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# Response of the Arctic Marine Inorganic Carbon System to Ice Algae and under-ice Phytoplankton Blooms

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UNIVERSITY OF CALGARY

Response of the Arctic Marine Inorganic Carbon System to Ice Algae and under-ice  
Phytoplankton Blooms

by

Jeremy Whitehead

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
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## Abstract

Research on the inorganic carbon cycle in the Arctic winter to spring transition process has revealed that ice algae could play a role in the inorganic carbon cycling under sea ice. A ten-week case study was conducted near Qikiqtarjuaq, NU, Canada, in which dissolved inorganic carbon (DIC) and was collected from the water column. Samples were collected near the start of an ice algae bloom, and continued until early stages of an under-ice phytoplankton bloom. During the ice algae bloom period, there was no significant decrease in DIC or  $p\text{CO}_{2\text{sw}}$  prior to sea ice melt. DIC fixation calculations show that previous studies may have overestimated the drawdown of DIC from ice algae, but that sloughing ice algae or an under-ice phytoplankton bloom can dramatically reduce DIC and  $p\text{CO}_{2\text{sw}}$ . This case study provided insights that under-ice phytoplankton blooms are a more important biological mechanism preconditioning the Arctic surface mixed layer.

## **Acknowledgements**

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## Chapter 1: Thesis Introduction

### *1.1 Thesis Design*

My advisor's research interests broadly lie with carbon dioxide in the Arctic's bodies of water. In particular, he researches air-sea gas exchange mechanisms, Arctic marine carbon cycles, ocean acidification, gas exchange through sea-ice, and remote sensing/modeling. Therefore, my initial research project's conception was to investigate biogeochemical processes affecting Arctic seawater CO<sub>2</sub> concentrations during the spring melt season. The key investigative query had to do with a specific time period - the spring melt transition. I was tasked with measuring and analyzing the combined drawdown effects of ice algae blooms, phytoplankton blooms, and sea ice melt, to identify significant air-sea exchanges of CO<sub>2</sub> during the spring break-up season in the Arctic Ocean. A major contribution for the project would be new insights into inorganic carbon parameters during spring time, which lack in quantity compared to summer time, sea-ice free waters. Examining this understudied time period and could help fill in the blanks on the Arctic carbon cycle as well as larger implications for climate change and mesoscale earth processes.

Progression to the thesis proposal gave birth to a new focus that was not fully conceived during the research focus. During the proposal process, it became clear that the time frame from late spring to early summer gave us insightful access to the ice algae bloom and growth period. While there was a focus on ice algae, the sampling period captured a rise, fall, and disappearance of ice algae chlorophyll, which allowed a direct comparison to the fluctuations in inorganic carbon that were also present. Key impact during the proposal phase were that the beginning and the end of sampling gave evidence to existing claims and possibly some refutes to current

research. The project gained a new, focused objective, which was to determine if the ice algae played a role in controlling the inorganic carbon of the underlying sea-water.

The final thesis research was able to answer the initial question of what the state of the inorganic carbon system was below the ice cover, and also to answer the new questions about the role that ice algae play. It turned out that ice algae did not play a significant role while mostly present in sea ice and that an under-ice phytoplankton bloom, which has only recently been investigated and discussed, is responsible for the large fluctuations in inorganic carbon. This thesis is the result of investigating some simple measurements, and enriching it with concepts and ideas that all fit and relate to inorganic carbon, ice algae, phytoplankton blooms, sea ice, and the Arctic.

## *1.2 Thesis Justification*

Understanding the inorganic carbon system has large implications for global problems such as ocean acidification and climate change. Research has been conducted on these issues to show that ocean acidification (Bates and Mathis, 2009) is resulting in lower pH levels and stress for biological organisms in the Arctic, and that climate change (Takahashi et al., 2009) is resulting in warmer temperatures, leading to further sea ice melt and sea surface stratification. This thesis research was undertaken in order to record and quantify changes in the inorganic carbon system under sea-ice during the understudied spring transition period. Past research has provided an imbalance of measurements during the summer open water period for measuring air-sea fluxes of carbon dioxide in the Arctic (Semiletov et al., 2007). This seasonal timing is a function of the lower ice cover during this time of year, lending to easier ship access and direct measurements of air-sea gas exchange. The spring to summer phytoplankton bloom also causes a drawdown (lowers) of dissolved carbon dioxide in the water, creating a large potential difference

between the surface water and atmosphere. Summer time in the Arctic is heavily studied for its role in absorbing and releasing atmospheric carbon dioxide and the impact of those processes. It has also been suggested that the spring period is important to study prior to open water, because there could be several preconditioning factors impacting the inorganic carbon system (Yager et al., 1995). These factors would change the marine carbon system prior to phytoplankton blooms, and aid or interfere with the potential difference between the surface water and atmosphere. These processes have the potential to impact the magnitude and direction that gas-exchange will flow once the ice melts. Few measurements exist for this spring period though, leaving ample opportunity to study concentrations of inorganic carbon beneath the sea ice, and enlighten on some processes that may or may not be impacting inorganic carbon.

There are several reasons to study the marine inorganic carbon system. First, the ocean is involved with direct exchange of carbon dioxide (and other gasses). This allows the ocean to control the atmospheric inventory of carbon dioxide. Second, the ocean is the largest reservoir of inorganic carbon, more than the atmosphere and terrestrial biosphere combined. The ocean is able to absorb atmospheric carbon dioxide, convert it into organic carbon, and export it to deep waters (Hansell et al., 2012). This allows the ocean to continually uptake more atmospheric carbon dioxide, moderating the increases from anthropogenic activities. Finally, oceanic pH (acidity and basicity) is also controlled by the inorganic carbon system. Increasing carbon dioxide concentrations in the ocean increases the amounts of hydrogen ions and decreases the pH of the water. This is the other carbon dioxide problem that is often neglected compared to global warming (Doney et al., 2009). It is important to understand the evolution of the inorganic carbon system in the Arctic to account for the changes that will occur with air sea exchange, the total carbon budget and ocean acidification.

It is well known that the spring and summer phytoplankton blooms in the Arctic drawdown carbon dioxide in seawater well below atmospheric concentrations (Else et al., 2012). This creates a strong carbon sink for most regions of the Arctic. What is currently not as well-known is the role that ice algae blooms play on carbon drawdown before the large phytoplankton blooms. Forest et al., (2011) reports that ice algae in the Amundsen Gulf are a minor fraction of the total primary production and biomass, with phytoplankton comprising 94% and ice algae comprising 6% of total biomass. Loose et al., (2011) similarly surmise that ice algae production is about 5% of total water column production. But it is important to understand as well that ice algae production and biomass is site specific, with the central Arctic Ocean having a larger ice algae biomass compared to areas such as Resolute, Canada (Michel, 2006). It is already known that ice algae drawdown nutrients and carbon from sea ice (Munro et al., 2010), but also some current research suggests that ice algae primary production is significant in quantity to drawdown noticeable amounts of nutrients and carbon dioxide from the surface mixed layer as well (Shadwick et al., 2011). Forest et al., (2011) also supports the statement from Shadwick et al., (2011), in that this noticeable biomass does have a contribution in the drawdown of inorganic carbon during spring. Ice algae could play a critical role because their bloom and growth period occur prior to the phytoplankton bloom (Leu et al., 2015). Brown et al. (2015) reports that  $p\text{CO}_2$  in the bottom centimeters of sea ice is significantly decreased over time from biological activity such as ice algae. Thus, ice algae have the potential to modify the inorganic carbon system of the water column prior to sea ice melt, making it important to quantify this preconditioning contribution to air-sea gas exchange in the Arctic.

The aim of this thesis research is to capture the changes of dissolved inorganic carbon under sea-ice prior to the spring and summer melt and the beginning of the phytoplankton bloom.

The specific objectives for this thesis work were therefore to: 1) to determine if the ice algae bloom modifies inorganic carbon parameters in the water column to an extent that would significantly impact air-sea exchange of CO<sub>2</sub>; and 2) to determine the significance of the ice algae bloom to the marine carbon system relative to under-ice phytoplankton blooms. This will allow the determination of relative contributions of ice algae and phytoplankton to the drawdown of inorganic carbon, and the impact that may have on air-sea CO<sub>2</sub> exchange in the summer season. This research is also performed to add more empirical data for inorganic carbon in the springtime period as well as to confirm and/or deny previous reports that ice algae play a significant role in the drawdown of carbon.

This research should expand our knowledge on the impacts that ice algae play on preconditioning the water prior to the open water phytoplankton blooms and air-sea exchange. Since this is the first study of its kind in landfast ice near Baffin Bay, there are also secondary objectives to comment on the potential for this region to act as a source or sink of atmospheric CO<sub>2</sub>, and to report on carbonate saturation states and the potential vulnerability of a local soft-shell clam fishery to ocean acidification.

## Chapter 2: Background and Literature Review

### 2.1 *The Arctic*

The Earth has two unique polar regions; the Arctic in the northern hemisphere and the Antarctic in the southern hemisphere. The Arctic is defined by several unique characteristics based on its location (**Figure 1**). The most visible factor that differentiates the Arctic from the Antarctic is the presence of a central ocean basin with surrounding land mass. This central ocean basin, called the Arctic Ocean, has first-year and multi-year sea-ice present. Sea-ice grows, melts, and extends into the many seas and bays that connect to it (**Figure 2**). The land surrounding the Arctic ocean contains large watersheds which provide the largest input of freshwater into any ocean basin (Peterson et al., 2002), producing slightly less saline waters than most other ocean basins. A more geographical definition of the Arctic polar regions is the area of the Earth lying above 66°34' N latitude. This latitude line was chosen as it represents a point at which above there is at least one day where the sun does not set (in the summer) or rise (in the winter). This is not the only definition however, and other characteristics provided by AMAP (Arctic Monitoring and Assessment Programme) such as the July 10 °C isotherm, sea ice extent, marine extent or the terrestrial vegetation treeline have been used to define the Arctic.

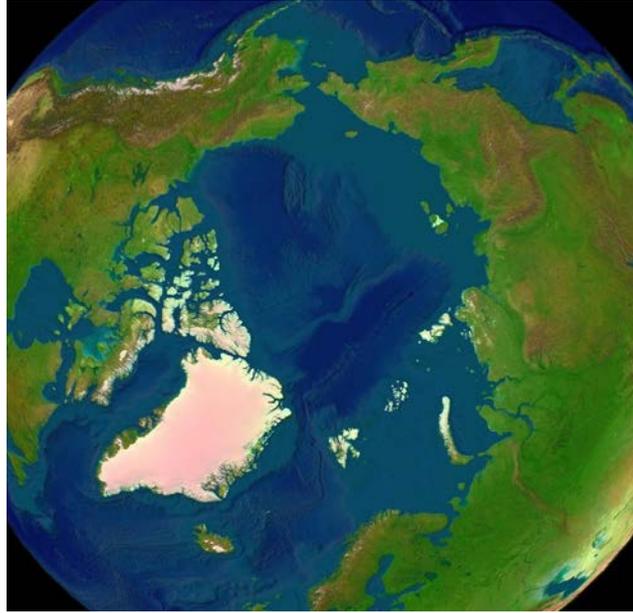


Figure 1: Topographical map of the Arctic clear of ocean sea-ice from NASA World Wind 3D visualization globe. Bathymetry of Arctic Ocean floor can also be seen.  
([https://commons.wikimedia.org/wiki/File:Arctica\\_surface.jpg](https://commons.wikimedia.org/wiki/File:Arctica_surface.jpg))

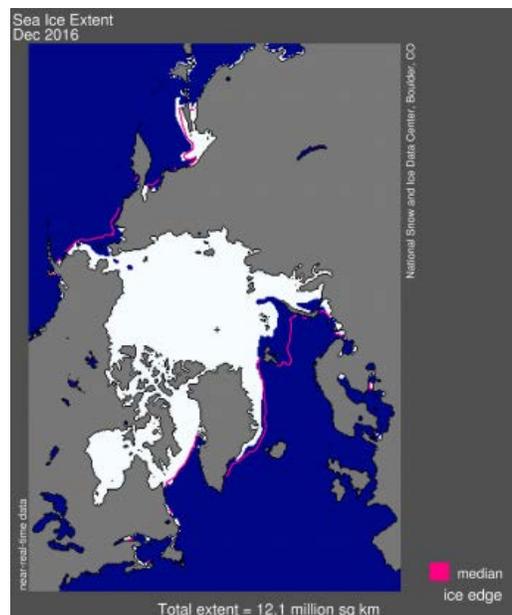


Figure 2: Current sea ice extent as of December 2016. The central arctic basin is covered and sea ice can be seen extending into and onto the landmasses further from the North Pole.  
([http://nsidc.org/arcticseaicenews/files/1999/12/n\\_extn\\_hires-859x1024.png](http://nsidc.org/arcticseaicenews/files/1999/12/n_extn_hires-859x1024.png))

Due to the nature of higher latitudes, the Arctic suffers from an energy deficit of incoming shortwave solar radiation, or insolation. This deficit arises for three main reasons. The first as mentioned in the Arctic definition, is the persistence of days to months of darkness in which no shortwave insolation reaches the Arctic. No sunlight corresponds to no incoming energy which leads to evidence of no photosynthesis (Rysgaard et al., 1999) and temperatures falling dramatically. The second reason is due to the effect of our planet's shape and the way that solar radiation reaches our planet (**Figure 3**). Because of the curvature of the earth, a parcel of sunlight has to distribute the same amount of energy over a greater surface area in the Arctic compared to a surface area around the equator. This makes any energy that does arrive less intense compared to lower latitudes. The final aspect is from insolation reflection known as albedo. High albedo of snow and ice reflects incoming shortwave radiation by as much as 80%, with snow playing a larger role (pure snow has an albedo generally between 0.8 to 0.9 in the UV/visible spectrum (Wiscombe and Warren, 1980)). This reflection reduces the total radiative energy that the surface can absorb, reducing the energy balance even further. The energy deficit from these three factors is somewhat offset by the warm surface waters of the Gulf Stream current, which release heat into the atmosphere before crossing the North Atlantic to Europe. In addition, some warm air from atmospheric circulation also contributes to negate the energy deficit. However these offsets do not supply enough energy or heat, and the overall energy deficit combinations allow the freezing process of water, which results in permafrost, glaciers, and the iconic sea-ice that covers the Arctic Ocean.

