113$, $R^2 = 0.75$, as well as the UWR site with a $p = 0.0168$, $R^2 = 0.71$ (see figure 14 & 15).

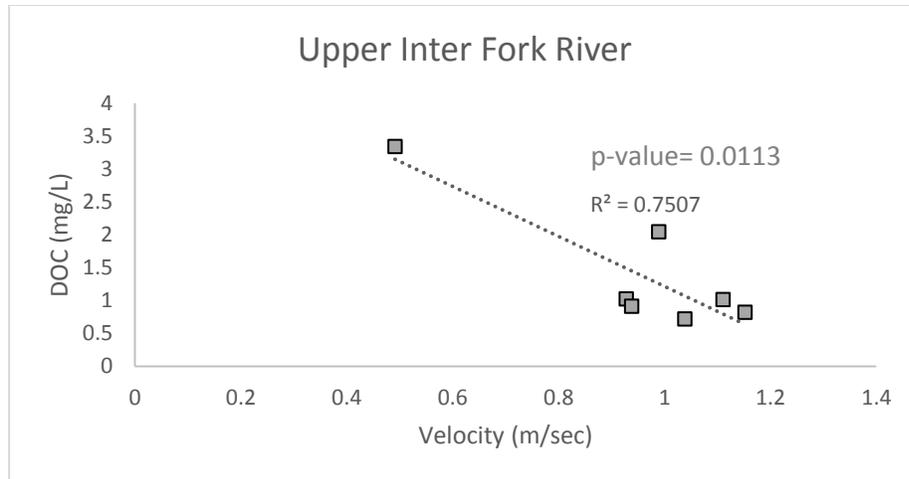


Figure 14: Relationship between DOC (mg L^{-1}) and velocity (m/sec) at the upper Inter Fork White River site.

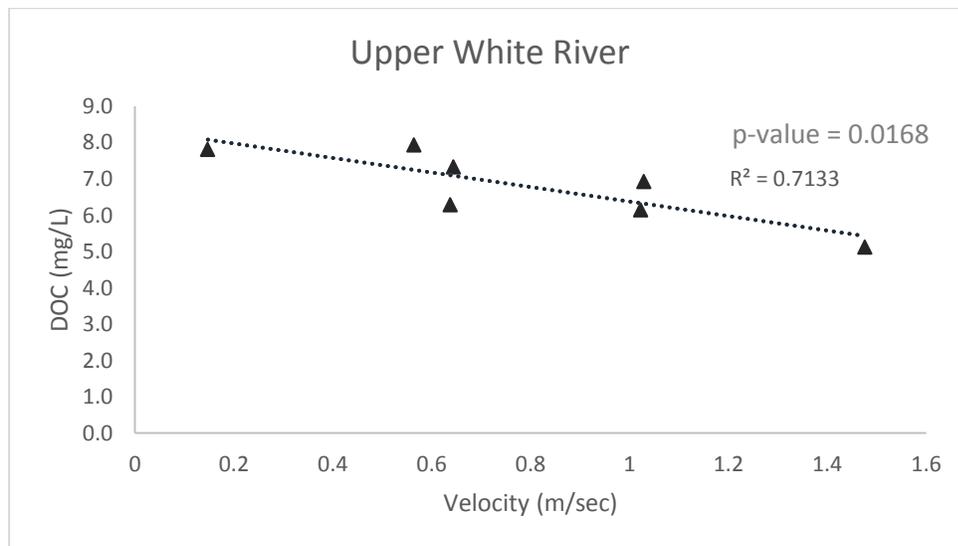


Figure 15: Relationship between DOC (mg L^{-1}) and velocity (m/sec) at the upper White River site.

Average temperatures on Mount Rainier ranged from -1.4 to 19 ± 17.3 °C throughout the field season (see table 1) (NOAA, 2016). Relationships between DOC concentrations and the daily average temperature from the day of sampling were not significant based on simple linear regression. Simple linear regressions were also performed on DOC

concentrations against a 7-day average temperature. The relationships between the 7-day average temperature and DOC were not significant (see table 2).

The daily precipitation totals varied from 0 to 2.4 cm during the sample collection period (see table 1) (NOAA, 2016). Based on simple linear regression, the relationship between DOC concentrations and the daily precipitation totals were significant for the UWR site displaying with a $p = 0.047$, $R^2 = 0.58$ (see figure 16). Simple linear regressions were also done using a 7-day precipitation total instead of the daily precipitation total to see if precipitation over time affected DOC export. The relationships between the 7-day precipitation totals and DOC were not significant (see table 2).

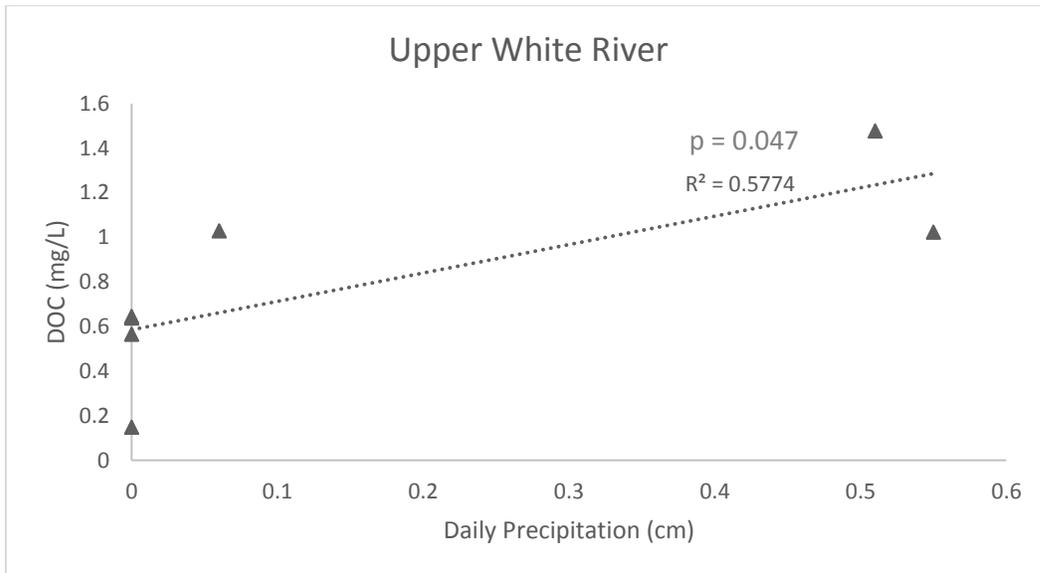


Figure 16: Relationship between DOC (mg L^{-1}) and daily precipitation (cm) at the upper White River site.

4.2 Other Parameters: pH, alkalinity and pCO_2

The pCO₂ values in the glacial streams were generally low, with some values less than atmospheric equilibrium values, and some higher (see table 3). Values at the UWR site ranged from 199.2 to 293.1 ppm with an average of 247.2 ± 15.5 ppm. The LWR site had values ranging from 214.8 to 594.9 ppm with an average value of 321.9 ± 45.4 ppm. The Inter Fork White River sites had much more variable pCO₂ values, but overall displayed higher values than the White River. The UIF values ranging from 289.5 to 618.9 ppm with an average of 454.4 ± 52.7 ppm and the LIF site had values ranging from 266.3 to 833.7 ppm with an average value of 494.4 ± 81.1 ppm. The NGC1 had pCO₂ values ranging from 259.3 to 637.7 ppm with an average of 434.8 ± 89.8 ppm and the NGC2 had pCO₂ values ranging from 607.1 to 753.9 ppm with an average of 655.4 ± 43.6 ppm.

Site/Date	pCO ₂ μatm or ppm							
	5.21.16	6.4.16	6.18.16	7.9.16	7.23.16	8.12.16	8.27.16	9.10.16
LWR	369	214.8	310.9	310.9	594.9	250.8	255.1	268.6
UWR		288.6	257.2	293.1	225.8	199.2	261.1	205.6
LIF	429	833.7	266.3	316.5	450	784	321.3	554.0
UIF		604	289.5	402.5	618.9	420.5	516.4	328.9
NGC1	259.3	610.9	281.5	384.6	637.7			
NGC2					607.1	753.9	586.8	673.8

Table 3: pCO₂ values at the glacial and non-glacial stream sites over the field season.

pH values that were used to calculate the pCO₂ values were gathered in the field (see table 4). Values for pH at all the sites was fairly consistent throughout the summer months, with the NGC2 displaying higher pH values than any other sites. At the UWR site the pH values ranged from 7.1 to 7.3 and at the LWR site pH ranged from 6.9 to 7.3. Values ranged from 7.0 to 7.3 at the UIF site and they ranged from 6.9 to 7.3 at the LIF site. The NCG1 displayed values ranging from 6.9 to 7.4 while the NGC2 had pH values ranging from 7.6 to 7.7.

pH Values								
Site/Date	5.21.16	6.4.16	6.18.16	7.9.16	7.23.16	8.12.16	8.27.16	9.10.16
LWR	7.3	7.1	7.2	7.3	6.9	7.3	7.2	7.3
UWR	7.3	7.1	7.3	7.2	7.2	7.3	7.1	7.3
LIF	7.3	7.0	7.3	7.2	7.1	6.9	7.2	7.1
UIF	7.3	7.1	7.2	7.1	7.0	7.2	7.1	7.3
NGC1	7.3	6.9	7.3	7.4	7.2			
NGC2					7.7	7.6	7.7	7.6

Table 4: pH values for the glacial and non-glacial sites over the field season.

Alkalinity values in both glacial streams were generally consistent throughout the summer, although both White River sites displayed a large dip in alkalinity values during early June while the Inter Fork River displayed a gradual decrease in alkalinity during that time (see figure 17, table 5). The alkalinity in the UWR ranged from 91.9 to 122.7 $\mu\text{eq L}^{-1}$, while the LWR site had values ranging from 68.4 to 243.2 $\mu\text{eq L}^{-1}$. The UIF has alkalinity values ranging from 139.2 to 205.2 $\mu\text{eq L}^{-1}$ and the LIF had values ranging from 132.4 to 256.9 $\mu\text{eq L}^{-1}$. The first non-glacial creek had alkalinity values in the same range as the glacial streams, but the alkalinity in NGC1 increased over time, while the glacial streams were generally decreasing over time. The alkalinity in NGC1 ranged from 134.1 to 275.4 $\mu\text{eq L}^{-1}$. The second glacial stream had alkalinity levels higher than any of the other glacial or non-glacial sites with values ranging from 669.7 to 718.8 $\mu\text{eq L}^{-1}$.

Alkalinity ($\mu\text{eq/L}$)								
Site/Date	5.21.16	6.4.16	6.18.16	7.9.16	7.23.16	8.12.16	8.27.16	9.10.16
LWR	243.2	68.4	159.6	166.8	126.1	137.8	127.6	146.5
UWR		91.9	178.1	138.2	95.7	109.5	110.5	122.7
LIF	256.9	224.1	145.0	140.9	132.4	152.1	143.3	180.7
UIF		205.2	143.1	148.5	139.2	146.8	160.3	182.2
NGC1	161.3	134.1	177.3	243.7	275.4			
NGC2					680.9	669.7	718.8	682.6

Table 5: Alkalinity values ($\mu\text{eq/L}$) for the glacial and non-glacial streams over the field season.