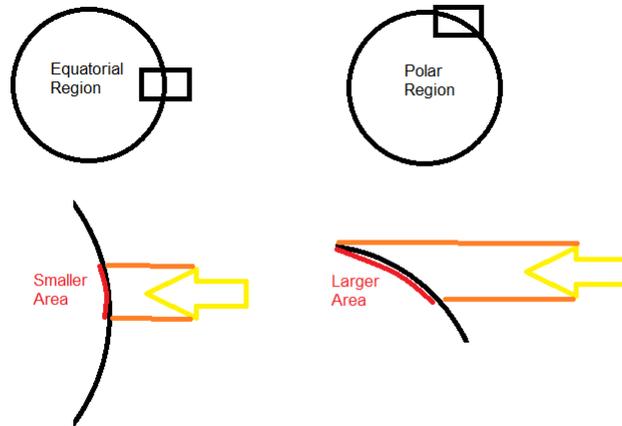


Figure 3: Model schematic showing how the same parcel of insolation reaches an equatorial and polar region of the Earth. The equatorial region has a smaller surface area to cover due to the small curvature, compared to the polar region with a larger area from a larger curvature.

The Arctic Ocean is a deep ocean basin with an average depth of around 3000 meters. The deepest part in the central of the basin can be greater than 4000 meters. The Arctic is the freshest ocean with salinities ranging from 26 to 34 (Steele et al., 2001) compared to other oceans which range from 31 to 35 due to its annual sea-ice melt and river influences. The Arctic waterways also receive deep Pacific water and mid to deep Atlantic waters through mixing and deep currents. The Pacific waters are identified by their richer nutrient content (Grebmeier et al., 2006), while the Atlantic is identified as warmer and more saline (Orvik and Niller, 2002). On the Eurasian side of the ocean, there are broad continental shelves, while on the Canadian side there is an Archipelago that breaks up the Arctic Ocean (Jakobsson et al., 2012). A unique characteristic that it shares with the Southern Ocean is the presence of sea ice. Two main categorizations of sea ice are either multi-year or first year sea ice. Sea ice is considered multi-year sea ice if it has survived multiple years of summer warming and is generally thick (between 2 to 4 meters) and restricted to the highest latitudes. First year sea ice is ice that forms for the first time in fall and winter, but usually disappears when summer returns. This ice is thinner

(generally less than 2 meters), more mobile, and can attach to the land to form landfast ice. One of the great threats to the Arctic is related to the melting of sea ice, especially multi-year sea ice from climate change. Evidence is already showing that climate change is having impacts on the Arctic (Serreze et al., 2000). Climate change is currently impacting the Arctic the greatest, a phenomenon known as Arctic amplification (Screen and Simmonds, 2010). There are many other climate change impacts due to feedbacks with sea ice which will be discussed in more detail in the next section.

## *2.2 Climate Change*

Due to Arctic amplification, the Arctic is experiencing the most dramatic effects of climate change (Serreze and Francis, 2006). Arctic amplification is a term that describes how the temperatures in the Arctic are much higher than the average global temperature increase due to greenhouse gasses (Deser et al., 2010; Screen and Simmonds, 2010). The effects of Arctic Amplification exist because of the ice-albedo feedback. As sea ice continues to decrease, snow cover on top of the sea ice consequently decreases. This lowers the albedo of the Arctic Ocean surface, which allows for further enhancement of insolation and continued warming. The positive feedback is present from additional sea ice melt as the ocean takes up more heat. The Arctic warms about 2 °C higher than other warming areas on the planet. Higher atmospheric temperatures increase the heat energy in the Arctic, decreasing the energy deficit for which the critical process of freezing water is needed. Higher atmospheric temperatures consequently lead to higher land and surface water temperatures, which result in decreasing sea ice extent, sea ice thickness, glacier melt, and permafrost melt (Guo and Wang, 2016).

The increase in atmospheric temperatures from the increase in carbon dioxide emissions has several effects. Rising temperatures of the atmosphere and ocean surface delays the timing of

when the surface becomes cold enough for sea ice to form (Stroeve et al., 2011). It will take a longer amount of time then for sea ice to reach its maximum extent from the additional heat. Likewise, warmer air temperatures hasten the time of when sea-ice begins to melt, increasing the duration of open water in summer and increases the area of open water during the winter (Markus et al., 2009). The warmer surface water will also inhibit the thickening of sea ice for both first-year and multi-year sea ice (Hansen et al., 2013) as more heat will hinder the freezing process. While sea ice thickness is decreasing, increased precipitation will be increasing snow thickness (Bintanja and Selten, 2014). This could potentially create a negative feedback, as more aerial snow cover reflects insolation off surfaces and heat is also insulated under thicker snow covers.

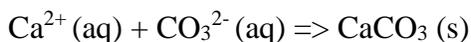
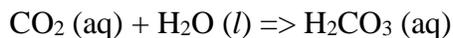
Because the ocean and atmosphere are in a dynamic state of equilibrium with carbon dioxide, the increase in carbon dioxide concentrations from anthropogenic sources leads to a direct increase in concentrations in the ocean. The carbon system controls the pH of the ocean from the chemical equilibrium reaction of carbon dioxide and water to create carbonic acid. Carbonic acid is a weak acid and reverts back to carbon dioxide and water, or it dissociates by losing a hydrogen ion (proton). The increase in hydrogen ions causes the pH to decrease on its scale, increasing the acidity of the water. While there is debate as to whether the Arctic will increase its ability to uptake carbon dioxide and release more hydrogen ions (Cai et al., 2010), current measurements have shown that the pH of the Arctic Ocean is decreasing over time (Yamamoto et al., 2012), and is projected to decrease with additional carbon emissions from models (Takahashi et al., 2014; Steiner et al., 2015).

Increasing temperatures are not only affecting the Arctic Ocean, but are also having consequences on the terrestrial side. There is currently an ongoing decrease in permafrost extent

(Blunden and Arndt, 2015). Thawing of permafrost is occurring to greater depths on land and near the surface of the ocean. Permafrost near the land surface is no longer forming further south, causing a northward retreat. Permafrost thawing is releasing groundwater and allowing old carbon that was once stored to be potentially released into the atmosphere and the oceans (Frey and McClelland, 2009). Increased river runoff from certain river basins, combined with the melting of sea-ice and permafrost, could lead to a freshening of the surface Arctic Ocean (Morison et al., 2012). This would create a stratified less saline surface layer, hindering the ability for deep water formation, an extremely critical component of climate control and mixing.

### 2.3 Carbon System and Cycles

The inorganic carbon system is comprised of four measurable aspects: dissolved inorganic carbon (DIC), total alkalinity (TA),  $p\text{CO}_{2\text{sw}}$  (partial pressure of carbon dioxide in seawater) and pH. Each of these four components can tell us something interesting about the marine environment:  $p\text{CO}_{2\text{sw}}$ , when measured near the surface tells us the magnitude of an ocean's ability to absorb or release  $\text{CO}_2$  from the atmosphere; DIC can provide insights into biological processes occurring throughout the water column; pH helps us understand ocean acidification and the ability of calcifying organisms to build their shells; and TA tells us the contribution of minor anions in solution (Dickson, 1981) with an application to see calcium carbonate precipitation, formation and dissolution. The carbonate system equations are as follow



Carbon cycles are strongly linked to climate through various feedback processes such as anthropogenic input, ocean uptake, and increasing or decreasing primary production. There are critical global factors that involve the carbon cycle and have been occurring throughout history (Friedlingstein et al., 2006; Giorgetta et al., 2013; Reichstein et al., 2013). The atmosphere, terrestrial biosphere, and oceans store, utilize, and sequester carbon. Carbon dioxide is a principle component for photosynthesis and is a greenhouse gas that helps maintain the global temperature. In modern times, carbon dioxide has been rapidly increasing from anthropogenic activities such as energy and agriculture (Searchinger et al., 2008), which have doubled emissions. In terms of the ocean, carbon has more roles that it can play. As stated, the ocean contains the largest reservoir of inorganic and organic carbon, with about sixty times more than the atmosphere, and seventeen times more than land (Hansell et al., 2009). Also mentioned before, carbon dioxide has a direct control on the pH of the ocean (Kroeker et al., 2010), with increasing carbon dioxide increasing the acidity and impacting many calcifying organisms. Carbon cycling in the ocean begins with fixing inorganic carbon and nutrients in the surface waters into organic matter, and then the organic matter is either consumed, remineralized, or is carried into the deep ocean where it becomes refractory or sequestered in the sediment. This transfer of carbon from the surface to the deep waters sequesters atmospheric carbon for long period of time, thus moderating the increase in atmospheric carbon dioxide to levels that would have become even higher.

Carbon in inorganic and organic forms follow a cyclic pattern in the global ocean (**Figure 4**). Inorganic carbon and nutrients (such as nitrogen and phosphorus) are transformed into organic carbon and oxygen through photosynthesis at the surface of the ocean. Some of the organic matter will be consumed by respiring organisms such as bacteria and larger heterotrophs,

and the rest will either sink as particulate organic matter (POM), or it will become part of the water column as dissolved organic matter (DOM) and will sink during downwelling events. Once the organic carbon is in deep water, POM can sink to the bottom sediments or DOM can transfer during downwelling events, providing food for benthic organisms or becoming buried underneath more sediment and sequestered (Smetacek et al., 2012). Some of the organic matter will become entrained in the deep water and become refractory, unconsumable carbon (Nebbioso & Piccolo 2013). The fraction of organic matter that is consumed and eventually remineralized into inorganic carbon and nutrients, can then be mixed and brought back to the surface through upwelling mechanisms, completing the biogeochemical cycle. An important outside influence from ocean cycle is air-sea exchange. Depending on the concentration gradient between the atmosphere and ocean surface, carbon dioxide will transfer between the two.

In most ocean regions, the marine inorganic carbon system parameters follow a typical seasonal pattern as described in the previous paragraph (Falkowski et al., 2000), with net autotrophy occurring in the spring and summer leading to DIC uptake, low  $p\text{CO}_{2\text{sw}}$ , and an increase in pH, followed by net heterotrophy in the fall and winter leading to DIC accumulation, increasing  $p\text{CO}_{2\text{sw}}$ , and lower pH. In the Arctic, the inorganic carbon system follows some of these established trends, but with added complications from seasonal sea ice growth and decay, and extreme variations in light availability. For example, in the fall and winter during sea-ice formation, brine rejection increases sea surface DIC and TA (Rysgaard et al., 2007), while during the spring and summer, DIC, TA, and  $p\text{CO}_{2\text{sw}}$  decrease due to dilution associated with sea ice melt. Unfortunately, the winter portion of this seasonal pattern is still not well understood, due mostly to a sampling bias towards the ice-free seasons. The lack of observations through the fall, winter, and particularly early spring, have led to different interpretations about how seasonal

processes affect the ability of Arctic seas to act as a CO<sub>2</sub> sink (Yager et al., 1995; Else et al., 2011) and uncertainty about their influence on carbonate saturation states (Fransson et al., 2009; Yamamoto-Kawai et al., 2013).

Because of these knowledge gaps, understanding the seasonal marine carbon system cycles in the Arctic remains a top research priority. In particular, emphasis has been put into developing a baseline understanding of whether the Arctic marine region as a whole acts as a net sink or source for CO<sub>2</sub> exchange. Bates and Mathis (2009) estimate that the Arctic accounts for between 5-14% of global marine CO<sub>2</sub> sinks, but there is some debate about the roles of coastal areas (Shadwick, 2010) and some continental shelf seas (Semiletov et al., 2007) being sources. This research is largely driven by a desire to understand how climate change is impacting the entire Arctic carbon cycle (McGuire et al., 2009). But this is a difficult task given that many of the processes controlling the marine carbon system are changing in the Arctic, including changes to sea ice extent (Stroeve et al., 2007; Stroeve et al., 2012) and thickness (Meier et al., 2014), river runoff (Wu, Wood, and Scott, 2005), glacial melt (Pritchard et al., 2009), sea surface temperature (Levitus et al., 2000), and (perhaps most importantly) biological production (Bates and Matthis, 2009; Cai et al., 2010).

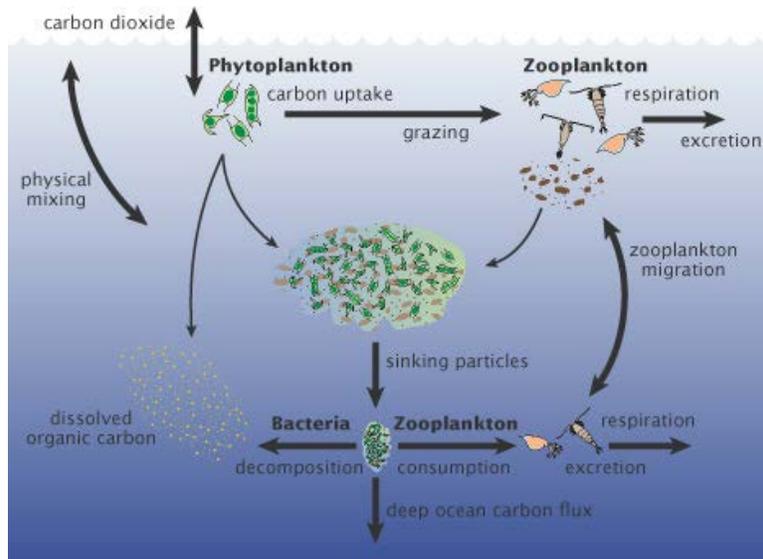


Figure 4: Schematic showing the processes and transfer of carbon through the ocean. ([https://earthobservatory.nasa.gov/Features/Phytoplankton/images/carbon\\_flux.jpg](https://earthobservatory.nasa.gov/Features/Phytoplankton/images/carbon_flux.jpg); adapted from [http://www1.whoi.edu/images/jgofs\\_brochure.pdf](http://www1.whoi.edu/images/jgofs_brochure.pdf))

The Arctic marine carbon cycle shares some characteristics with low latitude oceans, but with a few distinct differences (**Figure 5**). The most limiting factor is that of sunlight. During the winter, very little photosynthesis occurs in the Arctic and the drawdown of inorganic carbon and nutrients is not apparent (Rysgaard et al., 1999). In the late spring and summer as sunlight returns and sea ice melts, carbon and nutrients that have accumulated over the winter and are readily available for ice algae and phytoplankton to consume (Bates, 2006). The phytoplankton blooms are large and noticeable events that drawdown significant amounts of inorganic carbon (Popova et al., 2010). Yager et al., (1995 provided a first attempt at a description of the carbon cycle in ice-covered waters, summarizing what was known and hypothesized at that time. They proposed simply that inorganic carbon accumulates during the winter and is reduced during the summer. However, the only consideration for sea ice in their research is that it diluted the total carbon mass balance, not impacting air-sea exchange for sea ice covered areas. Their propositions and observations are lacking in the sense that there has been debate about the role of

the coastal oceans (Shadwick et al., 2010), evidence for air-sea exchange through sea ice (Papakyriakou & Miller, 2011), and sea ice processes that can enhance the way carbon is absorbed from the atmosphere (Anderson et al., 2004).

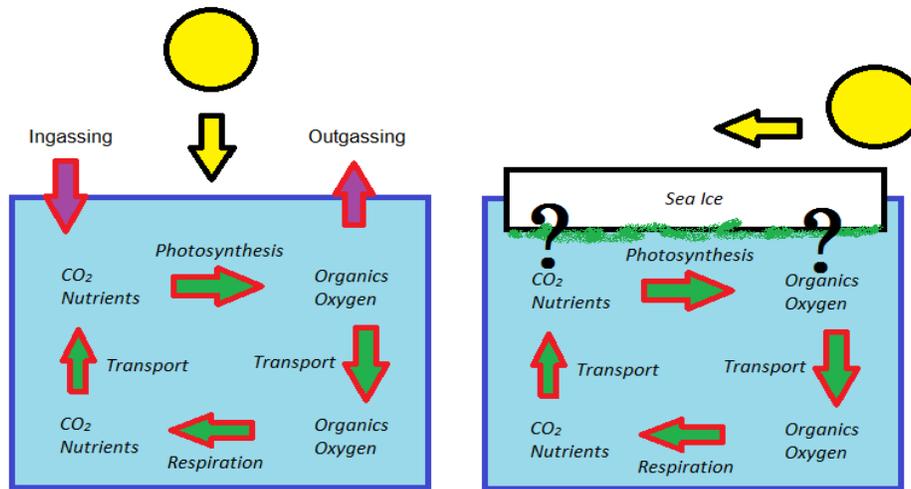


Figure 5: Model showing typical low latitude carbon cycling on the left, and typical high latitude cycling on the right, with the unknowns of sea-ice. The key differences are the lack of sunlight and the presence of sea ice in the Arctic, which limit water column photosynthesis and gas exchange respectively.

#### 2.4 Sea Ice Processes

Freshwater normally freezes at 0°C at 1 atmosphere of pressure. An important consideration to remember is that water can exist below 0°C, but ice cannot exist above 0°C. The salinity of the ocean lowers the freezing point, which make the freezing temperature of the ocean around -2 °C at 1 atmosphere of pressure. This specific value will also change depending on the salinity, with higher (lower) salinity waters having a higher (lower) freezing temperature. This is known as the freezing point depression (Potter et al., 1978) and has since been quantified based on how much salts and other impurities contribute (Bodnar, 1993). The beginning of sea ice formation begins when the atmosphere is cold enough that it cools the surface of the ocean,

creating the first ice called frazil ice. As more frazil ice accumulates at the surface, wind and waves push together the ice into slicks called grease ice. Depending on weather conditions, ice has two different stages: calm conditions lead to nilas ice, or harsh conditions lead to pancake ice. Once the surface has been covered with ice and temperatures remain low, consolidation begins. The consolidation process thickens sea ice in the water column. Thickening of ice does not necessarily mean that more ice crystals are accumulated, but that the ice grows by releasing heat into the ocean. Sea ice grows down deeper with a skeletal layer, or the thin and fragile layer below the consolidated layer. The skeletal layer is easily influenced by movement of water. Above the skeletal layer is the thick consolidated columnar ice. At some point, there is just too much heat coming from the ocean, and snow on top of the sea-ice insulates it from the freezing air. These physical limitations will stop sea ice from continually thickening and the thickness will remain generally consistent from winter to summer (Thomas, 2004)

The physical process of sea ice is easily seen, but there are some chemical composition changes to the sea-ice and ocean water that are not visible. During the freezing process, salts (sodium, chloride, carbonate, etc.) and organic matter (Giannelli et al., 2001) are expelled from the ice matrix. Ice forms by the strengthening and ordering of intermolecular bonds, which leaves no room for salt ions. As the skeletal layer grows, it expels the salts, creating highly saline waters. These waters either sink because they are denser than the underlying water (Talley, Reid, and Robbins, 2003), or they are trapped in the columnar ice and form brine pockets (Xie et al., 2009). These brine pockets are very dense, with salinities sometimes over 100. The high salinity inside the sea-ice increases the concentration of certain salts such as calcium carbonate, which subsequently precipitate out of the solution. The temperature of the sea-ice will determine the length, amount, and porosity of the brine channels. Colder ice will have smaller and lower water

content brine pockets, and warmer ice will have more interconnections and higher water content (Thomas, 2004).

The change of state of the surface ocean from water to ice involves the transfer of heat. The very cold atmospheric air and the cold, but stable ocean surface water cause the transfer of heat through the sea-ice matrix. Sea ice is not uniform in temperature, with the coldest temperatures near the surface, insulated by the snow, and the warmest temperatures at the sea-ice ocean interface, which generally are the same temperatures  $\sim -2^{\circ}\text{C}$  (Maykut & Untersteiner, 1971). This gradient causes the ocean to lose heat upwards through the ice. Thermodynamic properties state that ice has a lower heat capacity but a higher thermal conductivity than water, allowing for faster transfer of heat through the sea ice matrix. The gradient of temperature also allows sea ice to be more porous and have higher unfrozen water content near the ocean, and less porous ice near the atmosphere. Sea ice helps maintain temperatures at the sea ice-water interface, which is usually the most dramatic in the water column due to day and night cycles.

Once sea ice is present snow covers begin to appear on top of the ice. The snow has three main effects: snow has a high albedo ( $>0.8$ ) which reflects incoming shortwave radiation which would warm the surface of the ice. This reflection and attenuation due to high albedo limits the amount of radiation that can penetrate through the ice for primary producers to use, resulting in lowered production during fall to spring. Also, snow is a good insulator of heat, which keeps the top of the sea ice at a relatively stable temperature, moderating the temperature fluctuations compared to if no snow was present. Current research in regards to sea ice observations include the thinning of sea ice (Stroeve et al., 2011), increased precipitation and northern retreat of sea ice extent (Bintanja & Selten, 2014), and the timings of freeze up and melt (Markus, Stroeve, and Miller, 2009). Sea ice also has processes related to carbon and are discussed in the next

subsection. In general, the freezing mechanisms change the composition of seawater similar to the expulsion of salt as stated.

### *2.5 Impacts of Sea Ice on Seawater*

The freezing process of sea ice has significant impacts on the chemistry of the underlying seawater. As the ice forms its crystal matrix, salts and other impurities are expelled. This leads to dense brine just below sea ice from the intrusion and accumulation of salts. This process is a critical part of the global thermohaline circulation as it is the beginning formation of deep water masses (Dickson and Brown, 1994). With relation to carbon, sea ice also expels DIC to the underlying water column (Rysgaard et al., 2007). TA also increases as salts and other ions are expelled to the water. Bulk measurements of sea ice melt show that inorganic carbon and alkalinity are in lower concentration within the sea ice (Bates et al., 2014), but there are concentrated brine pockets with very high inorganic carbon and alkalinity values. In the opposite mechanism, the melting of sea-ice dilutes seawater with lower concentrations of DIC and TA, lowering the total concentrations of the surface waters (Bates et al., 2014). When trying to ignore the effects of expulsion and dilution, taking the normalized values to the salinity of the surface waters allows us to ignore the physical effects of sea ice processes on the water column and see how biological interactions instead impact DIC and TA. In contrast, sea ice has much higher normalized carbon and alkalinity compared to seawater (Geilfus et al., 2012). Current research is focusing on the drawdown of carbon from the atmosphere during freeze up (Rysgaard et al., 2007), the carbon composition above, inside, and below sea ice (Miller et al., 2011) and the increasing or decreasing ability of the Arctic to absorb carbon (Bates and Mathis, 2009; Cai et al., 2010).

## 2.6 Ice Algae Present in Sea Ice

Along with the physical and abiotic influences of sea ice processes on the water column, there are also biological communities that can play a role in the carbon cycles. One of the biological components unique to the Arctic is the ice algae community, which forms at the ice-water interface or inside the sea-ice matrix itself (Horner and Schrader, 1982). Ice algae primarily consist of numerous amounts of diatom taxa (Werner et al., 2007), but also contain other algae such as dinoflagellates and cyanobacteria. The sea-ice matrix also has a diverse range of ice bacteria (Junge et al., 2002) and other grazing organisms like copepods (Conover and Huntley, 1991) that consume ice algae, forming a food web community. Ice algae are important in the Arctic marine ecosystem because they are the first primary producer to take advantage of returning spring sunlight after winter darkness (Leu et al., 2015). Primary production from ice algae is significant during spring and early summer as it is up to two orders of magnitude greater than water column productivity in regions with a heavy ice algae biomass (Gradinger, 2009). As they are the first primary producers, they consume nutrients and carbon from inside the sea-ice matrix, which are in turn replenished by pulsing exchange with the underlying seawater (Niedrauer and Martin, 1979; Cota, 1987). Since ice algae are the first primary producers in the annual cycle, they may be of importance to understand the role they could play in affecting under-ice seawater chemistry and also the role that climate change will have on sea-ice and consequently ice algae production and life cycle (Leu et al., 2011).

As described by Miller et al. (2015), the past two decades have seen an acceleration in research to determine the biogeochemical role (Vancoppenolle, 2013) that ice algae play in sea-ice, including the potential to impact under-ice seawater. In the winter to spring transition, mixed layer DIC levels are generally at their peak, resulting from increased respiration raising  $p\text{CO}_{2\text{sw}}$

levels (Bates, 2006). As stated, ice algae take up the nutrients and dissolved carbon from within sea ice, but they could also impact nutrient and dissolved inorganic carbon in the water column after sea ice depletion. If this ultimately results in extraction of DIC and nutrients from the water column, it creates a scenario in which the seasonal increase in DIC/ $p\text{CO}_{2\text{sw}}$  may start to reverse. This may lead to undersaturation of  $p\text{CO}_{2\text{sw}}$  relative to the atmosphere, pre-conditioning the underlying water column for  $\text{CO}_2$  uptake once the ice cover is removed, or it becomes permeable to gas exchange (Yager et al., 1995; Else et al., 2011). The specific role that ice algae might play in this “seasonal rectification” is unclear due to an underrepresentation of the relationship between ice algae and dissolved inorganic carbon in the literature relative to the more easily studied phytoplankton and its inorganic carbon drawdown role.

### *2.7 Carbon System under Sea Ice*

The carbon system under sea ice is currently not fully understood and warrants the investigation of this thesis research. The Yager et al. (1995) hypothesis, proposes that dissolved carbon increases under sea ice from limited sunlight and net respiration, followed by dissolved inorganic carbon decreases during open water high sunlight periods (**Figure 6**). There does appear to be evidence for this general pattern (Else et al., 2012), but as stated previously this is not fully explored and there could be inconsistencies on when and where drawdown or enhancement is occurring.

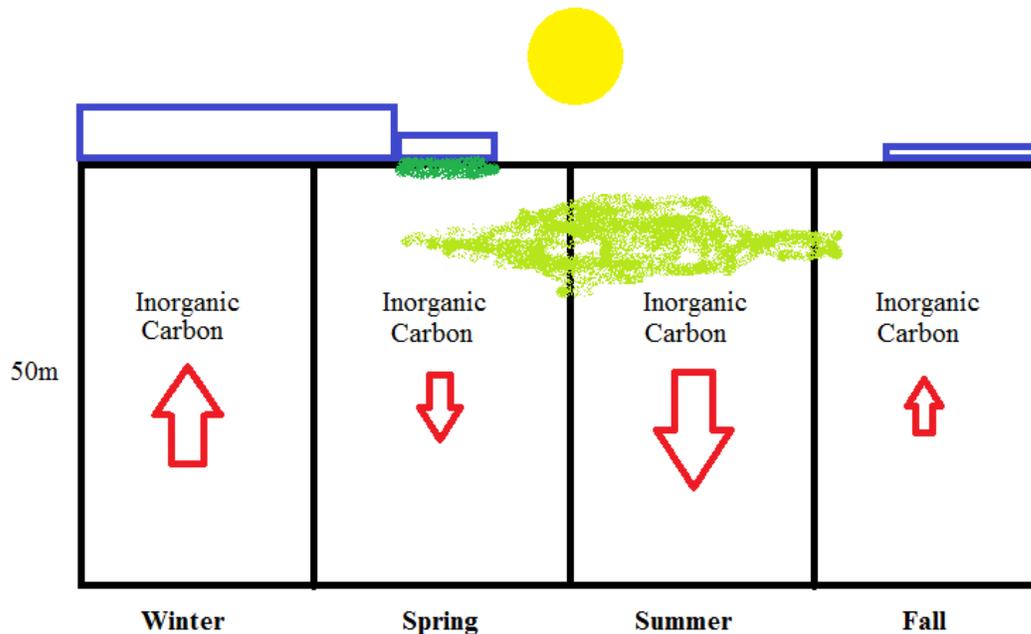


Figure 6: Schematic generalizing the Yager et al. (1995) hypothesis for dissolved inorganic carbon changes in the Arctic. In winter, there is no sunlight, extensive sea ice, and the carbon greatly increases in concentration. During spring, sunlight begins to return, sea ice becomes populated with ice algae, and a small phytoplankton bloom appears, which should decrease the carbon. Transitioning to summer, there is no more first year sea ice, and massive phytoplankton blooms occur, consuming carbon and nutrients from the surface waters. Finally in fall, the nutrients are consumed, phytoplankton blooms cease, and sea ice freezing processes begin.