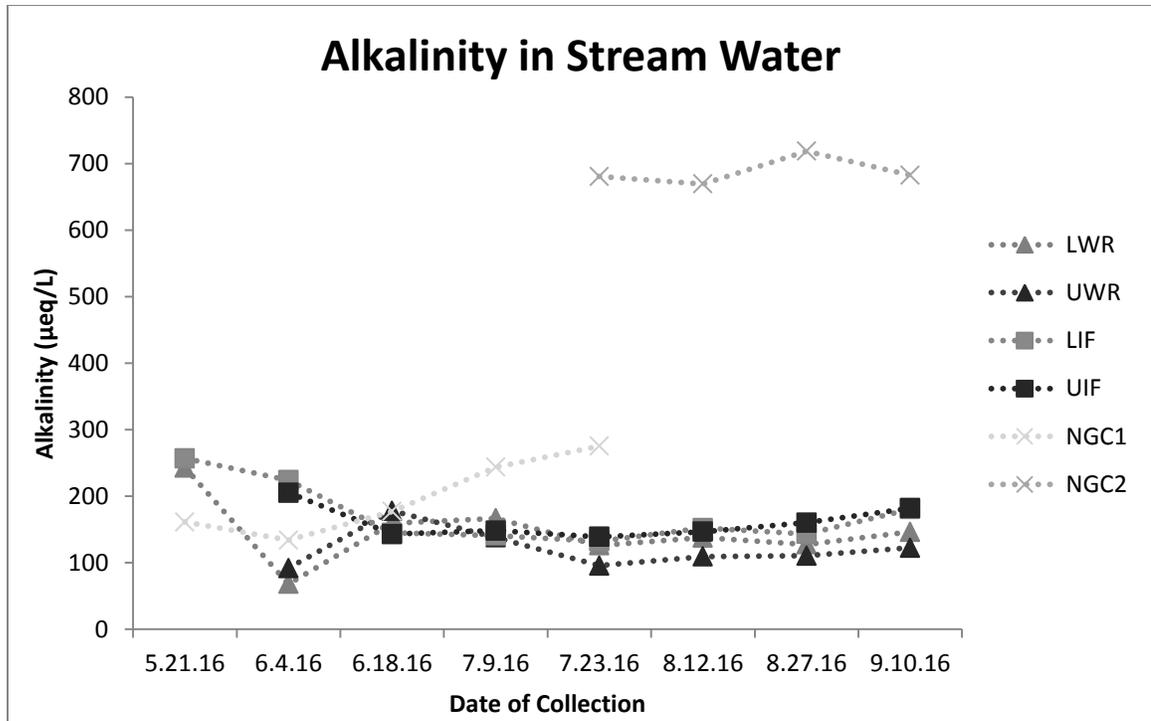


Figure 17: Alkalinity values ($\mu\text{eq L}^{-1}$) for all glacial and non-glacial streams throughout the field season.

4.3 Major Ion Analysis

The White River sites, the Inter Fork White River sites and the non-glacial creek all showed similar trends in the relative amounts of major ions in the stream water (see figures 18-23). At all the sites throughout the summer the general trend for the major cation concentrations was $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$. The general trend for the major anion concentrations was $\text{HCO}_3^- \geq \text{SO}_4^{2-}$. The K^+ , HCO_3^- , and SO_4^{2-} concentrations were very similar throughout the summer in all the White River and Inter Fork White River Sites (see table 6).

At the upper and lower White River sites, all the major ions generally have the highest concentrations early in the melt season and then the concentrations generally

decrease slightly over the summer months. The Ca^{2+} and Na^+ are much more variable throughout the summer months in comparison to the other major ions (K^+ , HCO_3^- , and SO_4^{2-}) which sustain lower and steadier concentrations throughout the summer (see figure 18 & 19). At the upper and lower Inter Fork White River sites, Ca^{2+} , Mg^{2+} and Na^+ initially have high concentrations, begin to decrease but then have peak concentrations again in late July. Similar to the White River, K^+ , HCO_3^- , and SO_4^{2-} sustain lower but steadier concentrations over the field season (see figure 20 & 21). The first NGC sampled began with peak concentrations in May with especially high concentrations of Ca^{2+} , Mg^{2+} and Na^+ . The concentrations of K^+ , HCO_3^- , and SO_4^{2-} are low similar to the other rivers. All the ion concentrations from the NGC1 decreased quickly through mid-July and the stream had dried up by late July (see figure 22). At the second NGC that was used after the first creek dried up displayed concentration values similar to the glacial creek ion concentrations with the exception of HCO_3^- that had really high concentrations (see figure 23).

Average Major Ion Concentrations ($\mu\text{eq/L}$)						
	UWR	LWR	UIF	LIF	NGC1	NGC2
Ca ²⁺	973.7 ± 106.4	887.5 ± 32.6	940.1 ± 67.4	1008.4 ± 102	885.5 ± 386.1	998.8 ± 192.4
Mg ²⁺	352.5 ± 39.5	339.3 ± 11.4	353.8 ± 26.3	349.7 ± 29.7	309.8 ± 135.8	372.1 ± 89.1
K ⁺	115.6 ± 16.8	128.5 ± 11.4	139.8 ± 19.6	125.9 ± 12.7	126.5 ± 63.3	121.2 ± 34.7
Na ⁺	719.6 ± 79.1	557.9 ± 93.2	546.8 ± 107	724.2 ± 159.8	920.4 ± 533.5	895.2 ± 140.9
SO ₄ ²⁻	135.4 ± 17.6	124.6 ± 14.3	106.1 ± 12	91.5 ± 12.5	28.2 ± 10.6	61.6 ± 2.4
HCO ₃ ⁻	120.6 ± 12.1	146.6 ± 18.5	160.4 ± 9.9	171.5 ± 17.2	197.9 ± 48.2	684.6 ± 12

Table 6: Average major ion concentrations ($\mu\text{eq/L}$) for all glacial and non-glacial stream sites.

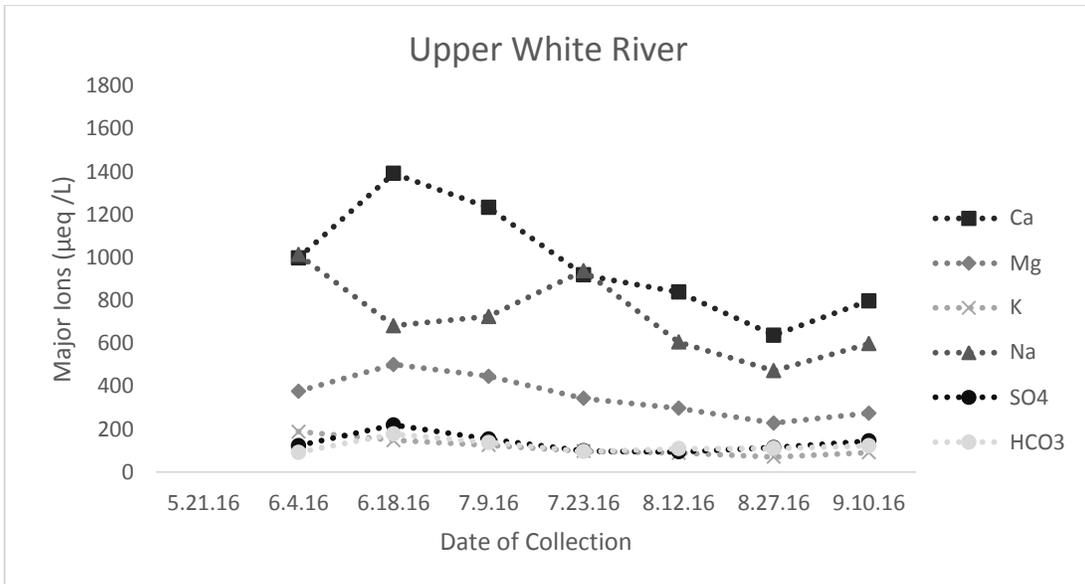


Figure 18: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the upper White River.

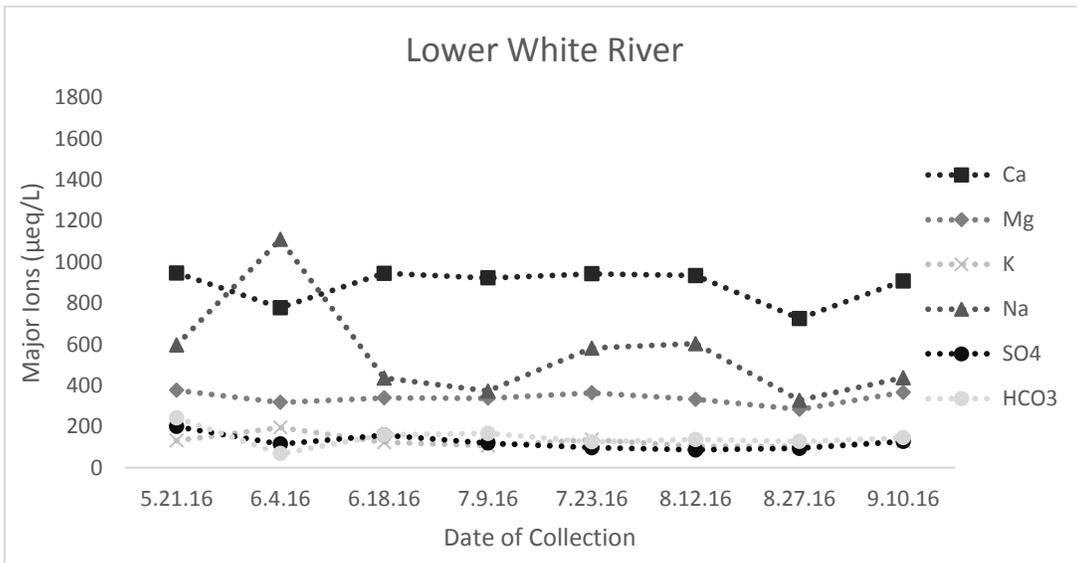


Figure 19: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the lower White River.

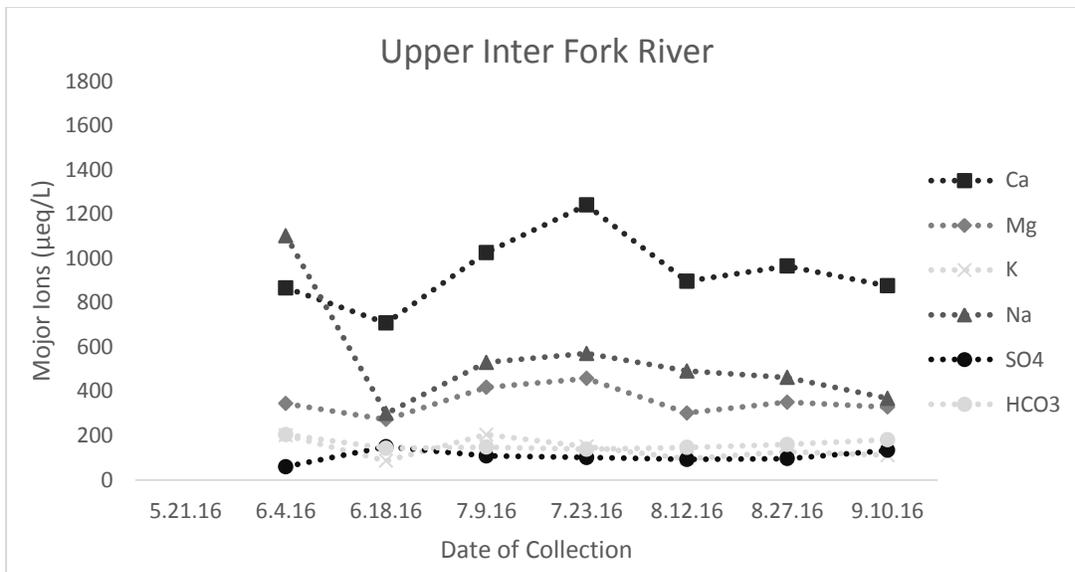


Figure 20: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the upper Inter Fork White River.