Debate is ongoing if there is in fact air-sea exchange within sea-ice covered areas.

Research by Rysgaard et al., (2012), break down carbon exchange into four categories: brine rejection and sinking of carbon rich water, blocking of air-exchange from sea ice, melt water carbon depleted but alkalinity enriched, and biological drawdown of carbon during spring and summer. Some new hypotheses state that there is not an ever increasing trend throughout the winter to spring period. Work by Shadwick et al., (2011) and Else et al., (2012) showed that ice algae, the lesser participant to open water phytoplankton, demonstrate the ability to show a

drawdown signal of carbon in the surface waters of the ocean beneath sea ice. If this is true, this would undersaturate the water further before open water and enhance the exchange with the atmosphere.

## Chapter 3: Methodology

### 3.1 Study Area

This research was conducted in the landfast ice adjacent to Baffin Bay, a deep body of water located between Greenland (Denmark) and Baffin Island (Canada) (**Figure 7**). The general circulation in Baffin Bay is cyclonic (Tang et al., 2004), with Atlantic and Greenland origin waters coming in from the south through the Labrador Sea, and Arctic origin surface waters coming from the north through the Canadian Arctic Archipelago. Baffin Bay is mostly covered by sea-ice except in August and September (Tang et al., 2004), but it has a well-known recurrent polynya at its northern extent (North Water Polynya, Miller et al., 2002).

The field program was conducted as part of the 2015 GreenEdge project (<http://www.greenedgeproject.info/icecamp.php>), which lasted approximately 10 weeks from April to July. The sampling site was southeast of Broughton Island (67.28774N, 63.47398W) and northeast of mainland Baffin Island, approximately 23km from the town of Qikiqtarjuaq, Nunavut, Canada (**Figure 7**). The sampling location was not in Baffin Bay itself, but within a fjord at the edge of the Bay where the water depth was 360-370 meters to the sediments. The sampling site was covered (ice concentration: 100%) by thick (>120 cm) first year landfast ice. A mobile ice zone was present approximately 25km offshore of the site, which had a mixture of thin (30-70 cm) and thick (>120 cm) first year sea ice with a coverage of 90-100%.

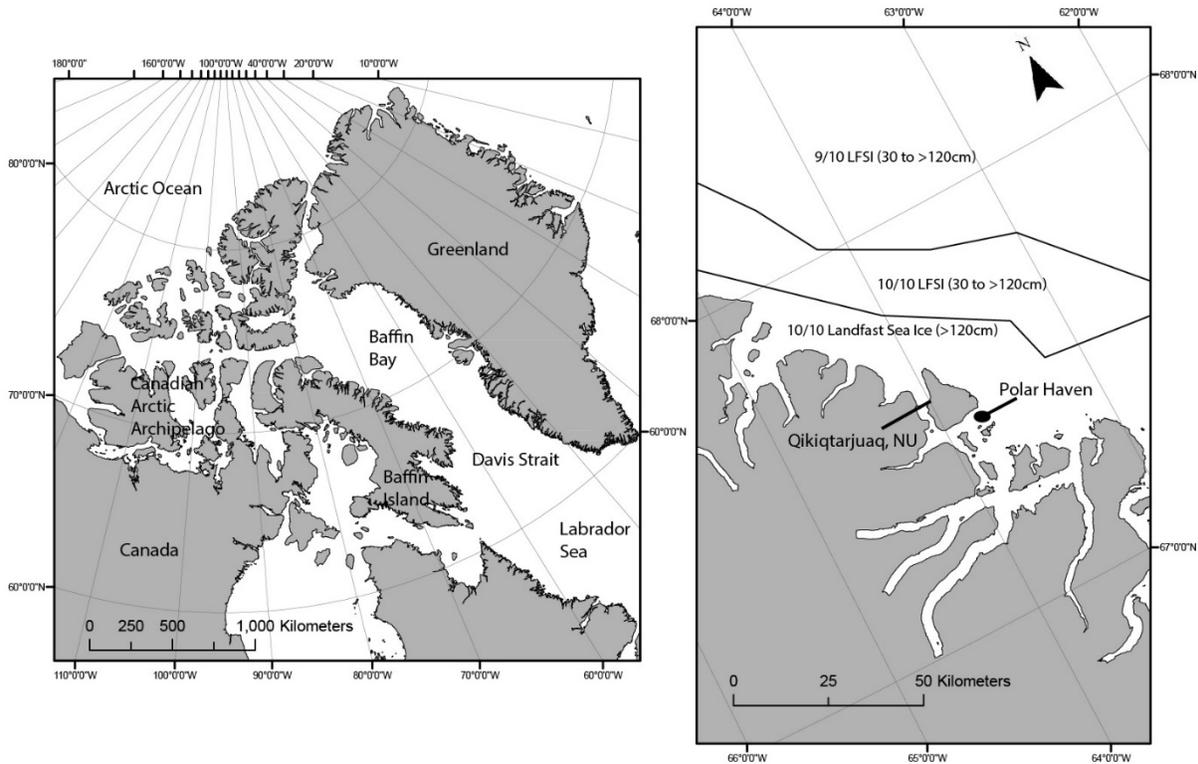


Figure 7: Map of the study area with sea ice characterization border in black lines (percentage of ice cover and thickness of sea ice also enclosed). Base of operations were maintained in the town of Qikiqtarjuaq, while sampling and experiments occurred at the ice camp (Polar Haven) approximately 23km from town. Polar Haven was not directly into the bay but in the coastal island chains on thick first year landfast ice.

### 3.2 Sampling and Analysis

To constrain atmospheric conditions, an automated weather station was set up near the Polar Haven (~500m to the southwest). Air temperature was recorded every 10 minutes with a shielded probe that ventilated 30 seconds prior to measurement, while snow depth was measured every 10 minutes using a Sonic Ranger 50 (Campbell Scientific) located 2m above the snow-ice

interface. Ice thickness was measured every three days (approximately) in the vicinity of the main sampling site using the average length of multiple ice core samples.

General ocean parameters (temperature, salinity, chlorophyll *a*) were collected using a Seabird model SBE9+ V2 CTD (conductivity [salinity], temperature, depth), which was calibrated prior to ice camp activities. CTD casts were made prior to water collection, descending at a rate of 0.3m/s down to a depth of 350m. Density was calculated from absolute salinity and conservative temperature using TEOS-10 Oceanographic Toolbox (McDougall and Barker, 2011). Surface current direction and magnitude was also measured near the sampling site, using a 1200 kHz RDI ADCP (acoustic doppler current profiler) deployed face up at 4.1 meters depth. Deployed in this configuration, the instrument was able to record velocities within a ~3m volume between the ice-water interface and the sensor. Velocities were sampled with 5cm bins every 25 minutes.

Seawater samples were collected approximately every three days from April 30 – July 10 through a 1x1 meter hole in the ice, which was covered by a ~35 m<sup>2</sup> tent (“Polar Haven”). DIC and TA samples were collected using 8-20 liter Niskin bottles by General Oceanics and deployed at set depths of 1.5 m, 5 m, 20 m, 40 m, and 60 m. Water from the ice-ocean interface was collected using a pump outside the ice camp deployed through an auger hole. After the retrieval of Niskin bottles, water was transferred via Tygon tubing into 12 mL vials (LabCo Exetainer 839W). Four samples were collected from each specified depth. Samples were preserved with 20 µl supersaturated HgCl<sub>2</sub>, stored in a dark cooler, and then refrigerated for storage (40 °C).

Analysis of DIC and TA occurred at the University of Manitoba after sample collection and storage. DIC was analyzed using an Apollo Sci Tech. DIC analyzer Model AS-C3 equipped with an infrared CO<sub>2</sub> detector (LiCor Model LI-7000). Instead of operating on a principle of

coulometric titration, the AS-C3 uses a non-dispersive infrared detector to quantify CO<sub>2</sub> gas. An additional advantage of this analyzer is the small volume size required for repeated samples. TA was analyzed by potentiometric titration using a Radiometer Analytical TIM840 titrator. Both instruments used 5% HCl to acidify samples. Seawater reference standards for DIC and TA were based from Scripps Institute of Oceanography, batch #144 to provide high accuracy measurements. All sample collection and analysis were based on the standard inorganic carbon procedures (Dickson et al., 2007), with slight modifications for the small-volume sampling protocols. Using the DIC and TA measurements, pH (total scale),  $p\text{CO}_{2\text{sw}}$ , and calcium carbonate saturation states ( $\Omega$ ) were calculated using the CO2SYS Excel Program (Pierrot, Lewis, and Wallace, 2006).

Samples for nitrogen nutrients in the form of nitrate (NO<sub>3</sub><sup>-</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>) were also collected from Niskin bottles at the same depths in 20 ml polyethylene flasks. Mercuric chloride (100 µL) were added to preserve the samples, which were then stored in the dark until analysis. Analyses were performed after returning the samples from the field, using an automated colorimetric procedure as described by Aminot and Kerouel, (2007). The reported nitrate concentrations are accurate up to 0.05 µmol L<sup>-1</sup> and nitrite up to 0.03 µmol L<sup>-1</sup>.

Chlorophyll *a* in sea ice was collected by taking two ice cores of 14.5 cm diameter and pooled and melted with a known volume of fresh filtered (0.2 µm) seawater overnight in a cooler prior to filtration. Chlorophyll *a* was measured in a six step process. First, samples were filtered under a vacuum through a FD/F 25 mm diameter glass fibre filter. The filter is soaked in 10 mL of acetone 90% in a glass scintillation under dark and freezing (-20°C) for 24 hours. The extract is poured into a cuvette and measured using the fluorometer by Tuner Design model AU-10. The sampled is then acidified with the resulting extract read by fluorometer again. The final

concentration of chlorophyll *a* and phaeopigments is calculated according to Yentsch and Menzel, (1963).

Seawater used for primary production measurements was transferred from the Niskin bottles with a Teflon tube into three 600 ml polycarbonate bottles. After addition of  $^{13}\text{C}$  tracer, samples were spiked with inorganic nitrogen labelled with  $^{15}\text{N}$ . One sample was spiked with 100 $\mu\text{l}$  of  $^{15}\text{N-NH}_4$ , and a second with 50 $\mu\text{l}$  of  $^{15}\text{N-NO}_3$ . After tracer addition, samples were placed into different plastic boxes covered by a nickel screen simulating different light intensity corresponding to the depths of sampling. Incubation was stopped after 24 hours and samples were immediately filtered on Whatman GF/F filters (25 mm in diameter) precombusted at 500°C. Filters were dried at 60°C during 12 hours and stored dry until mass-spectrometer analysis. Filtrates were poisoned with 1 ml  $\text{HgCl}_2$  (6g.l $^{-1}$ ) and stored until analysis.  $^{13}\text{C}/^{15}\text{N}$  enrichments on filters were measured on a CN-Sercon mass-spectrometer according Raimbault and Garcia, (2008).

## Chapter 4: Data and Results

### 4.1 Atmospheric/Sea-Ice conditions

Air temperatures (**Figure 8a**) remained mostly below 0°C for the first 6 weeks of the experiment, with the first above zero temperatures near the end of May. Late June and early July saw the daytime highs 5-10 degrees above zero. Snow depth (**Figure 8b**) remained fairly consistent for the first two weeks of the measurement period, with values in the range of 20-30 cm. Several large snowfall events during the month of May caused snow depth to reach peaks of about 50 cm. Following the final snowfall event, snow depth then declined steadily through the month of June, as a result of compaction and snow melt. Based on snow temperatures from the meteorological tower, snow melt appeared to start at the beginning of June in the upper centimeters. The first fully formed melt ponds appeared on June 24<sup>th</sup>. Sea ice thickness measurements varied around 120-140 cm with no distinctive trend through the month of May (**Figure 8c**). Ice thickness did decline through the month of June as a result of melt, reaching a minimum thickness of 105 cm at the end of sampling.

### 4.2 Oceanographic Conditions

Temperature, salinity, and density profiles from CTD casts at different points throughout the sampling period for the upper water column are shown in **Figure 9**. Throughout most of May and early June temperature, salinity, and density were fairly consistent with depth. The mixed layer depth for this time period (calculated following the de Boyer Montegut et al. (2004) definition of a density difference greater than 0.03 kg m<sup>-3</sup> at a threshold of 10m ( $\sigma > 0.03$  depth  $\geq$  10m)) was around 16 m.

**Figure 10a** shows density contour profiles throughout the sampling period to 350 m depth. The surface (upper 50 m) of the ocean does not change noticeably over time and there are

distinct density layers with increasing depth. To see actual changes in surface density, it is necessary to zoom in to the upper 10 meters. This is shown in **Figure 10b**, where mid-June has the first noticeable drop from the consistent  $1026 \text{ kg m}^{-3}$  (or  $\sigma_{26}$  for notation ( $\sigma = \text{Density} - 1000$ )), followed by a large decrease in density around July down to 1015, which signifies the intrusion of sea-ice meltwater. Indeed, this is reflected in the profiles from **Figure 7**, in which all three seasonal lines from June 24<sup>th</sup> and July 8<sup>th</sup> are different.

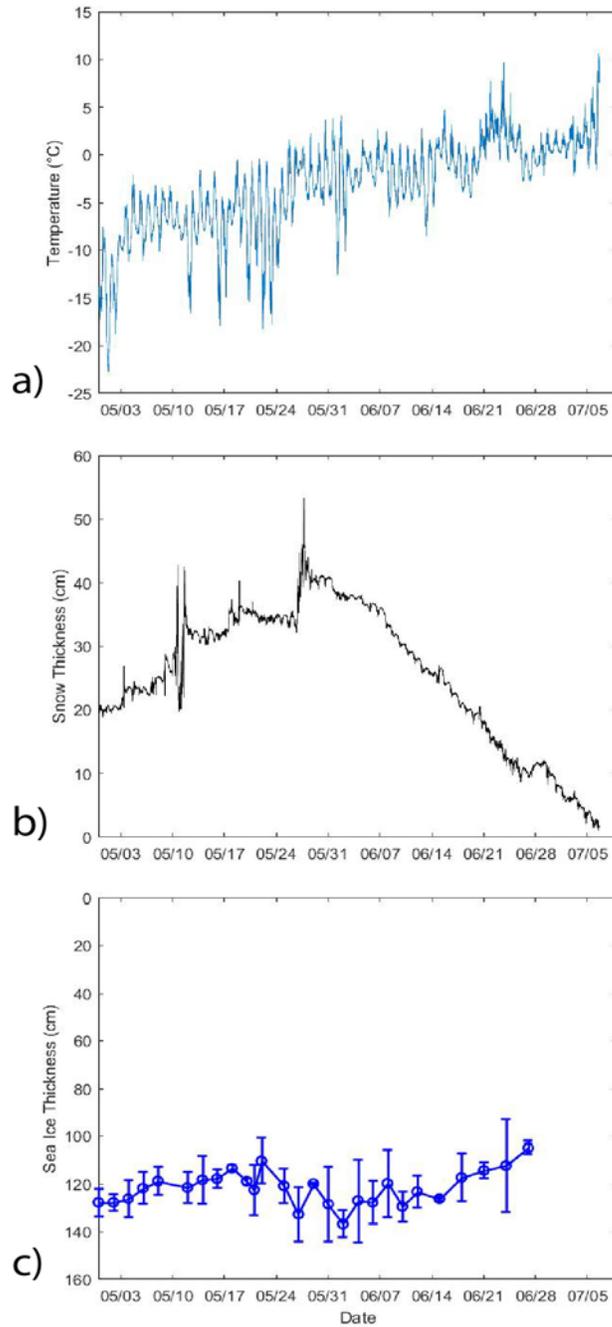


Figure 8: Select physical parameters measured at the Polar Haven: a) Air temperatures (°C) recorded every 10 minutes from meteorological tower. b) Snow depth (centimeters) recorded every 10 minutes from meteorological tower. c) Average sea ice thickness (centimeters) with standard deviations (3-4 cores) from ice core sampling.

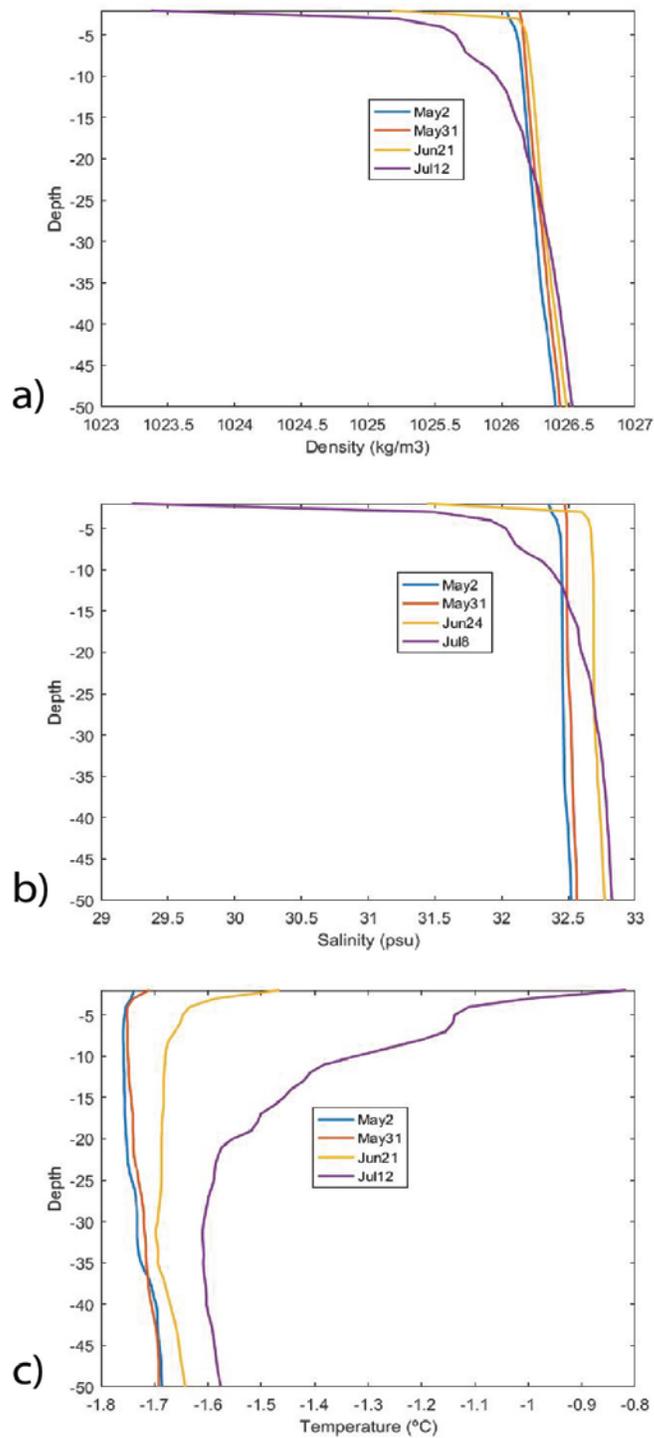


Figure 9: Water column profiles of a) density ( $\text{kg m}^{-3}$ ), b) salinity (psu), c) temperature ( $^{\circ}\text{C}$ ) for select dates; beginning of May (May 2<sup>nd</sup>), end of May (May 31<sup>st</sup>), beginning of summer (June 24<sup>th</sup>), and the last day of sampling (July 8<sup>th</sup>).

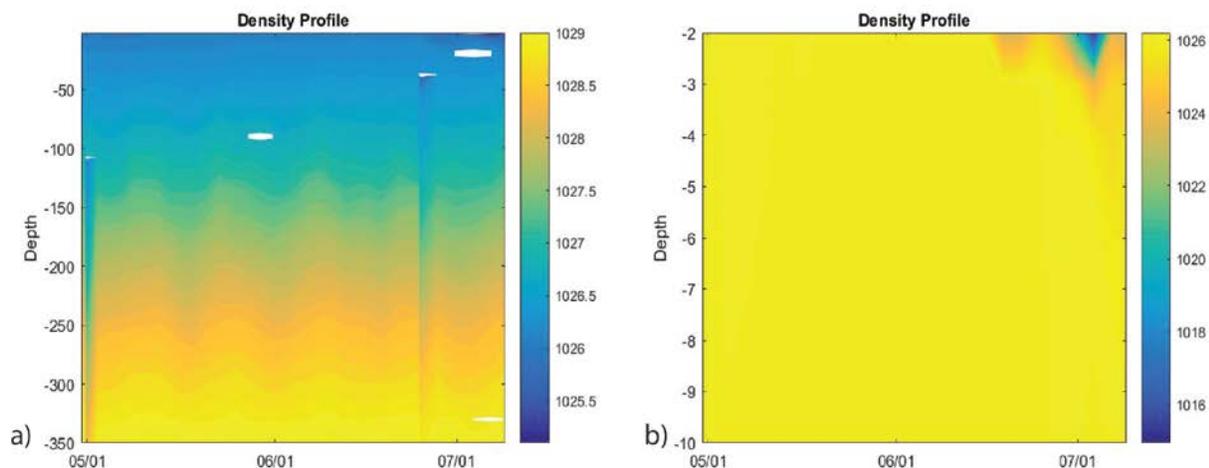


Figure 10: Contour density profiles ( $\text{kg m}^{-3}$ ) for the sampling period of a) the water column (350 meters) and b) upper 10 meters. Blank spaces indicate that temperature and/or salinity was not recorded for that depth.

#### 4.3 DIC/TA/Nutrient Conditions

The time series of carbon system parameters, nutrients, and near-surface salinity are shown in **Figure 11**. These tracers show remarkable coherence with the observations of sea ice and water column chlorophyll (**Figure 13b**). DIC, TA, and nitrate in the upper 5m (**Figure 11a-c**) gradually increased through May and early June, before dropping significantly on June 18<sup>th</sup>; the same date that chlorophyll in the ice reached minimum values, and chlorophyll in the seawater initially increased. This was followed by slight rebounds and fluctuations in all parameters over the course of the next week, and then a drastic decreases in DIC, TA, and nutrients after July 21<sup>st</sup>. The sudden late season decrease in these parameters matches the sudden accumulation of chlorophyll *a* in the water column (**Figure 4b**). The late season decreases also match to some extent the decreases observed in near surface salinity (**Figure 11d**), with the first decreases occurring on June 24<sup>th</sup>, followed by drastic decrease then rebound. **Figure 12** shows an extrapolated DIC concentration profile for the entire sampling period. Fluctuations only occurred in the upper 10 m of the surface water.

#### 4.4 Biological Conditions

**Figure 13a** shows sea ice chlorophyll *a* concentrations for the bottom 0-3 centimeters of ice at high snow (HS) and low snow (LS) sampling locations. Chlorophyll *a* concentrations peaked near the end of May, with values around 35 mg m<sup>-2</sup> under high snow, and greater than 40 mg m<sup>-2</sup> under low snow. After those dates, chlorophyll *a* concentrations fell, reaching minimum values around June 18<sup>th</sup>. The strongest decreases in chlorophyll *a* started around June 12<sup>th</sup>, closely coinciding with the first observations of melt water in the CTD profiles. **Figure 13c** shows the water column chlorophyll *a* at 2 and 5 m depths. Displaying opposite trends compared to sea ice, the chlorophyll *a* in the water column began to rise shortly after the appearance of melt water. It then fell rapidly back to pre-melt values, before increasing dramatically after the occurrence of melt ponds on June 24<sup>th</sup>.

Primary productivity for both sea ice (**Figure 13b**) and the water column (**Figure 13d**) are also shown. Productivity is different from chlorophyll *a*. Productivity is defined as the rate of fixation of carbon by primary production, and chlorophyll *a* is the concentration of biomass measured from the chlorophyll *a* pigments. Productivity remained low for April and May, but picked up for both sea ice and the water column during June, with maximum productivity occurring on the same date as maximum chlorophyll concentrations in (**Figure 13a**). Water column chlorophyll concentrations (**Figure 13c**) from CTD measurements are shown. A small increase in water column chlorophyll down to 5m occurred on June 18<sup>th</sup>, with a large increase in the water column chlorophyll on July 2<sup>nd</sup>, several days after the melt of the sea-ice.

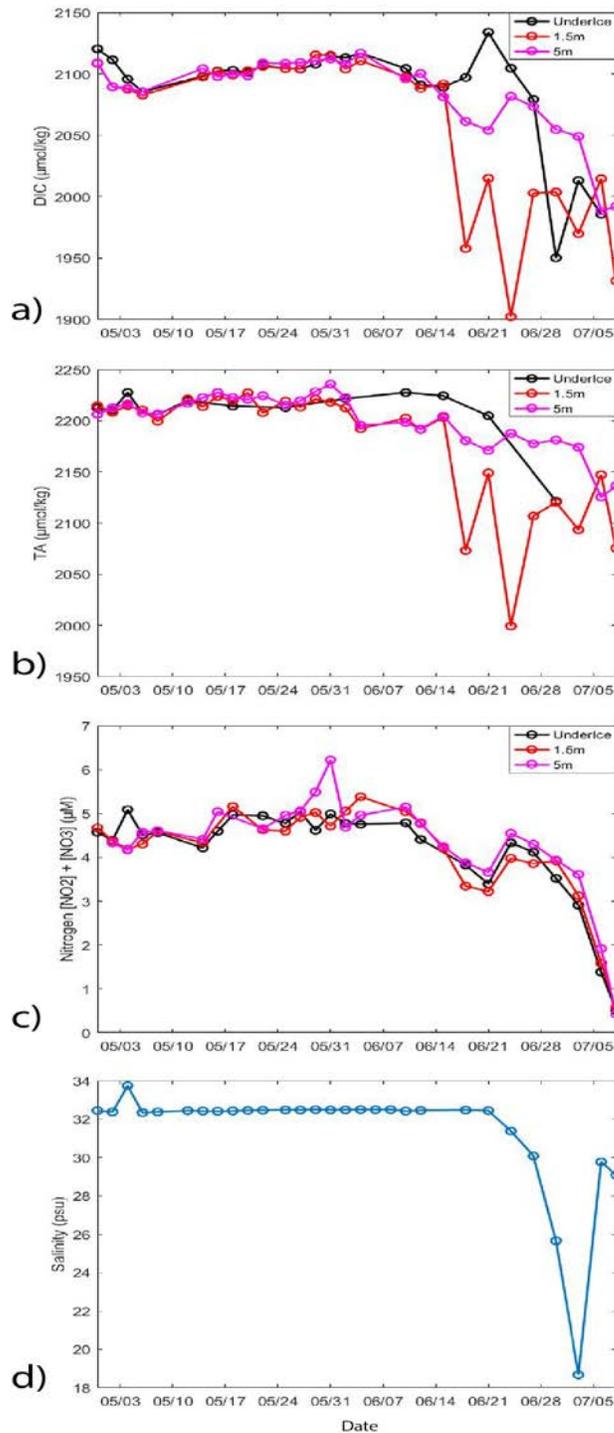


Figure 11: Chemical parameters of the water column: a) DIC (dissolved inorganic carbon) concentrations through sampling period for upper 5 meters. b) TA (total alkalinity) concentrations through sampling period for upper 5 meters. c) Nitrogen nutrients (Nitrate [NO<sub>3</sub><sup>-</sup>] and Nitrite [NO<sub>2</sub><sup>-</sup>]) concentrations through sampling period for upper 5 meters. d) Salinity at 2 meters from water surface (approximately 60-90 centimeters from the ice-water interface).