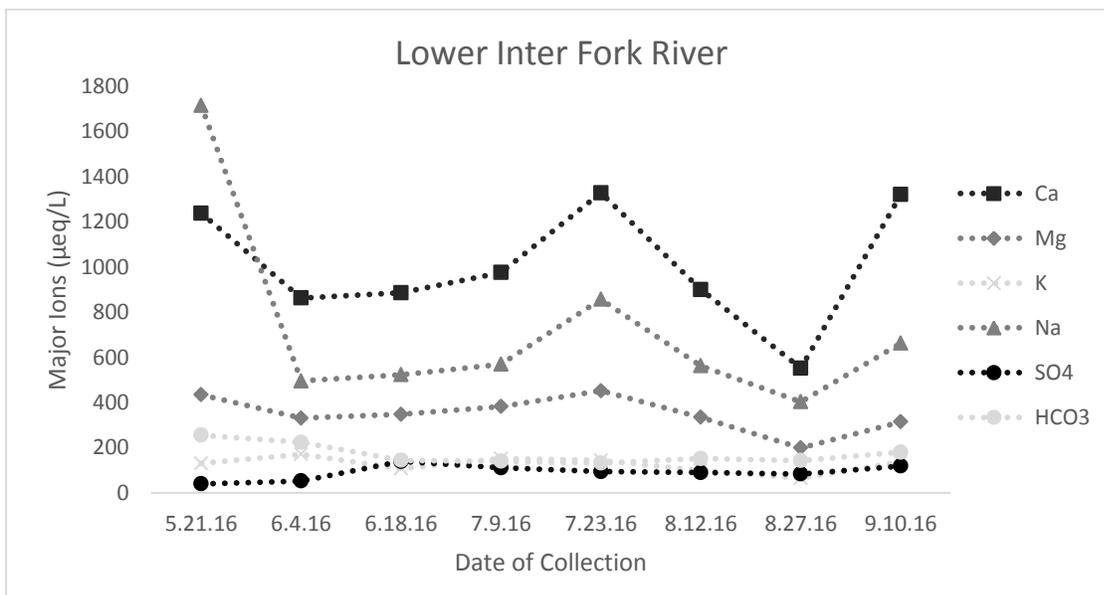


Figure 21: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the lower Inter Fork White River.

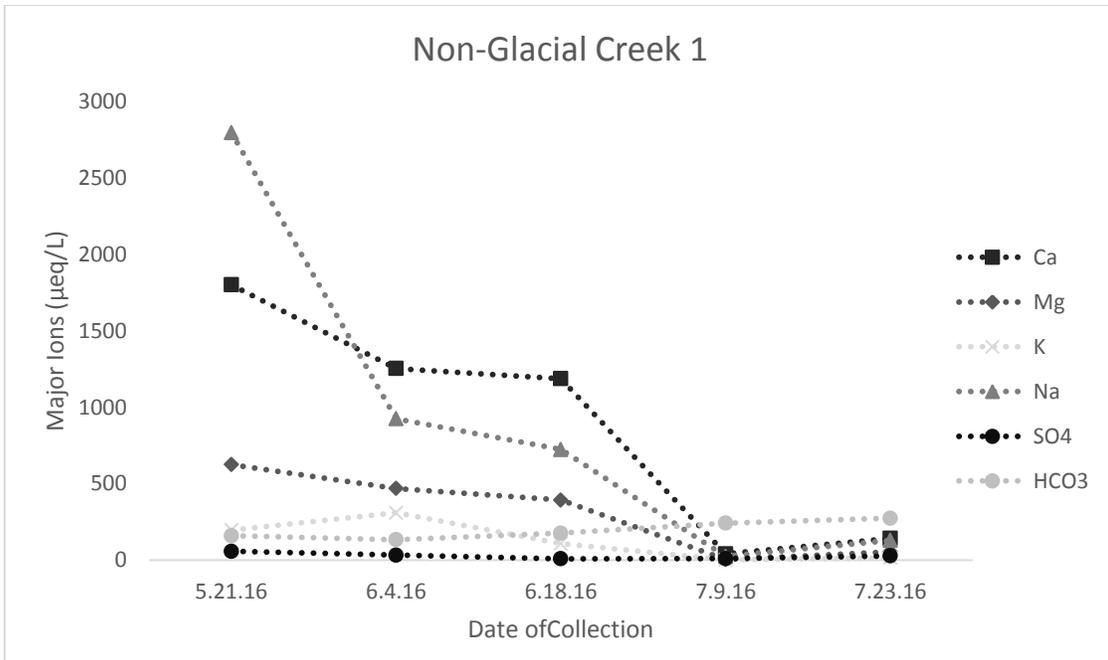


Figure 22: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the non-glacial creek 1. Major ion concentrations were much higher initially in the non-glacial creek, so y-axis has a different scale than all the other graphs.

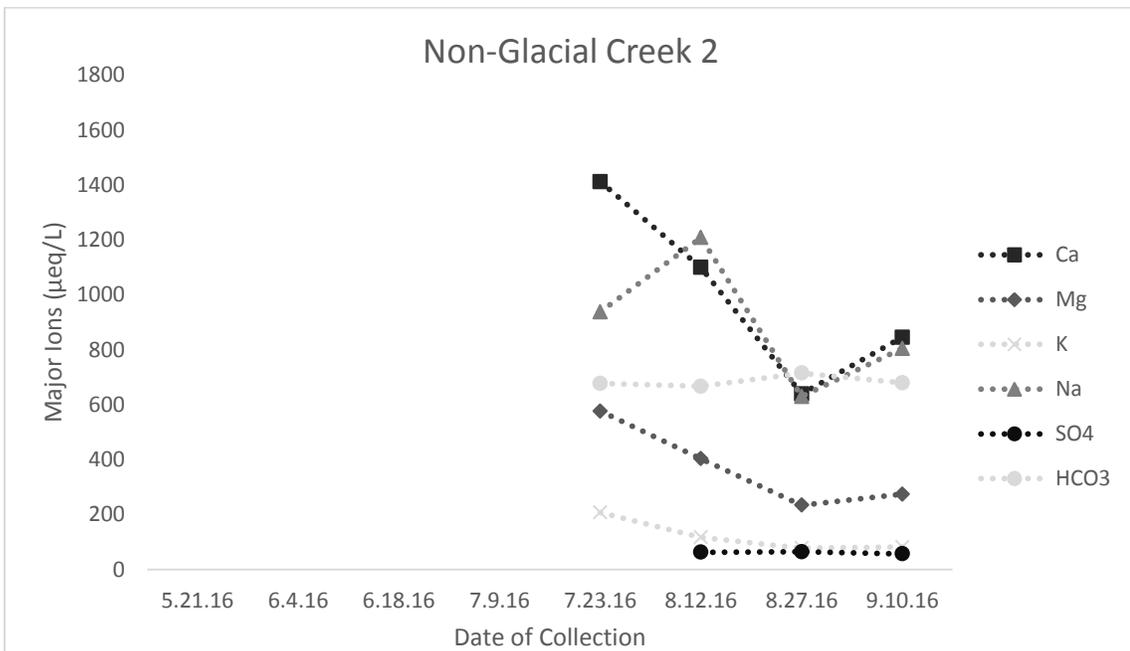


Figure 23: Temporal trends of the major ions ($\mu\text{eq L}^{-1}$) in the non-glacial creek 2.

The trends of HCO_3^- and SO_4^{2-} are important to look at using a smaller scale since they are important in the chemical weathering processes beneath the glacial ice. The HCO_3^- concentrations in the glacial streams start with low concentrations and in general slowly decrease over the summer months (see figure 24). In contrast, NGC1 starts with low concentrations that increase over time. NGC2 displays higher concentrations of HCO_3^- than any of the other glacial or non-glacial creeks. Both glacial streams and the NGC1 have HCO_3^- concentrations ranging from 68.3 to 274.8 $\mu\text{eq L}^{-1}$, while NGC2 has HCO_3^- concentrations ranging from 668.8 to 714.7 $\mu\text{eq L}^{-1}$.

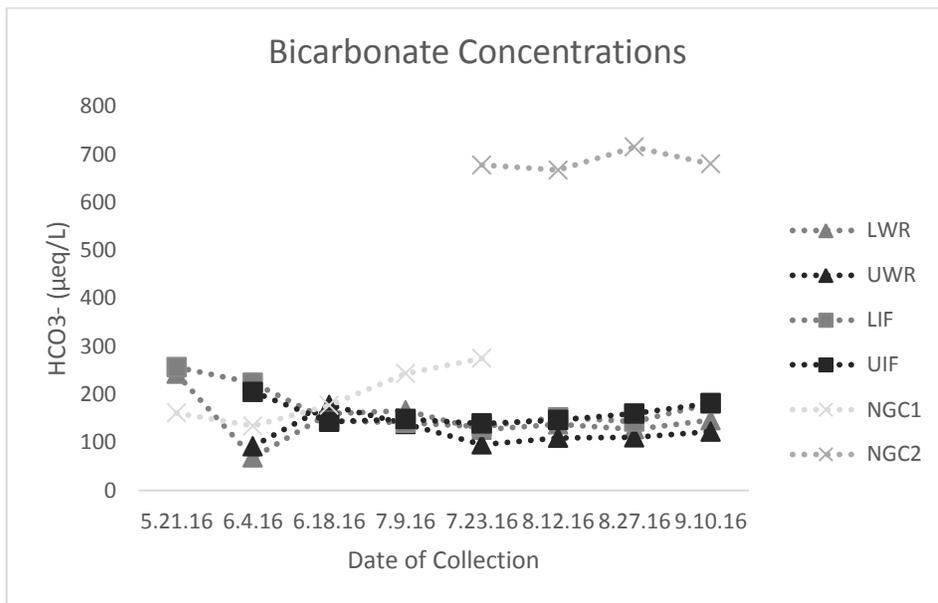
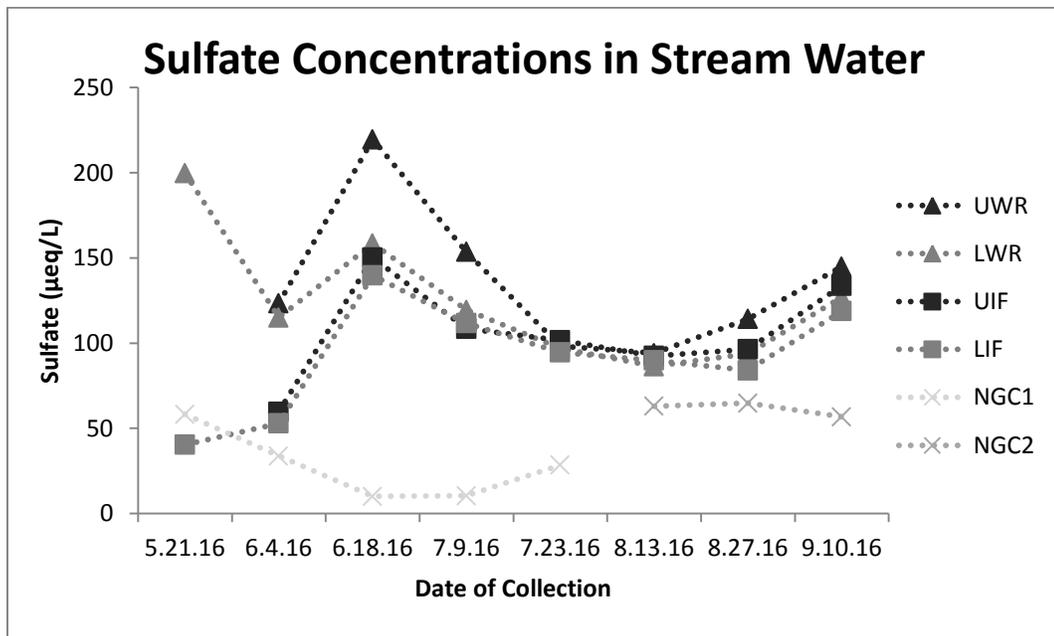


Figure 24: HCO_3^- concentrations ($\mu\text{eq L}^{-1}$) in the glacial and non-glacial streams over the field season.