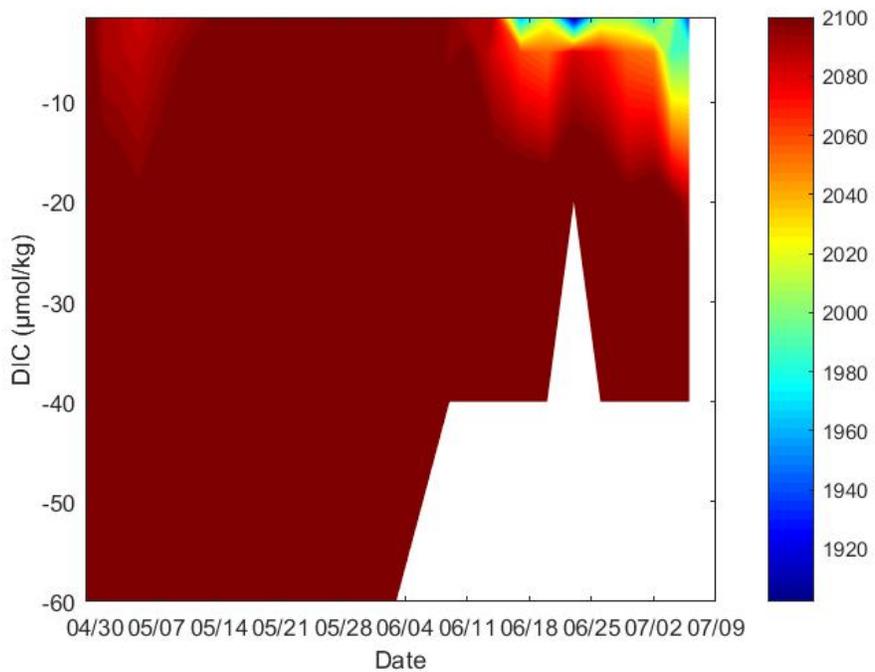


Figure 12: DIC ( $\mu\text{mol kg}^{-1}$ ) extrapolated contour plot of the sampling period from Figure 11a. Blank spaces indicate that DIC was not sampled from that depth.

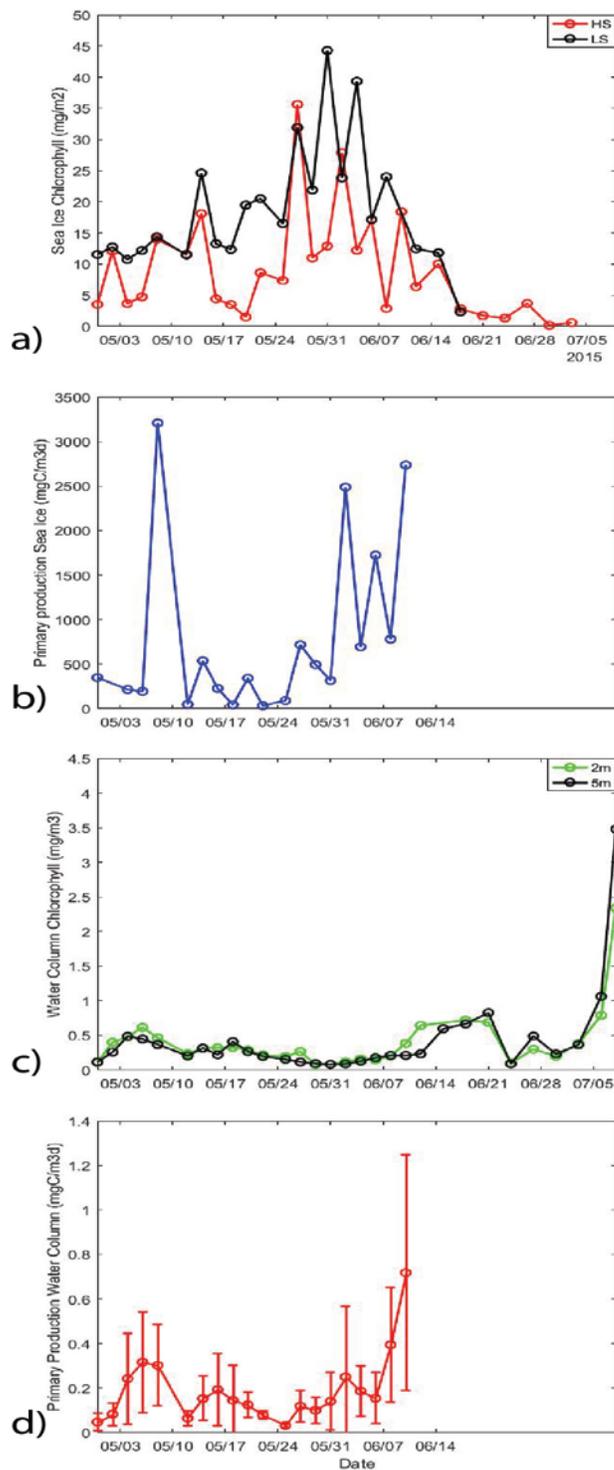


Figure 13: Chlorophyll *a* concentrations of sea ice: a) Chlorophyll concentrations of the bottom 3 centimeters of sea ice. HS and LS refers to high snow and low snow respectively above the measurement site. b) Sea ice primary productivity. c) Water column chlorophyll concentrations from CTD measurements. d) Water column productivity.

## Chapter 5: Discussion

### 5.1 Ice Algae

As discussed in the introductory section, the timing of DIC drawdown in the Arctic, and the biological community responsible for it, is subject to some debate. Based on a year-long study in a spring-opening polynya region, Shadwick et al., (2011), and Else et al. (2012) observed a reduction of DIC and  $p\text{CO}_{2\text{sw}}$  (respectively) in the mixed layer beneath the ice cover in early April, which they attributed to the onset of the ice algae bloom. Brown et al. (2015) noted a large drawdown of  $p\text{CO}_{2\text{sw}}$  in the bottom centimeters of bulk sea ice, but saw no such impact of ice algae on  $p\text{CO}_{2\text{sw}}$  in the water column through the peak of an intense ice algae bloom near Resolute Bay, Nunavut. The results from this present study fall more in line with the observations of Brown et al. (2015), with no significant DIC drawdown in the water column through the ice algae period (**Figure 11a**). In fact, the results show a slight increase in DIC/TA (**Figure 11a&b**) during the peak of the ice algae bloom (approximately May 26<sup>th</sup> to June 8<sup>th</sup>, **Figure 13a**). The beginning of the ice algae measurements show that there was already a substantial amount of chlorophyll in the sea ice. While there are no DIC/TA measurements made prior to the start of the initial sampling, **Figure 14** shows an extended ice algae chlorophyll measurement (note that the concentrations are in  $\text{mg m}^{-3}$ ), which includes chlorophyll *a* a few weeks prior to the first DIC/TA sampling. As seen there was an initial bloom of ice algae, but these concentrations mimic the final outcome of the ice algae at very low concentrations compared to the growth period.

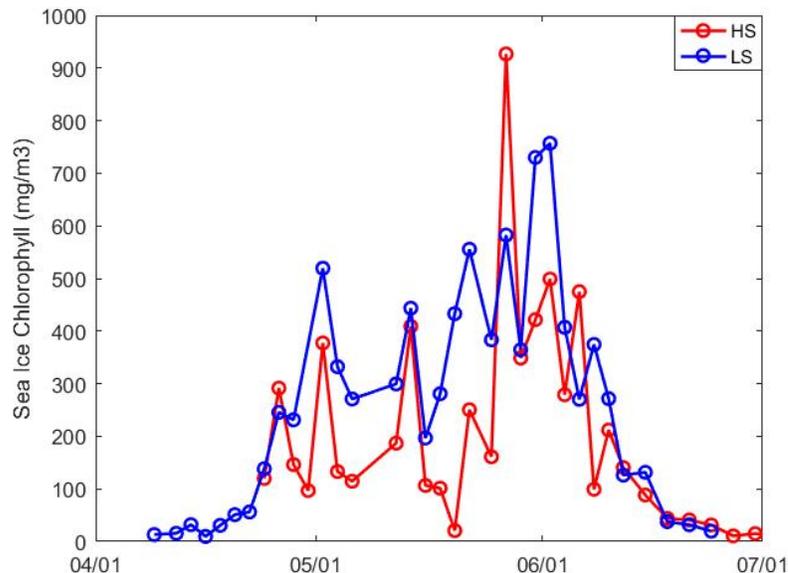


Figure 14: Extended sea ice chlorophyll *a* measurements (note the change in units to  $\text{mg m}^{-3}$  from **Figure 13**). Extra measurements made a few weeks prior to first DIC/TA sampling. The algae concentrations during the month of April were similar to the end of June.

This apparent conflict regarding the impact of ice algae blooms on the carbonate system of the underlying ocean could of course be the result of regional differences in bloom magnitude. However, the study conducted by Brown et al. (2015) at Resolute experienced exceptionally high bottom ice chlorophyll *a* (max  $\sim 80 \text{ mg m}^{-2}$ ) compared to Shadwick et al. (2011) ( $\sim 20 \text{ mg m}^{-2}$ ) in Amundsen Gulf. In the study, peak bottom ice chlorophyll *a* fell between these two examples, with values between  $30\text{-}45 \text{ mg m}^{-2}$  (**Figure 5a**). If ice algae do have a significant influence on the under-ice carbonate system, it is expected that the change would be most noticeable in regions with stronger ice algae blooms. It is therefore curious that Shadwick et al. (2011) observed an impact on seawater DIC/ $p\text{CO}_{2\text{sw}}$  while neither the present research, nor Brown et al. (2015) observed anything similar.

Taking a wider view, the magnitude of the ice algae bloom experienced in the research does appear to be typical of landfast ice in the North America Arctic (Leu et al., 2015). While Resolute experiences a much stronger ice algal bloom due to the continual resupply of nutrients from Pacific-water intrusion and mixing (Michel et al., 2006), other sites in the Canadian Arctic Archipelago, the North Water Polynya, and Barrow (Alaska) show peak chlorophyll *a* concentrations closer to the observations (Leu et al., 2015). The timing of peak sea-ice chlorophyll *a* in the research was late May/early June (**Figure 13a**), which is somewhat later (by ~14-21 days) than observed in Resolute and the North Water Polynya, and quite a bit later (by ~30 days) than in Amundsen Gulf. During the study, there were two large snowfall events (section 3.1) which may have played a role in limiting or delaying ice algae photosynthesis (Lee, Whitley, and Kang, 2008) through impacts on light transmission (Mundy et al., 2005).

Nevertheless, the similar bloom timing and magnitude to most locations in the North American Arctic make the observations useful for further understanding the potential role of sympagic production on the under-ice carbon system. Looking at the DIC concentration difference from May 2<sup>nd</sup> (the start of the observations) to June 4<sup>th</sup> (the end of the ice algae bloom), observed a  $0.15 \mu\text{mol kg}^{-1}\text{d}^{-1}$  increase at 1.5 and 5m depth, Furthermore, fluctuations of DIC concentrations in **Figure 11a** do not correlate well with fluctuations of chlorophyll *a* in **Figure 13a**. This suggests negligible control of ice algae production on the mixed layer carbonate system, and that the slight increase observed is the result of respiration in the water column.

If this fairly typical ice algae bloom did not affect the under-ice carbon system, it is curious if different regions are reflective of different mechanisms, or the suspicion on the general hypothesis that ice algae can exert a significant control on the under-ice carbonate system

throughout the mixed layer (Else et al. 2012; Shadwick et al. 2011). Simple carbon budget calculations can be used to further elucidate this point. During the period in which ice chlorophyll *a* was accumulating (Apr. 30 to May 31, Figure 4a), fellow collaborators observed an increase in total particulate carbon from ~600-1200 mg m<sup>-2</sup> in the bottom 10 cm of the ice (not shown). If it is assumed that all of this carbon was fixed from the DIC pool in the mixed layer, it can be calculated that this change would impart to DIC concentrations ( $\Delta DIC$ ) via:

$$\Delta DIC = \frac{\Delta TPC}{MLD \cdot \rho} \quad (1)$$

Where  $\Delta TPC$  is the change in total particulate carbon (600 mg m<sup>-2</sup>), MLD is the mixed layer depth (~16 m), and  $\rho$  is the density of seawater (1026 kg m<sup>-3</sup>). This amount of carbon fixation yields a decrease in mixed layer DIC of only 3.0  $\mu\text{mol kg}^{-1}$ . Even if it is assumed that all of the particulate carbon present in sea ice at the peak of the ice algae bloom (1200 mg m<sup>-2</sup>) was derived from the mixed layer, this would only produce a decrease in DIC of 6.0  $\mu\text{mol kg}^{-1}$ . Observations of slight increases in DIC over the ice algae accumulation period suggest that net respiration in the water column overwhelms the modest uptake of DIC afforded by the ice algae. In contrast, Shadwick et al. (2011) attributed a 20  $\mu\text{mol kg}^{-1}$  decrease in a 50 m deep mixed layer to ice algae production. This would require an accumulation of approximately 12 000 mg m<sup>-2</sup> of particulate carbon in the sea ice. Assuming a carbon:chlorophyll *a* ratio of 30:1 (Riemann, et al., 1989) (similar to what is observed, and similar to other observations in the vicinity of Amundsen Gulf), this would require bottom-ice chlorophyll *a* values in excess of 400 mg m<sup>-2</sup>, more than an order of magnitude higher than the ~20 mg chlorophyll *a* m<sup>-2</sup> actually observed (Leu et al., 2015). In fact, those concentrations would be at least twice as high as any values reported in the pan-Arctic summary reported by Leu et al. (2015). Simply put, there is not enough biomass in the sea ice to impart a significant change in mixed layer DIC.