Using a smaller scale to look at SO_4^{2-} concentrations over time the differences between the glacial creeks and the non-glacial creek concentrations can be observed. The SO_4^{2-} concentrations in all the glacial creek sites peaked in mid-June with the highest concentrations ranging from 139.8 to 219.5 $\mu\text{eq L}^{-1}$ (see figure 25). The highest

concentration of $219.5 \mu\text{eq L}^{-1}$ is from the UWR river site which is located closest to the terminus of Emmon's Glacier. The peak in sulfate levels in the glacial streams generally coincides with the peak DOC concentrations (see figure 26 and 27). In contrast, the SO_4^{2-} concentrations in NGC1 started low and dropped lower when the glacial creeks were experiencing the peak concentrations. The non-glacial creeks had SO_4^{2-} concentrations ranging from 10.1 to $64.8 \mu\text{eq L}^{-1}$. There were no significant relationships between DOC and sulfate when a simple linear regression was ran comparing the two variables.



NOWData sets

Figure 25: Concentrations of SO_4^{2-} ($\mu\text{eq L}^{-1}$) for the glacial and non-glacial streams over the field season.

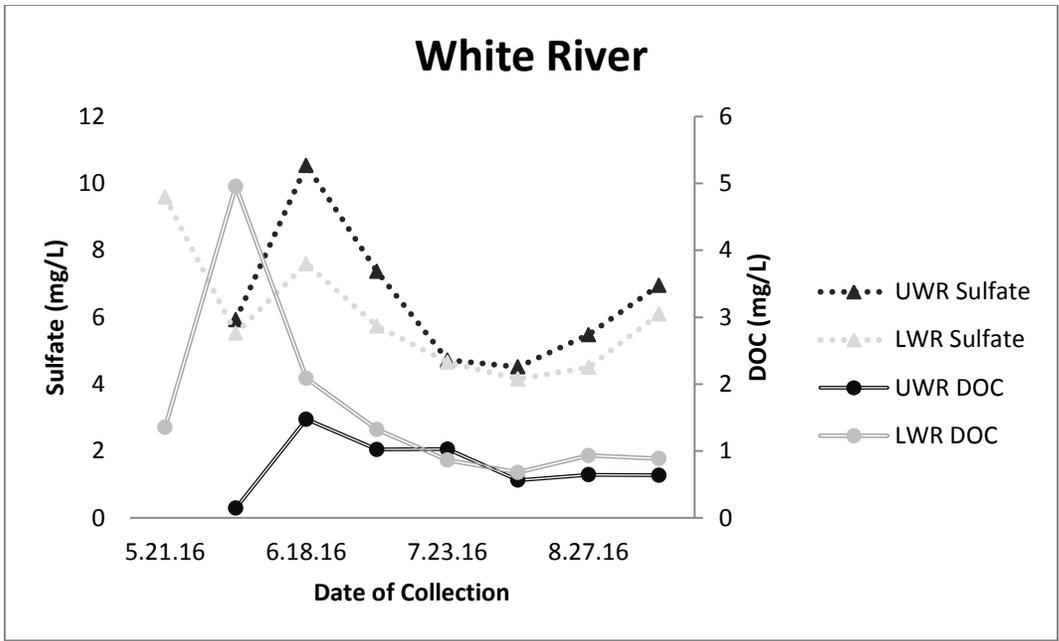


Figure 26: Visual comparison of SO_4^{2-} ($\mu\text{eq L}^{-1}$) and DOC (mg L^{-1}) at both White River sites over the field season.

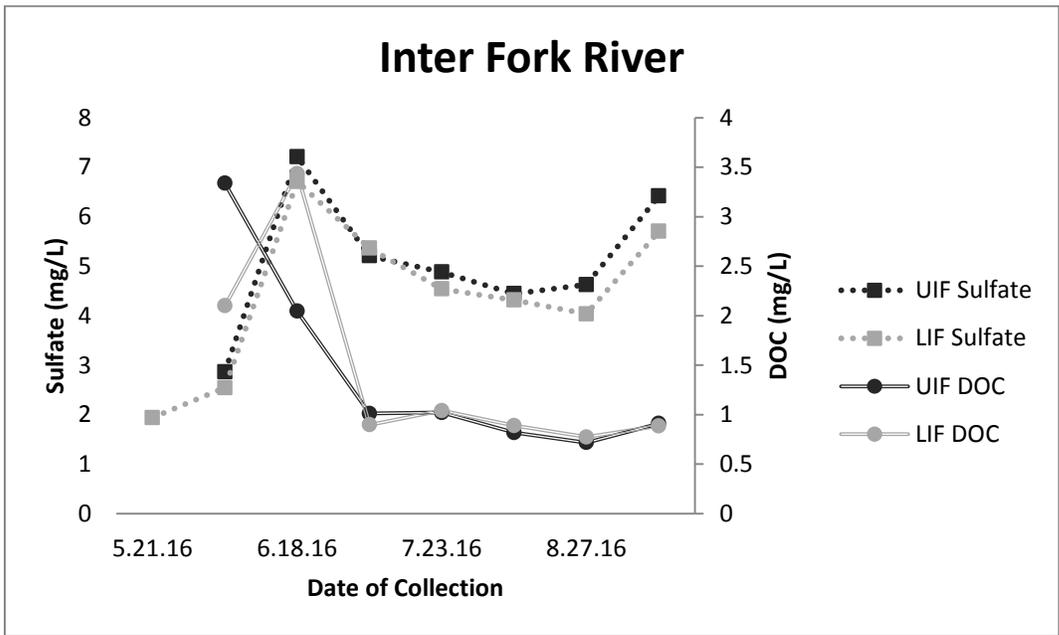


Figure 27: Visual comparison of SO_4^{2-} ($\mu\text{eq L}^{-1}$) and DOC (mg L^{-1}) at both Inter Fork River sites over the field season.

A general understanding of the chemical weathering occurring beneath the glacial ice can be inferred using associations of the major ions in proglacial stream water following procedures similar to those found in Wadham et al., 2010 and Bhatia et al., 2013. This method is typically conducted on borehole meltwaters. That said, this data may not be completely accurate since the samples were gathered after the water exits the subglacial environment and mixes with englacial and supraglacial waters as well as coming in contact with the atmosphere. Research comparing borehole waters and proglacial stream waters has shown that ion concentrations in boreholes are much higher than that of the proglacial streams but proglacial stream water samples can still be used to get an overall idea of the chemical weathering patterns occurring subglacially (Brown, 2002).

One ion association, the C-ratio ratio $[\text{HCO}_3^- / (\text{HCO}_3^- + \text{SO}_4^{2-})]$ (see figure 28), can provide an understanding of the main processes driving chemical weathering beneath the ice which are carbonate dissolution and sulfide oxidation. The UWR had a generally consistent C-ratio throughout the summer, ranging from 0.37 to 0.54. The LWR displayed similar trends to the UWR, with a C-ratio ranging from 0.37 to 0.61 as the summer progressed. The UIF site had a C-ratio ranging from 0.49 to 0.77, with the highest C-ratio's occurring in late spring. The LIF site showed similar trends to the UIF site with a C-ratio ranging from 0.51 to 0.86 and the highest values occurring in late spring. The first non-glacial creek had the highest values for the C-ratio, ranging from 0.73 to 0.96, while the second non-glacial creek had values ranging from 0.91 to 1.

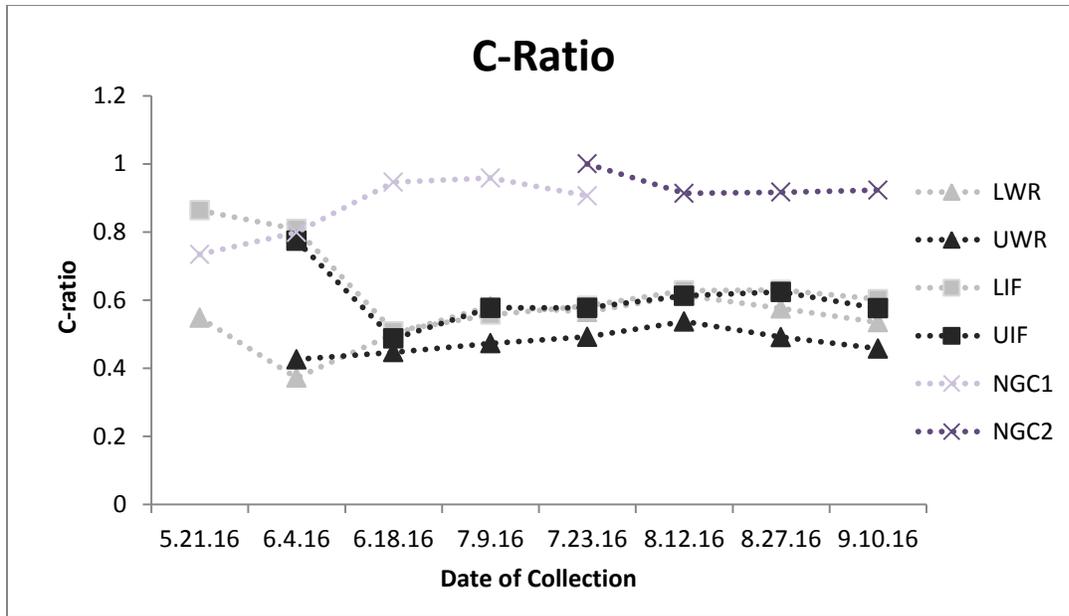


Figure 28: C-ratio values for the White River, the Inter Fork White River and the non-glacial creeks over the field season.

The last ion association utilized was plotting SO_4^- against HCO_3^- which has been used in prior research to gather evidence of microbial activity in the subglacial environment (see figure x). The regression equation of the association between SO_4^- and HCO_3^- should result in a y-intercept of $220 \mu\text{eq L}^{-1}$ based on the theoretical solubility of calcite in meltwater at 0°C (Raiswell, 1984). Y-intercepts larger than this indicates that there must be an additional source of CO_2 to account for the higher concentrations of HCO_3^- if the drainage system is closed to the atmosphere (Bhatia et al., 2013; Raiswell, 1984; Wadham et al., 2010). The association of SO_4^- and HCO_3^- in the UWR resulted in a $p = 0.001$, $R^2 = 0.86$ and a y-intercept of $34.6 \mu\text{eq L}^{-1}$ (see figure 29). The LWR had a $p = 0.03$, $R^2 = 0.57$ and a y-intercept of $25.4 \mu\text{eq L}^{-1}$ (see figure 30). while the LIF had a $p = 0.03$, $R^2 = 0.57$ with a y-intercept of $266.1 \mu\text{eq L}^{-1}$ (see figure 32). The results of the plot for SO_4^- against HCO_3^- at the UIF site were not significant (see figure 31).