## 5.2 Under-ice Phytoplankton

A possible explanation for the Shadwick et al. (2011) discrepancy is that uptake of DIC by an under-ice phytoplankton bloom was misattributed to the ice algae bloom. Our measurements show a rapid DIC drawdown of  $\sim 90 \mu\text{mol kg}^{-1}$  from June 15<sup>th</sup> to July 8<sup>th</sup> at 5m depth, and greater drawdown at 1.5m, (**Figure 11a**). There was also a short ( $\sim 1$  week) and less intense decrease in DIC/TA/nutrients and increase in chlorophyll *a* that preceded the sustained changes in late June. That brief departure may have been caused by sea ice algae flushing off of the ice as meltwater (with low DIC/TA/nutrient concentrations due to dilution) percolated through the sea ice. As Mundy et al. (2009) describe, when sea ice algae are released to the water column, they can seed a subsequent under-ice phytoplankton bloom. The period of intense DIC decline after June 24<sup>th</sup> can likely be attributed to such a bloom. One other potential cause of the DIC drop could be dilution from sea ice melt, however salinity normalized DIC and TA concentrations at 5 meters (**Figure 15**) still shows a significant decline of  $55 \mu\text{mol kg}^{-1}$  over that time period, suggesting that biological drawdown was the main factor. With the onset of melt ponds on June 24<sup>th</sup> and residual snow cover being  $< 5\text{cm}$  in the beginning of July (**Figure 8b**), it is likely that further light penetration into the water column occurred, triggering the under-ice phytoplankton bloom. The response of the carbonate system to this bloom suggests a far more important role for this community than the ice algae community in controlling water column carbonate chemistry.

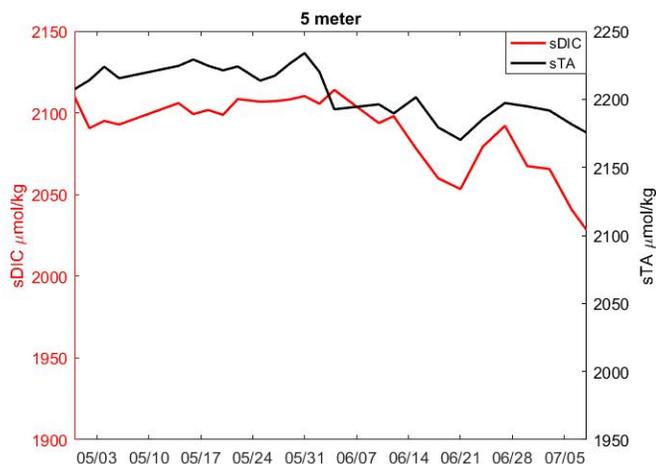


Figure 15: Normalized DIC (sDIC) and TA (sTA) at 5 meters from Figure 4 a) and b) to a salinity value of 32.46. Meltwater did not intrude into 5 meters until the end of sampling.

### 5.3 Advection

A common concern in marine biogeochemical time-series studies is that ocean currents make it impossible to measure the same seawater twice. This is not a problem in highly homogenous regions, as the processes occurring “upstream” of the sampling site should be consistent with the sampling site itself. It may, however, be a concern in the study area, where processes occurring in the mobile ice of Baffin Bay may be quite different than those occurring along adjacent landfast ice regions (**Figure 7**). This would be particularly concerning during periods of significant open water in Baffin Bay. If advection transported water from Baffin Bay into the landfast ice region, the time-series based conclusions may be compromised.

As shown in **Figure 16**, the study region was heavily enclosed by thick first year sea-ice. Even at the end of sampling in early July, western Baffin Bay still had significant amounts of sea-ice present. This alleviates to some extent concerns that biogeochemical processes in Baffin Bay would be significantly different than at the sample site. The ice also would have prevented any large scale horizontal wind-driven advection, particularly since sea-ice roughness reduces surface water velocities through drag.

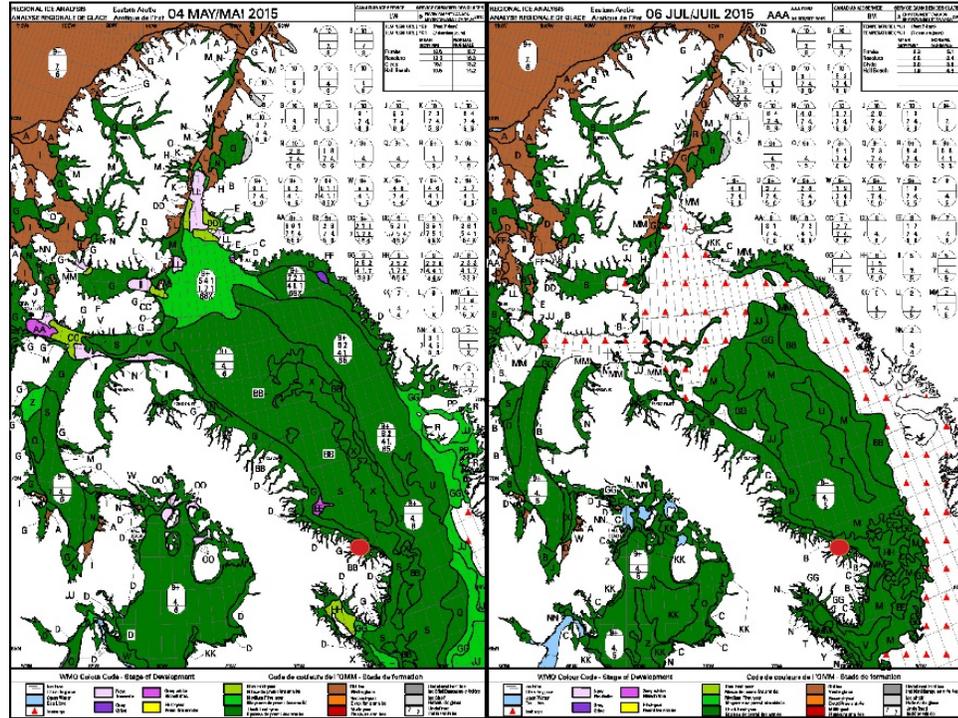


Figure 16: Sea ice extent provided by Canadian Ice Service on May 4<sup>th</sup>, 2015 and July 2<sup>nd</sup>, 2015. Red dot is the study site. Dates were as close to beginning and end of sampling as available from archives. Thick first year sea-ice covered the entire bay during spring. Northern and eastern portions of the bay experienced melt first, with western sea-ice still remaining thick into early summer.

To further rule out advection as a source of error, the ADCP data was compiled into daily means and plotted as vectors to show net daily water movement (**Figure 17**). Averaging the raw daily current vectors for the sampling period created a mean vector for the measurement period with a net water movement to the NNE at  $0.7 \text{ cm s}^{-1}$ . Therefore, the upper 4 m of the water column traveled on average  $584 \text{ m d}^{-1}$ , and for the sampling period, the underlying water mass traveled 40.32 km. This means that the upper layer source water for sampling was within  $\sim 40 \text{ km}$  to the SSW. As **Figure 7** shows, this current direction serves to transport water towards Baffin Bay, from source areas dominated by landfast ice to the SSW. The water source should therefore

have little to no influence from the central Bay, and there is higher confidence that biogeochemical measurements are representative of landfast sea ice.

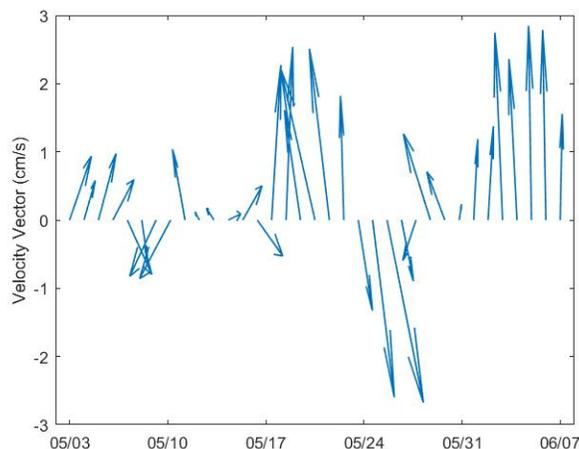


Figure 17: Daily current vector plot of seawater from the upper 3 meters below sea-ice. Vector direction indicates water movement with north being up, and east being right. The magnitude of the vector is the average sum of the water velocity from 3 meters below the ice. The velocity vector axis is identical for both y (north, south) and x (east, west) directional movement. Velocity vectors from raw data were averaged to give a sampling site vector of  $0.6763 \text{ cm s}^{-1}$  to the NNE.

#### 5.4 Sea Ice Melt

Sea-ice formation and decay are physical mechanisms which change the concentration of carbon in seawater. Enhanced gas exchange during the freezing process (Anderson et al., 2004) and brine rejection (Rysgaard, 2007; Miller et al., 2011) increase the concentrations of DIC in the water column. Contrastingly, the decay or melting process initially causes DIC concentrations to decrease as DIC depleted meltwater is introduced to the underlying water column (Rysgaard et al., 2011). Sea-ice impact by climate change is already increasing production and the growing season (Arrigo et al., 2008) and is assumed that carbon will also be affected by these changes (Bates and Matthis, 2009).

Sea ice thickness measurements had little variation through most of the research period (**Figure 8c**). From April 30<sup>th</sup> until June 27<sup>th</sup>, there was a thickness maximum range of 32 cm, with the ice being thinnest at 104.8 cm on June 27<sup>th</sup>. Values for DIC concentrations and sea ice thickness from April 30<sup>th</sup> to June 15<sup>th</sup>, which was prior to melt, had consistent values with minimal overall change; start and end date 1.5 meter DIC measurements changed  $16.8 \mu\text{mol kg}^{-1}$ , and sea ice thickness average changed by 1.5 cm. On June 21<sup>st</sup>, sea ice was melting as noted by 2m salinity steadily decreasing. Initial sea ice melt started earlier on June 18<sup>th</sup> from 1m salinity values which coincided with the large DIC drawdown (1m salinity values are excluded from detailed analysis as measurements were made inside the sampling hole and subject to contamination and/or error). Sea ice thickness continually decreased by 21.5 cm, and there are large fluctuations and lower concentrations in DIC at 1.5 m of up to  $112 \mu\text{mol kg}^{-1}$ . Normalized values of sDIC and sTA at 5 m (**Figure 15**) had a range of 85.5 and  $63.5 \mu\text{mol kg}^{-1}$  respectively.

### *5.5 $p\text{CO}_{2\text{sw}}$ Calculations*

Arctic marine systems generally absorb  $\text{CO}_2$  from the atmosphere, but considerable variability has been observed between open seas and coastal seas like the ones under investigation here (Bates and Mathis (2009); Shadwick (2010)). Although most  $\text{CO}_2$  exchange is thought to occur in open water during summer and fall, it is still useful to examine  $p\text{CO}_{2\text{sw}}$  – the determining factor in a region’s source/sink status – in the ice covered season during spring. As first postulated by Yager et al. (1995) and later developed by Else et al. (2012), biogeochemical processes during the ice-covered season precondition  $p\text{CO}_{2\text{sw}}$  prior to ice break-up, and to a large extent determine the direction and magnitude of annual  $\text{CO}_2$  flux budgets.

Using DIC/TA measurements (and other appropriate general ocean parameters) to calculate  $p\text{CO}_{2\text{sw}}$ , it is found that seawater  $p\text{CO}_{2\text{sw}}$  at all sampling depths was essentially

undersaturated (below the atmospheric value of  $\sim 400 \mu\text{atm}$ ) throughout the entire sampling period (**Figure 18**). Concentrations ranged between 300-350  $\mu\text{atm}$  throughout the month of May, and with few exceptions the June measurements also stayed between 300-350  $\mu\text{atm}$ . In July, when ice melt was well underway and the phytoplankton bloom had been initiated, concentrations fell below 300  $\mu\text{atm}$ .

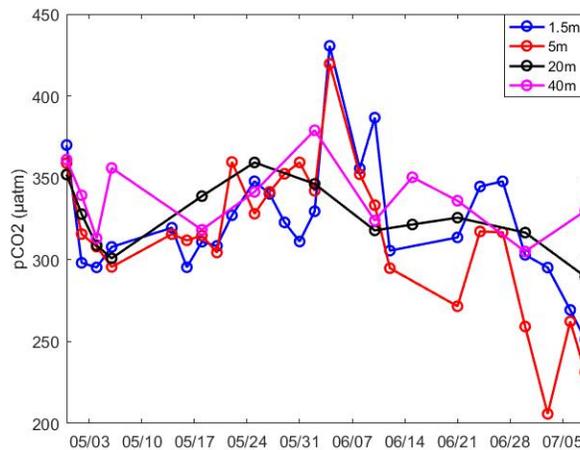


Figure 18:  $p\text{CO}_{2\text{sw}}$  concentrations ( $\mu\text{atm}$ ) through the sampling period for the upper 40 meters calculated with  $\text{CO}_2\text{SYS}$ . There is a marked undersaturation for the entire surface of the water column.