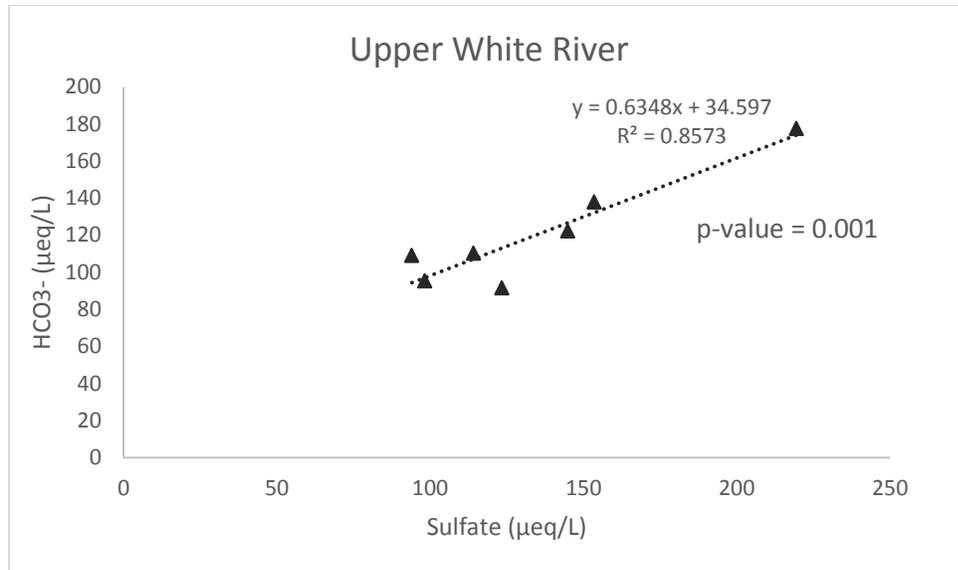


Figure 29: The comparisons of HCO_3^- ($\mu\text{eq L}^{-1}$) and SO_4^{2-} ($\mu\text{eq L}^{-1}$) for the upper White River site.

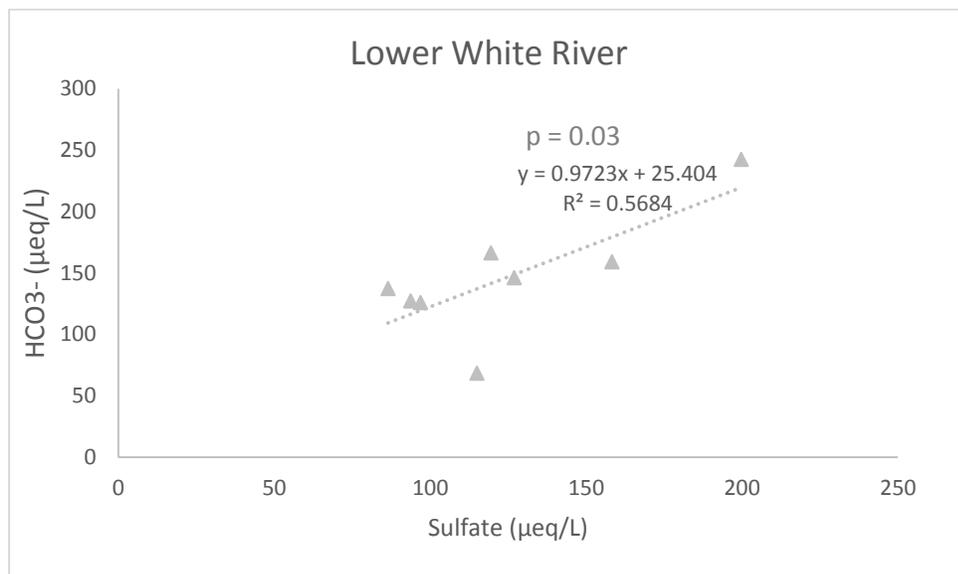


Figure 30: The comparisons of HCO_3^- ($\mu\text{eq L}^{-1}$) and SO_4^{2-} ($\mu\text{eq L}^{-1}$) for the lower White River site.

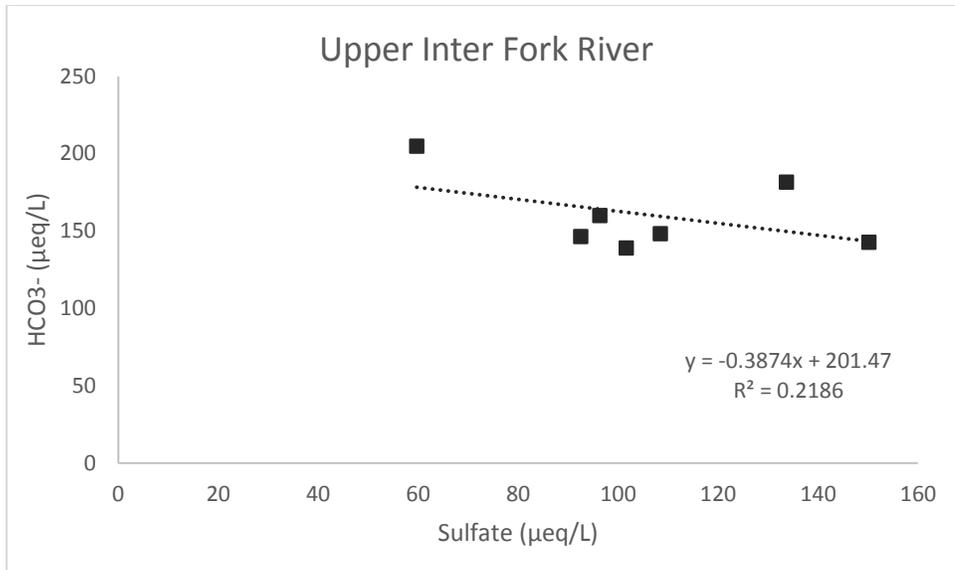


Figure 31: The comparisons of HCO₃⁻ (µeq L⁻¹) and SO₄²⁻ (µeq L⁻¹) for the upper Inter Fork White River site.

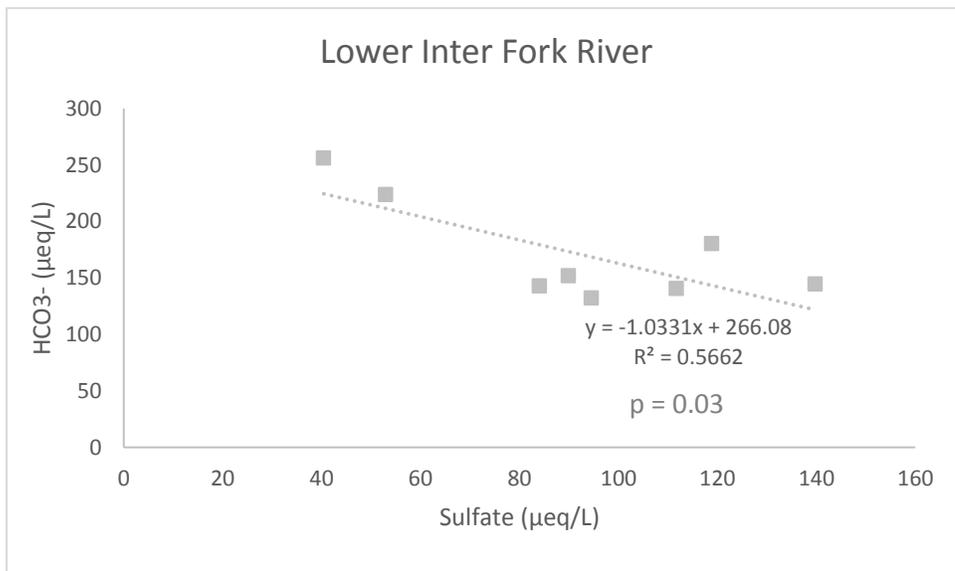


Figure 32: The comparisons of HCO₃⁻ (µeq L⁻¹) and SO₄²⁻ (µeq L⁻¹) for the lower Inter Fork White River site.

5. Discussion

5.1 Temporal and spatial patterns of DOC export

Current DOC export from the two glacial streams studied on Mount Rainier show similar temporal patterns over the melt season. DOC concentrations displayed the most variability during May and June, with the peak concentrations (1.5 to 4.9 mg L^{-1}) occurring in early to mid-June. After the peak in late spring, DOC concentrations in all the glacial streams decreased and leveled off to < 1 mg L^{-1} in July. The DOC concentrations stayed low through mid-September when the melt season ends and snow begins to accumulate for the winter. This DOC data is similar to results found in other studies, which generally found that DOC concentrations in glacial meltwater ranges from about 0.1 to 4.0 mg L^{-1} with peak concentrations occurring early in the melt season (Bhatia et al., 2013; Fellman et al., 2014; Hood et al., 2009; Lafreniere & Sharp, 2004).

The UWR and UIF sites are likely to have the most influence from glacial meltwater since these sites are located very close to the glaciers' terminus. These sites are less likely to have DOC inputs from other sources, like vegetation, soils, non-glacial streams or groundwater intrusion (Fellman et al., 2014; Hood & Scott, 2008). The LWR had the highest DOC concentration of all the glacial stream sites with a concentration of 4.9 mg L^{-1} C. The LWR site is located the furthest downstream from either glacial terminus. Multiple non-glacial streams tributaries, and the Inter Fork White River have merged into the White River at this location. The LWR site is also below the tree line, so it seems that DOC from any terrestrial sources are contributing to this higher concentration. The UWR site, which is close to the terminus of Emmon's Glacier, has

much lower DOC values during the peak export in comparison to the LWR, with a concentration of $1.5 \text{ mg L}^{-1} \text{ C}$. The lower peak DOC concentration is more representative of the proglacial waters that are most influenced by the glacial environment and least influenced by terrestrial carbon sources, which is expected.

The UIF and LIF sites had much more similar values during the peak export, with concentrations of $3.3 \text{ mg L}^{-1} \text{ C}$ and $3.4 \text{ mg L}^{-1} \text{ C}$ respectively. These sites were both located in areas that were in the tree line, so were not only receiving inputs of carbon from the glacial environment but from terrestrial sources as well. The UIF site should have less influence from terrestrial sources, because it is closer to the Inter Glacier's terminus.

By July, DOC concentrations at all the glacial stream sites decreased and displayed similar concentrations throughout the rest of the summer. All sites had generally low concentrations, ranging from $0.6 \text{ mg L}^{-1} \text{ C}$ to $1.0 \text{ mg L}^{-1} \text{ C}$. The non-glacial creek showed a much flashier pattern of DOC export, with high peaks observed in mid-May and in mid-June. By mid-July this non-glacial stream dried up. This indicates the importance of the glacial meltwater during the warm, dry months of summer. The glacial streams provide a consistent supply of cool, freshwater and DOC to downstream aquatic ecosystems. In contrast, the non-glacial streams that rely on precipitation often dry up and no longer provide freshwater or DOC to downstream aquatic environments. With recent studies showing that the DOC from glacial environments is more labile in quality compared to other DOC sources (Hood et al., 2009; Hood et al., 2015) this DOC input from glacial meltwater is important to proglacial aquatic ecosystems, even if it is being exported in small concentrations. A study completed by Fellman et al., (2015)

demonstrated that glacially derived DOC is utilized throughout the food web from biofilm to invertebrates and different fish species. This illustrates how important this source of DOC is to these aquatic environments.

At the proglacial stream sites on Mount Rainier, peak DOC concentrations occurred during the period of snow melt and lower concentrations occurred later in the season when glacial melt dominated. One theory is that the peak DOC concentrations in the glacial streams during spring is partly due to the flushing of open cryoconite holes on the surface of the glacier as the snow melts. Based on the significant results of simple linear regression plots of DOC concentrations against snowmelt ($p < 0.05$) this seems like a possible theory. When there is still snow on top of the glacial ice, the snow melt permeates through the remaining snow and firn cover until it reaches the ice surface where it either travels across the ice and exits from the supraglacial environment into a proglacial environment or it travels to the subglacial environment through crevasses in the ice (Fountain & Walder, 1998; Lafreniere & Sharp, 2004). This process of the melt water traveling across the ice surface and exiting the supraglacial environment is one that could flush any exposed cryoconite holes early in the melt season. This snowmelt can also wash terrestrial carbon into streams from plants and soils, so this may also be a source of DOC resulting in the peak DOC concentrations. Since the UWR site and the UIF site are closer to the terminus of the glaciers the terrestrial carbon sources should not be as influential as at the lower glacial river sites.

A second theory is based on the coinciding peaks of the DOC and SO_4^{2-} concentrations in the glacial streams during late spring. Studies have demonstrated that snow and supraglacial water generally have very low levels or no SO_4^{2-} present compared

to subglacial waters that become enriched with SO_4^{2-} (Anderson, Longacre and Krall, 2003; Mitchell et al., 2013). The acquisition of SO_4^{2-} into meltwater occurs when water in the subglacial environment comes in contact with the rock flour generated by the movement of the glacier (Brown, 2002; Mitchell et al., 2013; Raiswell, 1984). This rock flour contains fresh surfaces of the mineral pyrite and these fresh mineral surfaces quickly react with O_2 and H_2O , which results in the addition of SO_4^{2-} into the subglacial meltwater (Brown, 2002; Raiswell, 1984).

Since there is a peak in SO_4^{2-} concentrations in late spring, it seems to indicate that meltwater may be originating from the subglacial environment to produce this peak. This could be the point in the melt season when enough of the glacier's ice surface is exposed and crevasses begin to form, causing more meltwater to flow to the subglacial environment, which begins the evolution of the drainage system from a distributed, slow flowing system to a channelized, quicker flowing drainage system (Fountain & Walder, 1998). As this drainage system transitions due to the influx of meltwater in the subglacial environment, the flow in the subglacial drainage system increases, which could result in the peak SO_4^{2-} concentrations. If the ice on Emmon's glacier at lower elevations was snow free during this time of the year it would provide conditions for the evolution of the drainage system as described above. Since DOC concentrations peak around the same time as the SO_4^{2-} concentrations, that could indicate that some of the DOC is from carbon pools beneath the glacier.

Based on the significant p-values ($p < 0.05$) for the plots of velocity against DOC concentrations at the UWR site and the UIF site, it seems higher DOC concentrations occur with lower velocities of the stream water. Velocities in the White

River and Inter Fork White River were the highest mid-June through the end of August when the DOC concentrations were the lowest. This could indicate that the higher velocities may be diluting the DOC and sulfate concentrations in the meltwater. By gathering future data on meltwater from bore holes drilled through the glacial ice, a more accurate understanding of these concentrations during the summer months is possible.

The Inter Fork White River sites are more complicated than the White River sites because they are located in the forest and have a tree canopy over the stream. This means that there will be carbon from terrestrial sources influencing the DOC concentrations in these stream samples. To tease out the contribution of each different source of carbon in glacial streams, future research will need to focus on $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$ analyses and radiocarbon dating. This allows researchers to understand what portion of the DOC is likely from glacially derived sources versus terrestrial sources so a more intricate data set of glacial DOC export over the melt season can be gathered. All the glacial stream sites display a similar temporal pattern, so although data on the DOC sources can get more detailed with future research, this current data still shows the general trend of DOC export from glacial meltwater. When compared to the temporal pattern of DOC concentrations in the non-glacial creeks, the glacial streams display a different DOC export pattern.

To understand what factors were most important in controlling DOC export from glacial environments, the relationships between DOC export and multiple parameters were examined. Plots of DOC concentration against snow depth, snowmelt, and velocity all had significant p-values as well as relatively high R^2 values, although these values varied from site to site. DOC concentrations plotted against temperature and precipitation

had less significant p-values overall compared to the other parameters. One explanation for the varying p-values is the lower sites on the White River and Inter Fork White River are influenced by the mixing of non-glacial streams and terrestrial DOC inputs. These confounding factors could obscure the data since the influence of glacial melt on DOC export would be diluted by other sources of DOC. Overall, it seems that all parameters have an influence on the DOC export in the glacial bulk meltwaters, with snow depth, snowmelt and velocity having the strongest influence on DOC export.

5.2 Chemical weathering patterns in the subglacial environment

The major ions that are exported by glacial melt water during the summer months gives can provide a general insight into the chemical weathering that is occurring in the subglacial environment. They also can provide evidence for the presence or absence microbial communities beneath the ice. The cation concentrations found in the White River and the Inter Fork White River were generally high compared to other studies done on glacial meltwater (Bhatia et al., 2013; Brown, 2002; Singh et al., 2014). The anion concentrations were generally on the low end in comparison to other studies done on glacial meltwater (Brown, 2002; Singh et al., 2014; Wadham et al., 2010). These ion concentrations are reasonable based on the composition of the andesitic lava beneath the glaciers. Andesite is composed of ~50% SiO₂ (Schuman, 1993) The major mineral assemblages include plagioclase, pyroxenes, hornblende, with possible minor mineral assemblages of biotite, magnetite, apatite, zircon, ilmenite and garnet (Schuman,1993). Researcher have also found pyrite minerals present in volcanic rock on Mount Rainier,

which provides a source of sulphate for chemical weathering processes (John et al., 2008).

Using the associations of different ion concentrations in the meltwater, a general understanding of the chemical weathering processes occurring in the subglacial drainage system of the Emmon's Glacier and the Inter Glacier can be gathered. Here I discuss the results of these major ion concentrations from the upper White River site and the upper Inter Fork site. These sites were located closest to the glacial terminus, so the results from these sites represent the bulk glacial meltwaters before they are complexed by other water sources or weathering regimes.

Upper White River

Acid hydrolysis is the most important weathering reaction occurring beneath the ice (Brown, 2002; Raiswell, 1984). This reaction occurs as protons (H^+) drive acid hydrolysis and weather ions out of the rocks or rock flour, which is crushed up rock particles from glacial erosion (Sharp, Richards & Tranter, 1998). The dissolution and dissociation of atmospheric CO_2 (carbonate dissolution), and sulfide oxidation are the main reactions that produce H^+ protons in the subglacial environments (Brown, 2002; Raiswell, 1984). In general, silicates, aluminosilicates and carbonates dominate in the rocks found beneath glaciers, with accessory pyrite minerals sometimes present that represent the source of sulphate in meltwater (Raiswell, 1984). By using the C-ratio $[HCO_3^- / (HCO_3^- + SO_4^{2-})]$ the dominate source of protons driving the acid hydrolysis can be determined (Brown, 2002; Raiswell, 1984).

The C-ratio calculated for the White River sites revealed a value around 0.5 throughout the entire glacial melt season. This value indicates that there is coupled sulphate oxidation and carbonate dissolution occurring in the subglacial environment of Emmons glacier. The C-ratio indicates that the source of the protons beneath Emmon's Glacier are derived from the sulfide oxidation and the dissolution and dissociation of atmospheric CO₂.

pCO₂ values for the UWR are consistently below 300 ppm throughout the field season. This could indicate the subglacial drainage system was out of contact with the atmosphere (~409 ppm) (NOAA, 2017) and although my sites were in contact with the atmosphere, equilibration of the CO₂ had not occurred yet (Brown, 2002). The low pCO₂ values are a common occurrence when a fresh source of water, like snowmelt, comes in contact with a large amount of newly ground rock flour (Brown, 2002). The pCO₂ values at the LWR site are below 400 ppm except for a peak from early July to early August that reaches 595 ppm. High pCO₂ values can also indicate a closed drainage system that is receiving protons faster than they are used for chemical weathering, which could be the result of snowmelt or an increase in sulfide oxidation (Brown, 2002). The LWR site is further downstream from the glaciers terminus than the UWR site, so it has likely been more heavily influenced by contact with the atmosphere. Looking at the UWR site which is closer to the terminus of the glacier, the pCO₂ levels provide evidence for a closed drainage system beneath the glacier.

By plotting HCO₃⁻ versus SO₄²⁻ the resulting regression line can give insight into any potential presence of microbial communities beneath the ice. When subglacial flour comes in contact with meltwater, carbonate hydrolysis occurs due to the high reactivity of

the rock flour (Bhatia et al., 2013; Wadham et al., 2010). The carbonate dissolution reaction results in the production of HCO_3^- at a rate quicker than SO_4^{2-} is produced, so there HCO_3^- concentrations will increase in the meltwater before SO_4^{2-} concentrations begin increasing (Bhatia et al., 2013; Tranter et al., 2002; Wadham et al., 2010). Based on the theoretical solubility of calcite in meltwater at 0°C , this reaction should result in around $220 \mu\text{eq L}^{-1}$ of HCO_3^- in the water. Y-intercepts larger than this indicates that if the subglacial drainage system is closed to the atmosphere, there must be an additional source of CO_2 to account for the higher HCO_3^- concentrations in the meltwaters. (Bhatia et al., 2013; Brown, 2002; Wadham et al., 2010). Some studies reason that y-intercepts higher than $220 \mu\text{eq L}^{-1}$ suggest microbial communities are present in the subglacial environment that oxidize organic carbon generating additional CO_2 , which produces more protons that drive the chemical weathering processes (Bhatia et al., 2013; Tranter et al., 2002; Wadham et al., 2010). The plot of HCO_3^- versus SO_4^{2-} from the UWR resulted in a regression line with a y-intercept $< 220 \mu\text{eq L}^{-1}$. This data does not provide evidence to suggest that there are microbial communities producing additional CO_2 beneath Emmon's Glacier.

These results of the plots are likely skewed due to the fact that they were analyzed from bulk meltwater samples, which have come in contact with atmospheric CO_2 although at some sites it seemed equilibration of the CO_2 had not occurred yet. Future research should focus on gathering meltwater samples from boreholes in the glacier. This would provide more accurate data on the subject since boreholes allow researchers to gather water samples that are out of direct contact with the atmosphere. Studies done comparing borehole waters to bulk meltwaters indicate there is a substantial difference in

data depending on where you gather the glacial waters from (Brown, 2002; Bhatia et al., 2013; Tranter et al., 2002; Wadham et al., 2010). Although there is no evidence from this data suggesting there are microbial communities in the subglacial environment of Emmons Glacier, there are still consistent concentrations of DOC supplied to the White River throughout the melt season. Although the sources of the DOC cannot be fully understood without further research, some of the DOC is likely from the subglacial environment where soils and vegetation were overrun by the ice during the last ice age. Even if microbial communities are not altering this carbon source, the subglacial environment is likely still be a source of DOC to downstream ecosystems.

Upper Inter Fork White River

The C-ratio in the Inter Fork White River samples was around 0.8 early in the season and then evolved to around a 0.55 in mid-June to July and stayed fairly consistent throughout the rest of the summer months. These values indicate that carbonate reactions, or the dissolution and dissociation of atmospheric CO₂, are the dominate source of protons beneath the Inter Glacier early in the melt season. The chemical weathering reactions shift from being dominated by carbonate dissolution to coupled sulfide oxidation and carbonate dissolution by mid-June and this trend continues for the rest of the melt season.

pCO₂ values for the UIF had much greater variation than the UWR. The values ranged from 289.5 to 618.9 ppm. The LIF displayed values similar to the UIF with values ranging from 266.3 to 833.7 ppm. Both sites displayed the lowest pCO₂ values in mid-June similar to all the other glacial and non-glacial sites. With the UIF closer to the Inter

Glacier's terminus, it displays the trends most influenced by the glacial meltwater. Overall the UIF displays values lower than the values of the LIF site, likely because the water at the LIF site had more of an influence from contact with the atmosphere and has had time for the CO₂ in the stream to reach equilibrium.

The plot of HCO₃⁻ versus SO₄²⁻ from the UIF site resulted in y-intercept < 220 µeq L⁻¹. This result is similar to the results obtained for the UWR and they do not provide evidence for microbial activity in the subglacial environment. Again, these results are likely skewed due to the water samples being in contact with atmospheric CO₂. The UIF site may also have slightly differing results than the UWR site because it is located in an area with tree cover. Overall, this data does not provide evidence for microbial activity in the subglacial environment of the Inter Glacier.