Table 1 shows reported  $p\text{CO}_{2\text{sw}}$  measurements in various sea-ice covered regions during similar seasons (late winter, prior to sea-ice melt). This summary, in conjunction with the present results, shows a convergence towards the general observation that Arctic seas are undersaturated at the end of winter, prior to the onset of sea ice melt and phytoplankton blooms. This is in contrast with the original hypothesis of Yager (1995) which predicted supersaturation beneath sea ice prior to spring blooms, and is more in line with the model proposed by Else et al. (2012).

Table 1:  $p\text{CO}_{2\text{sw}}$  from previous studies during the spring (April, May, early June) time period. Measurements were made under sea-ice but prior to sea-ice melt decay and the phytoplankton blooms.

Study	Time Period	Region	$p\text{CO}_{2\text{sw}}$ ( $\mu\text{atm}$ )
Geilfus (2012)	April-June 2008	Amundsen Gulf, Beaufort Sea	April: 396 May: 528
Else (2012)	April-June 2008	Amundsen Gulf	April: 363 May: 305
Else (2012)	May 2008	Banks Island	May: 301
Shadwick (2011)	April-June 2008	Amundsen Gulf	April: 350-400 May: 300-350 June: 300-250
Papakyriakou (2011)	April-June 2002	McDougall Sound	May: 440-380 June: 370-350
Omar (2007)	April-June 1990-1999	Barents Sea	April: 340 May: 330 June: 300
Bates (2006)	Springtime 2002	Central Chukchi Sea shelf, (Perennial sea-ice)	300-350 (200-250)

Because sampling ceased in early July while sea-ice was still in the melting process, there were no measurements into the open water summer season. However, since nutrients were still available at the end of the sampling period, the phytoplankton growing season should have continued to reduce  $p\text{CO}_{2\text{sw}}$  further into the summer. Sea ice melt and dilution would also have continued, making this region a significant sink for atmospheric  $\text{CO}_2$  once open water had been achieved. Furthermore, observations show that significant under saturation prevails until at least 40m depth (**Figure 18**), indicating that a considerable volume of surface water would need to reach saturation before atmospheric  $\text{CO}_2$  uptake ceased.

The sensitivity of  $p\text{CO}_{2\text{sw}}$  changes in DIC is called the Revelle factor, which is an indicator for potential  $\text{CO}_2$  uptake and buffering capacity (Revelle and Suess, 1957). **Figure 19** shows the change in Revelle factor for the sampling site. At the end of sampling, values were

around 14 from the melting water as dilution increased temperatures (Millero, 1995) and reduced the  $p\text{CO}_{2\text{sw}}$  concentrations. The Revelle factor would have continued to decrease below 14 by the time sea-ice fully melted from less saline, warmer surface waters, and a reduction in  $p\text{CO}_{2\text{sw}}$ . Standard ocean Revelle factors are around the order of 10 (Egleston et al., 2010), with tropical waters being lower and high latitude waters being higher. Even though the Revelle factor for the site is high, with such a large gradient possibility ( $\Delta p\text{CO}_2 > 200 \mu\text{atm}$ ) between the ocean and atmosphere, this area in Baffin Bay should serve as a major  $\text{CO}_2$  sink.

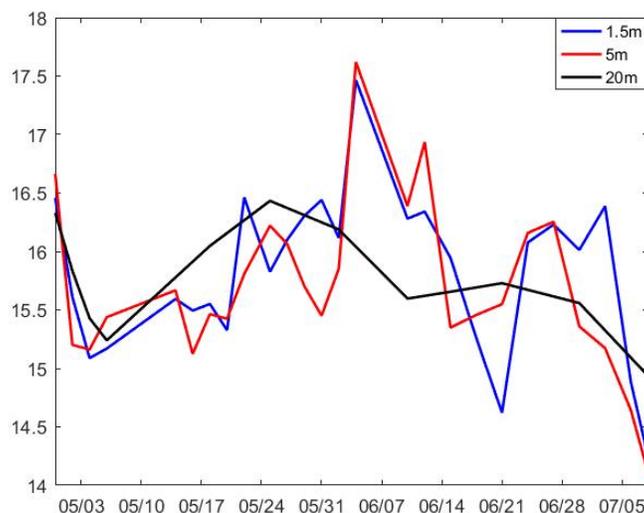


Figure 19: Revelle Factor values through the sampling period (no units). Values mimic the increases and decreases of  $p\text{CO}_{2\text{sw}}$  from Figure 8.

### 5.6 Carbonate saturation calculations

Qikiqtarjuaq is home to a small-scale commercial clam fishery, which a review of Nunavut fisheries identified as having potential for economic development (Brubacher 2004). The soft-shell clams (*Mya spp.*) are harvested by scuba divers, at depths of 10-20 m (Misiuk et al., 2014). Soft clams are very susceptible to aragonite dissolution from acidification, with dissolution even prior to  $\Omega=1$  (Ries et al., 2016). Gazeau et al., (2013) reviewed multiple works

examining the effects of lowered pH values on calcifying organisms (mostly gastropods and bivalves), conducted through incubations with controlled pH changes based on end century projections. They reported that with a 0.1 decrease from ambient pH levels, the calcifying abilities of soft-shelled clams are significantly impacted. Since the sampling coincides with the clam harvesting depth, and was conducted during the season with expected minimum pH values, it seemed appropriate to report the calcium carbonate saturation states based on the measured carbon system parameters (Table 2).

Table 2: Average calcium carbonate saturation states of calcite ( $\Omega_C$ ) and aragonite ( $\Omega_A$ ) with standard deviations calculated from CO<sub>2</sub>SYS.

	<b>Average <math>\Omega_C</math></b>	<b>Standard deviation</b>	<b>Average <math>\Omega_A</math></b>	<b>Standard deviation</b>
1.5 meters	2.15	0.196	1.33	0.115
5 meters	2.16	0.181	1.35	0.113
20 meters	2.17	0.119	1.36	0.0746
40 meters	1.91	0.104	1.32	0.0720

During the sampling period, calcium carbonate saturation states for both aragonite and calcite for the water column were  $\Omega > 1$ , so seawater was supersaturated with respect to calcium carbonate (Rossum and Merrill, 1983). Saturation levels were lower for 1.5 m and 5 m than 20 m because of the higher  $p\text{CO}_{2\text{sw}}$  values. Saturation levels for 40m were lowest because of colder temperatures and constant  $p\text{CO}_{2\text{sw}}$  values. Aragonite was close to saturated levels at the surface, although both calcite and aragonite's  $\Omega$  value increased as further production lowered  $p\text{CO}_{2\text{sw}}$  values (not shown).

Saturation states calculated are higher than those reported for Baffin Bay by Azetsu-Scott et al., (2010), who reported calcite and aragonite saturation values of around 1.76 and 1.10 respectively, with an aragonite saturation depth of 200-500m. Those measurements were made

further out in Baffin Bay, at a different time of year (July) and nearly a decade earlier (2003), which are all factors that could explain the slightly higher values at the site. In general, our values are consistent with other Arctic regions, falling somewhere in the middle. For example, the study site had lower surface saturation levels than the western Canadian Arctic Archipelago, the Chukchi Sea, Beaufort Sea, and southern Baffin Bay/Labrador Sea (Chierici and Fransson, 2009), but higher saturation levels than the central Canadian Arctic Archipelago and Amundsen Gulf (Chierici and Fransson, 2009).

It is well known that increased CO<sub>2</sub> and enhanced sea-ice melt results in lower, even unsaturated conditions in certain Arctic regions (Yamamoto-Kawai et al., 2009; Robbins et al., 2013). The earth system model presented by Steinacher et al., (2008) predicts that the entire Arctic Ocean water column will have undersaturation (except between 1000-2000m) by 2100. There will be undersaturation of at least 10% of Arctic surface waters within a decade, with over 50% of the Arctic surface waters undersaturated by year 2050 in the A2 emissions scenario (IPCC classification). For the Baffin Bay region in particular, Steiner et al., (2015) predicts that the saturation depth of aragonite will rise about 60m per decade. Building from the observation that the site near Qikiqtarjuaq is fairly typical for the Arctic, these projections suggest aragonite undersaturation at the depth of the clam shelves within three to four decades, potentially putting the clam fishery in peril.

## Chapter 6: Conclusion

The main conclusion of this thesis is that ice algae primary production while they are in sea ice does not affect mixed layer DIC/ $p\text{CO}_{2\text{sw}}$  concentrations to an extent that would significantly impact air-sea exchange of  $\text{CO}_2$  in the ice-free season. While I have only presented observations for a single case study, calculations of the ice algae biomass needed to impart a significant change on mixed layer DIC/  $p\text{CO}_{2\text{sw}}$  suggest that this null result would apply to most Arctic regions. This conclusion is in conflict with one major field study that did identify ice algae as a cause of significant drawdown of mixed layer DIC (Shadwick et al., 2011) and reduction in  $p\text{CO}_{2\text{sw}}$  (Else et al. 2012). It is also at odds with the original “seasonal rectification” hypothesis which proposed that seasonal sea ice areas are net sinks for  $\text{CO}_2$  because of preconditioning by ice algae prior to the open water season (Yager et al., 1995). But I argue here that those observations may have been misattributed to ice algae that sloughed off into the water column, or should perhaps have been attributed to the under-ice phytoplankton bloom as well. This problem may have arisen in the Shadwick et al. (2011) study because the DIC budget they presented was calculated for monthly time intervals, which may not have been a high enough temporal resolution to differentiate between the long ice algae bloom period (~6 weeks in that region (Riedel et al., (2006)), and a rapid under ice phytoplankton bloom (**Figure 13**). The Else et al. (2012) study does actually includes a figure showing water column chlorophyll *a* increasing in early April, indicative of an under-ice phytoplankton bloom, but the authors attributed that signal (likely erroneously) to ice algae production.

One possible reason for the persistent idea that ice algae influence mixed layer DIC/ $p\text{CO}_{2\text{sw}}$  is that the role of under ice phytoplankton blooms has only come to light in recent years. Although observed at least two decades ago (Fortier et al., 2002), their importance-

particularly in the changing Arctic icescape- has only been identified recently (Mundy et al., 2009; Arrigo et al., 2012). Even more recent is the discovery that melt ponds are not the only windows that can allow enough light into the surface ocean to trigger phytoplankton blooms; small cracks and leads can have a similar effect (Assmy et al., 2017). This could explain the onset of DIC/ $p\text{CO}_{2\text{sw}}$  drawdown in the heavily fractured Amundsen Gulf region well before the melt pond season (Shadwick et al., 2011; Else et al., 2012), and the misattribution of those drawdowns to the ice algae community.

It is also possible that this misunderstanding has arisen out of the different scales those studying ice algae biochemistry work in, compared to those studying air-sea gas exchange. Within the micro-scale ice algae habitat itself (the brine channels and skeletal layer of the sea ice), nutrient depletion and  $p\text{CO}_{2\text{sw}}$  drawdown has been noted (Brown et al., 2015; Delille et al., 2007). But if these restricted structures within the sea ice are not freely exchanging water with the much larger reservoir of the mixed layer, it is not surprising that the biogeochemical impact is not observed beyond the sea ice. One could imagine a scenario in which the mixed layer exchanges freely with the bottom ice structures, leading to greater modification of the mixed layer, and there is evidence to suggest that stronger under-ice currents do enhance exchange, reducing ice algae nutrient limitation and producing higher algal biomass (Cota et al., 1987). But there may be a physical limit to this process whereby the currents become too strong, and either wash the algae off the ice, or erode the ice structures that the algae inhabit. It may therefore be the case that even if waters from the mixed layer are being cycled effectively through the bottom ice layers, biogeochemical modifications to the mixed layer will remain minimal.

The second interesting conclusion of this thesis is that  $p\text{CO}_{2\text{sw}}$  was undersaturated (with respect to the atmosphere) as the region emerged from polar night into its spring awakening.

This to some extent confirms the “seasonal rectification hypothesis” (Yager et al., 1995), as there was undersaturation of  $p\text{CO}_{2\text{sw}}$  before sea ice melt and air-sea exchange. As illustrated in Table 1, this observation seems to be widespread as well. What is noteworthy is that  $p\text{CO}_{2\text{sw}}$  is undersaturated *before* any significant biological impact on  $\text{DIC}/p\text{CO}_{2\text{sw}}$  occurs. This is in contrast with the Yager et al., (1995) hypothesis that respiration under the ice should lead to supersaturation. It is not immediately clear why this widespread undersaturation beneath the ice cover exists. One possibility, first raised by Else et al. (2012), is that fall phytoplankton blooms lower  $\text{DIC}/p\text{CO}_{2\text{sw}}$  just before the ice cover forms, which prevents replacement of  $\text{CO}_2$  by air-sea gas exchange. Rapid mixed layer cooling in the fall, and the associated thermodynamic reduction in  $p\text{CO}_{2\text{sw}}$  (Takahashi et al., 1993) may further contribute to this process. Once the ice cover has been established, and the ecosystem has entered polar night, respiration must dominate. But perhaps the cold temperatures limit respiration rates, and slow the accumulation of  $\text{DIC}$  to the point that  $p\text{CO}_{2\text{sw}}$  is still below saturation when light returns to the mixed layer. Clearly, more work and study should be put into the fall and winter time periods for inorganic carbon analysis.

The final contribution of this research is a first measurement of carbonate saturation states near Qikiqtarjuaq. While this single measurement alone cannot tell us much about the vulnerability of this site to ocean acidification, it is useful to have, especially considering the presence of the unique, and potentially vulnerable soft-shell clam fishery. The measurements were made at what is to be the expected peak for the seasonal  $\text{DIC}$  cycle, and hence the seasonal minimum for  $\text{pH}$  and carbonate saturation states. These measurements may therefore represent a useful baseline for future research. It does seem that the observed saturation states are typical for Baffin Bay, and for the North American Arctic in general. Based on projections for those regions, it is suggested that carbonate undersaturation may be a concern in this region over the

coming decades at the depths of the clam shelves, and that the health of the clam populations should be carefully monitored.

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