There is still a steady flux of DOC to the Inter Fork River throughout the summer with a peak in the late spring, indicating there is a source of DOC in this area consistently providing DOC to the stream. The DOC concentrations from the bulk meltwaters of the Inter Fork White River does displays trends similar to the DOC concentrations from the White River, but does not display trends similar to the non-glacial creek. This suggests the data gathered for the glacial streams are displaying the general trends of DOC exported from glacial meltwater. As mentioned previously, future research could gather a more detailed understanding of the proportions of glacially derived carbon sources and terrestrial carbon sources by analyzing the δ¹³C, Δ¹⁴C and doing radiocarbon dating. The results from the UIF and UWR demonstrate that DOC export occurs throughout the glacial melt season to proglacial streams, whether this carbon source is glacially derived or from terrestrial sources.

5.3 The effects of glacial area on DOC and major ion export: The implications of continued glacial recession and climate change

This study gives insight into how DOC concentrations and chemical weathering regimes differ depending on the glacial area at the headwaters. Emmon's Glacier is the largest glacier on Mount Rainier (11.1 km²), the Inter Glacier is one of the smallest glaciers (0.8 km²) and the non-glacial creek is fed by lake waters and precipitation. Although stream water that is fed by lake waters may not be the ideal in some circumstances as a reference, it can be more effective when looking at changes between streams with differing glacial area at the headwaters. This is because as glaciers recede, they often leave behind large chunks of ice, which melt into lakes in these alpine environments. By comparing data between these three sites it can give insight into the changes that may occur as glaciers in the region continue to recede. I only used the data from the UWR and the UIF to compare to one another and with the non-glacial creek since they represent the purest glacial bulk meltwater.

The DOC peak concentrations were lowest in the White River (Emmon's Glacier), with higher peak concentrations in the Inter Fork White River (Inter Glacier) and the highest concentrations in the non-glacial creek. Prior research suggests that DOC sources may change as glacial recession results in less glacial area for cryoconite holes to form and less subglacial area for microbial communities to mobilize the organic carbon left beneath the ice (Fellman et al., 2014; Hood & Scott 2008). Instead more terrestrial sources of organic carbon will be input into the streams and rivers as terrestrial

succession follows glacial retreat, which results in higher concentrations of DOC. Not only do the sources of carbon shift, but the timing of the peak DOC export will shift as factors like snowmelt and precipitation patterns shift in timing (Hood & Scott, 2008; Hood et al., 2009). Models on snowmelt and precipitation done by the IPCC (2014) indicate that snowmelt will happen earlier in the season and precipitation will shift from snow to rain earlier in the season. The likely change in the timing of peak DOC concentrations could have an effect on the heterotrophic communities that rely on this DOC source (Fellman et al., 2015; Hood & Scott, 2008). An indication of this possible shift in the peak DOC concentrations is the non-glacial creek displayed the highest DOC concentrations earlier in the spring than the glacial streams. The current timing of the peak DOC export in the study, will likely occur earlier in the calendar year in coming decades since snowmelt and snow depth seemed to play a role in DOC export. The temporal trends of DOC export from meltwater needs to be monitored in the coming decades to really gather firm evidence of how these patterns may shift.

Since the DOC from glacial environments has been found to be more labile in nature than DOC from other sources, this shift in available labile DOC to the downstream aquatic environments could result in a shift in the structure of the aquatic food web (Hood & Scott, 2008; Hood et al., 2009,). If glaciers end up disappearing altogether, this would result in a shift from stream environments receiving predominately bioavailable glacially derived DOC to receiving predominately terrestrial DOC, which would likely result in a shift in the local aquatic food webs (Fellman et al., 2014). That is because the bioavailable glacially derived DOC stimulates production in the heterotrophic communities which make up the base of food webs (Fellman et al., 2014; Hood & Scott,

2008). Without any input of glacial DOC, the heterotrophic communities would likely change in structure with effects rippling through the aquatic ecosystem.

Not only will the recession of glaciers result in a decreasing export of glacially-derived DOC to downstream environments, it will also result in a decreasing supply of fresh, cool water to these streams and rivers. During the hot, dry summer months, glacial meltwater supplies streams with a constant supply of water. The non-glacial streams and creeks that are reliant on precipitation events or lake water often dry up part way through the summer, like what occurred to NGC1 in this study. There was a notable difference between the discharge of the White River, the Inter Fork White River and the non-glacial creek based on physical observation in the field. When glaciers are receding, the discharge has been shown to initially increase (Fountain & Tangborn, 1985) and then it begins to decrease until it becomes a non-glacial stream reliant on precipitation. This change in water input would likely have an impact on downstream aquatic ecosystems. In the Pacific Northwest, salmon species rely on high flows to reach their spawning grounds and cool temperatures to induce spawning. Without the freshwater input from glaciers, species like the salmon would be negatively impacted by the disappearing glaciers.

Looking at the C-ratio, it seems likely that as the glaciers recede a shift in weathering regimes may occur. The C-ratio in the spring at the UWR (Emmon's Glacier) was ~ 0.5, while the C-ratio at the UIF (Inter Glacier) and the NGC1 was ~0.8. This indicates there could possibly be a shift from coupled sulfide oxidation and carbonate dissolution producing protons for chemical weathering to primarily carbonate dissolution producing the protons for chemical weathering as glacier size decreases. This could be likely due to the glaciers covering less rock surface as they recede causing less chemical

weathering from the rock-water-ice contact. Instead, succession of vegetation in the area where glacial ice once covered rock will develop more soils for the vegetation and result in a different chemical weathering regime more indicative of the soils properties. This could also be due to differences in the underlying geology. Overall, this data demonstrates that there are differences in the concentrations of DOC and major ions in streams with differing glacial area at the headwaters. By monitoring this data into the future, a more concise understanding of the changes that may occur with receding glaciers can be gathered.

7. Conclusion

Glacier meltwaters from Mount Rainier are an important source of DOC to local proglacial environments. Both glaciers studied on Mount Rainier showed similar temporal patterns of DOC export compared to nearby non-glacial creeks indicating glaciers have unique properties that influence this export. By comparing glacial streams with different glacial coverage at the headwaters, this study provides insight into how DOC and major ion export may change as glaciers recede. Taking into consideration future climate scenarios it seems that not only will the DOC concentrations change as glaciers recede, but the timing of the peak DOC concentrations will likely shift in time and occur earlier in the season. Changes in DOC export from glacial environments are liable to cause changes to the aquatic food web. This could be problematic for important river organisms, including salmon and trout which are an economically and traditionally important species in the Pacific Northwest. Future research using stable isotope analysis

and radiocarbon analysis would allow for a more detailed understanding of the DOC sources and ages found in glacial watersheds on Mount Rainier. These techniques can also be used to track glacially derived carbon through the food web. Understanding if important fish species in our region are in any way reliant on this glacial carbon is crucial in keeping these fish populations strong.

When ancient DOC in the subglacial environment is mobilized it can stimulate heterotrophic communities in the glacial streams (Hood et al., 2009; Lawson et al., 2014; Spencer et al., 2014). Finding evidence of microbes in the subglacial environment by using these ion associations may suggest that they are helping mobilize some of the ancient DOC. The associations of the major ions found in the bulk meltwaters on Mount Rainier did not provide evidence for microbial communities beneath the ice. A more detailed study is needed in order to understand if there are microbial communities in the subglacial drainage system.

The chemical weathering pattern in the subglacial environments indicates that the current chemical weathering regime beneath Emmon's Glacier and Inter Glacier is generally coupled carbonate dissolution and sulfide oxidation. The slight differences in the C-ratio early in the melt season imply that the source of the meltwaters may come from different regions beneath the ice, so microbial communities may be present in some regions beneath the ice but not others warranting the need for more research. A study by Wadham et al. (2010) indicated that harder bed rock (high silica content) beneath glaciers provide less substrate for microbes than soft bedrock (sedimentary rocks). This may be the case on Mount Rainier since the glaciers are located on top of Andesite lava flows which are high in silica content. Future research should use borehole investigations to get

a more accurate idea of the DOC and major ion concentrations in the subglacial environments. The bore hole investigations drill a hole through the glacier to gather a water sample from beneath the ice. By doing this, complicating factors like exposure to atmospheric CO₂ can be eliminated.

This study provides data on the current spatial and temporal trends of DOC and major ion export in glacial streams on Mount Rainier. This data can provide insight into the local glacial chemical weathering regimes and the changes that may occur to these patterns as climate change causes the glaciers to recede. This data is beneficial for any researchers interested in continuing to monitor carbon export from glaciers in the Pacific Northwest. It would also be valuable to natural resource managers or policy makers to use when making decisions about protecting our natural resources, like salmon or trout. Understanding glacial dynamics is complicated, yet important on a global and local scale. Ice sheets and mountain glaciers are contributing labile DOC to proglacial coastal and freshwater environments. As these ice sheets and mountain glaciers recede proglacial aquatic environments will all likely undergo shifts to the local food webs. This study has provided a first glimpse into the local trends in glacial carbon cycling and discussed the implications of the recession of the glaciers on Mount Rainier which will continue as the climate continues to change.

References

- Anderson, S. P., Longacre, S. A., & Kraal, E. R. (2003). Patterns of water chemistry and discharge in glacier-fed Kennicott River, Alaska: Evidence for subglacial water storage cycles. *Chemical Geology*, 202, 291-312.
- Anesio, A. M., Hodson, A.J., Fritz, A., Psenner, R., & Sattler, B. (2009). High microbial activity on glaciers: importance to the global carbon cycle. *Global Change*, 15 (4), 955-960.
- Anesio, A. M., Sattler, B., Foreman, C., Telling, J., Hodson, A., Tranter, M., & Psenne, R. (2010). Carbon fluxes through bacterial communities on glacier surfaces. *Annals of Glaciology*, 51 (56), 32-40.
- Barker, J. D., Sharp, M. J., Fitzsimons, S. J., & Turner, R. J. (2006). Abundance and dynamics of dissolved organic carbon in glacier systems. *Arctic, Antarctic, and Alpine Research*, 38(2), 163–172.
- Bennett, M., & Glasser, N.F. (1996). *Glacial geology: ice sheets and landforms*. Chichester, England: John Wiley.
- Berner, E. K., & Berner, R. A. (2012). *Global environment: Water, air and geochemical cycles*. Princeton, New Jersey: Princeton University Press,
- Bhatia, M. P., Das, S. B., Xu, L., Charette, M. A., Wadham, J. L., & Kujawinski, E. B. (2013). Organic carbon export from the Greenland ice sheet. *Geochimica et Cosmochimica Acta* , 109, 329-344.
- Brown, Giles H. (2002). Glacier meltwater hydrochemistry. *Applied Geochemistry*. 17, 855-883.
- Collins, D. (1979). Hydrochemistry of meltwaters draining from an alpine glacier. *Arctic and Alpine Research*, 11(3). DOI: 10.2307/1550419.
- Fellman, J. B., Hood, E., Spencer, R. G. M., Stubbins, A., & Raymond, P. A. (2014). Watershed glacier coverage influences dissolved organic matter biogeochemistry in coastal watersheds of southeast Alaska. *Ecosystems*. DOI 10.1007/s10021-014-9777-1.
- Fellman, J. B., Hood, E., Raymond, P. A., Hudson, J., Bozeman, M., & Arimitsu, M. (2015). Evidence for the assimilation of ancient glacier organic carbon in a proglacial food web. *Limnology and Oceanography* 1-11. Doi: 10.1002/lno.10088.

- Fountain, A. G., & Tangborn, W. V. (1985). The effect of glaciers on streamflow variation. *Water Resources Research*, 21(4), 579-586.
- Fountain, A. G., & Walder, J. S. (1998). Water flow through temperate glaciers. *Reviews of Geophysics*, 36(3), 299-328.
- Gleick, P. H. (1996) Water resources. In S. H. Schneider (Ed). *Encyclopedia of Climate and Weather* (pp. 817-823). New York: Oxford University Press.
- Granshaw, F. D., & Fountain, A. G. (2006). Glacier change (1958–1998) in the north cascades national park complex, Washington, USA. *Journal of Glaciology*, 52(177), 251-256.
- Hasnain, S.I. (1999a). *Himalayan glaciers: hydrology and hydrochemistry*. New Delhi: Allied Publishers (P) Ltd.
- Hasnain, S. I., & Thayyen, R. J. (1999b). Controls on the major-ion chemistry of the Dokriani glacier. *Journal of Glaciology*, 45(149), 87–92.
- Hekkers, M., & Thorneycroft, K. (2011). *Glaciers of Washington: Glaciers of the American West*. Retrieved from <http://glaciers.us/glaciers-washington>.
- Hindshaw, R. S., Tipper, E. T., Reynolds, B. C., Lemarchand, E., Wiederhold, J. G., Magnusson, J., & Bourdon, B. (2011). Hydrological control of stream water chemistry in a glacial catchment (Damma Glacier, Switzerland). *Chemical Geology*, 285(1–4), 215–230. <https://doi.org/10.1016/j.chemgeo.2011.04.012>
- Hood, E., & Scott, D. (2008). Riverine organic matter and nutrients in southeast Alaska affected by glacial coverage. *Nature Geoscience*, 1(9), 583–587. <https://doi.org/10.1038/ngeo280>
- Hood, E., Fellman, J., Spencer, R. G., Hernes, P. J., Edwards, R., & D'Amore, D. (2009). Glaciers as a Source of Ancient and Labile Organic Matter to the Marine Environment. *Nature*, 462, 1044-1047. doi:10.1038/nature08580
- Hood, E., Battin, T. J., Fellman, J., O'Neel, S., & Spencer, R. J. (2015). Storage and release of organic carbon from glaciers and ice sheets. *Nature Geosciences*, 1-6. DOI: 10.1038/NGEO2331
- IPCC, 2014: Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part B: Regional Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Barros, V. R., C. B. Field, D. J. Dokken, M. D. Mastrandrea, K. J. Mach, T. E. Bilir, M. Chatterjee, K. L. Ebi, Y. O. Estrada, R. C. Genova, B. Girma, E. S. Kissel, A.

- N. Levy, S. MacCracken, P.R. Mastrandrea, & L.L. White (eds.)]. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press, pp. 688.
- John, D. A., Sisson, T. W., Breit, G. N., Rye, R. O. & Vallance, J. W. (2008). Characteristics, extent and origin of hydrothermal alteration at Mount Rainier Volcano, Cascades Arc, USA: Implications for debris-flow hazards and mineral deposits. *Journal of Volcanology and Geothermal Research*, 175, 289–314. doi:10.1016/j.jvolgeores.2008.04.004.
- Lafreniere, M.J., & Sharp, M. J. (2004). The concentration and fluorescence of dissolved organic carbon (DOC) in glacial and nonglacial catchments: interpreting hydrological flow routing and DOC sources. *Arctic, Antarctic, and Alpine Research*, 36,(2), 156–165.
- Lawson, E. C., Wadham, J. L., Tranter, M., Stibal, M., Lis, G. P., Butler, C.E. H., Laybourn-Parry, J., Nienow, P., Chandler, D., & Dewsbury, P. (2014). Greenland ice sheet exports labile organic carbon to the Arctic oceans. *Biogeoscience*, 11, 4015-4028.
- Lundquist, J., & Roche, J. (2009). Climate change and water supply in western national parks. *Park Science*, 26(1), 31-34.
- Mitchell, A.C., Lafrenière, M. J., Skidmore, M. L., & Boyd, E. S. (2013). Influence of bedrock mineral composition on microbial diversity in a subglacial environment. *Geology*, 41(8), 855–858.
- Mote, P. W., & Salathe Jr, E. P. (2010). Future climate in the Pacific Northwest. *Climatic Change*, Springer. DOI 10.1007/s10584-010-9848-z.
- National Oceanic and Atmospheric Administration [NOAA]. (2016). *NOAData - NOAA Online Weather Data*. Retrieved from <http://w2.weather.gov/climate/xmacis.php?wfo=sew>.
- National Park Service (NPS). (2005). Mount Rainier national park: geologic resource evaluation report. *Natural Resource Report*. National Parks Service. U.S. Department of the Interior. Retrieved from https://www.nature.nps.gov/geology/inventory/publications/reports/mora_gre_rpt_view.pdf.
- National Park Service (NPS). (2007). Mount Rainier: the forest communities of Mount Rainier national park. *Park History*. National Parks Service. U.S. Department of the Interior. Retrieved from https://www.nps.gov/parkhistory/online_books/science/19/chap5.htm

- National Park Service (NPS). (2016) Glaciers. *Glacial Features*. National Parks Service. U.S. Department of the Interior. Retrieved from <http://www.nps.gov/noca/learn/nature/glaciers.htm>.
- Nylen, T. H. (2001). *Spatial and temporal variations of glaciers (1913-1994) on Mt. Rainier and the relation with climate*. Retrieved from Portland State University.
- Porazinska, D. L., Fountain, A. G., Nylen, T. H., Tranter, M., Virginia, R. A., & Wall, D. H. The biodiversity and biogeochemistry of cryoconite holes from McMurdo Dry Valley glaciers, *Antarctica Arctic, Antarctic, and Alpine Research*, 36(1), 84-91.
- Raiswell, R. (1984). Chemical models of solute acquisition in glacial melt waters. *Journal of Glaciology*, 30(104), 49-57.
- Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., & Hoover, M. (2013). Global carbon dioxide emissions from inland waters. *Nature*, 503 (7476), 355-359.
- Riedel, J., & Larrabee, M. A. (2011). North cascades national park complex glacier mass balance monitoring annual report, water year 2009: North coast and cascades network. National Park Service, Fort Collins, Colorado.
- Schuman, W. (1993). *Handbook of rocks, minerals & gemstones*. Boston & New York: HarperCollins Publishers & Houghton Mifflin Company.
- Sharp, M., Richards, K. S., & Tranter, M. (1998). *Glacier Hydrology and Hydrochemistry*. Chichester, England: John Wiley & Sons LTD.
- Sharp, M., Parkes, J., Cragg, B., Fairchild, I. J., Lamb, H., & Tranter, M. (1999). Widespread bacterial populations at glacier beds and their relationship to rock weathering and carbon cycling. *Geology*, 27, 107-110.
- Singer, G. A. (2012). Biogeochemically diverse organic matter in Alpine glaciers and its downstream fate. *Nature Geosciences*, 5, 710–714.
- Singh, V. B., Ramanathan, A., Pottackkai, J. G., Sharma, P., Linda, A., Azam, M. F., & Chatterjee, C. (2014). Chemical characterization of meltwater draining from Gangotri Glacier, Garhwal Himalaya, India. *Journal of Earth Sciences*, 121(3), 625-636.

- Spencer, R. J., Vermilyea, A., Fellman, J., Raymond, P., Stubbins, A., & Scott, D. (2014). Seasonal variability of organic matter composition in an Alaskan glacier outflow: insight into glacier carbon sources. *Environmental Research Letters*, *9*, 1-7.
- Slemmons, K. E. H., Saros, J. E., & Simon, K. (2013). The influence of glacial meltwater on alpine aquatic ecosystems: a review. *Environmental Science: Processes & Impacts*, *15*(10). <https://doi.org/10.1039/c3em00243h>
- Skidmore, M. L., Foght, J. M., & Sharp, M. J. (2000). Microbial life beneath a high Arctic glacier. *Applied and Environmental Microbiology*, *66*(8), 3214–3220.
- Stewart, I. T., Cayan, D. R. & Dettinger, M. D. (2005). Changes toward earlier streamflow timing across western north america. *Journal of Climate*, *18*, 1136-1155.
- Stibal, M., & Tranter, M. (2007). Laboratory investigation of inorganic carbon uptake by cryoconite debris from Werenskioldbreen, Svalbard. *Journal of Geophysical Research Atmospheres*, *112*(G4).
- Tarnocai, C., Canadell, J. G., Schuur, E. A. G., Kuhry, P., Mazhitova, G., & Zimov, S. (2009). Soil organic carbon pools in the northern circumpolar permafrost region. *Global biogeochemical cycles*, *23*(GB2023). doi:10.1029/2008GB003327,
- Tranter, M., Brown, G. H., Hodson, A., & Gurnell, A.M. (1996). Hydrochemistry as an indicator of subglacial drainage system structure: a comparison of Alpine and Sub-Polar environments. *Hydrological Processes*, *10*, 541–556.
- Tranter, M., Sharp, M. J., Lamb, H. R., Brown, G. H., Hubbard, B. P., & Willis, I. C. (2002). Geochemical weathering at the bed of Haut Glacier d’Arolla, Switzerland—a new model. *Hydrological Processes*, *16*, 959–993. DOI: 10.1002/hyp.309.
- U.S Environmental Protection Agency (EPA). (1983). Sample preservation. *Methods for chemical analysis of water and wastes*. Cincinnati, Ohio, U.S EPA. Retrieved from <http://sisbl.uga.edu/epatab1.html>.
- U.S Environmental Protection Agency (EPA). (1994). Method 200.8, Revision 5.4: Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry.

- United States Geological Survey (USGS). (2014). Glaciers Help to Shape Mount Rainier. *Volcano Hazards Program: Mount Rainier*. Retrieved from https://volcanoes.usgs.gov/volcanoes/mount_rainier/geo_hist_glaciers.html.
- United States Geologic Society (USGS). (2014). Geology and History Summary for Mount Rainier. *Mount Rainer*. Retrieved from https://volcanoes.usgs.gov/volcanoes/mount_rainier/geo_hist_summary.html.
- United States Geologic Society (USGS). (2016). Ice, snow, and glaciers: the water cycle. *The Water Cycle - USGS Water Science School*. Retrieved from <https://water.usgs.gov/edu/watercycleice.html>.
- Wadham, J. L., S. Bottrell, M. Tranter, and R. Raiswell (2004), Stable isotope evidence for microbial sulphate reduction at the bed of a polythermal high Arctic glacier, Earth Planet. *Science Letters*, 219, 341–355.
- Wadham, J. L., Tranter, M., Skidmore, M., Hodson, A. J., Priscu, J., Lyons, W. B., Sharp, M., Wynn, P., & Jackson, M. (2010). Biogeochemical weathering under ice: size matters. *Global Biogeochemical Cycles*, 24 (3025). doi:10.1029/2009GB003688.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophysical Research*, 97, 7373–7382, doi:10.1029/92JC00188.
- Washington Department of Ecology (DOE). (2007). Facts about Washington's retreating glaciers and declining snow pack. *Ecology's Water Resource Program*. Retrieved from <https://fortress.wa.gov/ecy/publications/publications/0711016.pdf>.
- Washington Department of Fish and Wildlife (WDFW). (2008). Economic Analysis of the Non-Treaty Commercial and Recreational Fisheries in Washington State. *Publications*. Retrieved from <http://wdfw.wa.gov/publications/00464/>.
- Washington Department of Fish and Wildlife (WDFW). (2016). Hatcheries. *Conservation*. Retrieved from http://wdfw.wa.gov/hatcheries/mass_marking.html.
- Washington Department of Fish and Wildlife (WDFW). (2016). Recreational Salmon Fishing. *Fishing and Shellfishing*. Retrieved from <http://wdfw.wa.gov/fishing/salmon/species.html>.
- Washington Department of Fish and Wildlife (WDFW). (2017). Conservation. *Species of Concern*. Retrieved from <http://wdfw.wa.gov/conservation/endangered/All/#>.

Weiss (1974). Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chemistry*, 2, 203–215, doi:10.1016/0304-4203(74)90015-2.

