

Biogenic Silica Dynamics of Arctic Marine Ecosystems

by

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B. Sc. Honours, University of Victoria, 2007

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Abstract

Marine diatoms are the dominant primary producers in coastal and shelf regions, and contribute to about 20% of the annual photosynthesis on Earth. Diatoms also exert a major control on the marine silicon (Si) cycle through the formation of biogenic silica (bSiO₂). Continental shelves account for half of the total marine area in the Arctic, yet our knowledge of the cycling of Si for this critically climate-impacted region is limited. The overall objective of this thesis was to improve our understanding of marine bSiO₂ dynamics and Si cycling in marine Arctic and Subarctic ecosystems using novel techniques. Phytoplankton and nutrient observations, including dissolved and particulate silica concentrations, are presented from a period of ten years within five biological ‘hotspots’ in the Bering and Chukchi Seas. The first measurements of bSiO₂ production and dissolution rates are also presented from a period of four years at the same sites. Results from this work show that (i) although interannual variability is high, diatoms are responsible for most of the high primary productivity in the Bering and Chukchi Seas, (ii) bSiO₂ is primarily re-dissolved within the euphotic zone rather than exported, and (iii) phytoplankton phenology and marine Si cycling are affected by short-term climatic changes in this region. We also present the first measurements of bSiO₂ production rates along a transect from the Canadian Arctic Archipelago (CAA), through Baffin Bay and into the Labrador Sea. We show that diatoms are both abundant and productive throughout these regions in summer, despite widespread Si limitation in the low-nutrient surface waters. Finally, we also investigated the natural variations in the Si isotopic composition of silicic acid ($\delta^{30}\text{Si}(\text{OH})_4$). On a transect through the Bering and Chukchi Seas, Canada Basin and CAA, and finally to Baffin Bay and the Labrador Sea, we found that $\delta^{30}\text{Si}(\text{OH})_4$ signals reflect water mass composition, the dissolution of bSiO₂ throughout the water column, and the biological utilization of Si in surface waters. Ultimately, this work provides insight into the processes controlling marine Si cycling within the Arctic and its links to the global marine Si cycle and other biogeochemical cycles.

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Dedication

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General Introduction

Understanding the marine biogeochemical cycling of elements such as carbon (C), nitrogen (N), and silicon (Si) requires a clear knowledge of the underlying processes that control their distributions. In the face of ongoing climate and other anthropogenic-induced environmental changes (e.g. Stocker et al., 2013), research has primarily focused on the cycles of C and N (e.g. Vitousek et al. 1997; Falkowski et al. 2000), leaving our understanding of marine Si cycling comparatively limited. The largest consumers of dissolved Si (dSi^1 ; in the form of $\text{Si}(\text{OH})_4$) in the oceans are the diatoms (Figure 1). Diatoms are a ubiquitous group of microscopic algae with siliceous cell walls (frustules). These organisms account for almost half of the global annual marine biological C fixation (Nelson et al., 1995; Smetacek, 1999) and generate, through the photosynthetic process, a strong coupling between the marine cycles of Si, C and N (e.g. Brzezinski et al. 2003; Marchetti et al. 2010). Ballasted by their heavy silica frustules, diatoms also make up a significant portion of the biological export of carbon from the surface to the deep ocean (Buesseler, 1998). Despite the importance of these organisms to the C, N and especially Si cycles, studies aimed at quantifying the processes that control the marine biogeochemistry of Si and generating Si budgets for the world ocean only began in the latter half of the twentieth century (e.g. Nelson et al., 1995; Ragueneau et al., 2000) and there still remain large uncertainties in many of these estimates (Tréguer and De La Rocha, 2013). In order to better understand ecosystem-



Figure 1. False colour image of a chain-forming marine diatom of the genus *Chaetoceros* at 100x magnification. Collected from Saanich Inlet (March 2014). Original micrograph courtesy of J. Long.

¹ dSi in seawater consists of ~95% $\text{Si}(\text{OH})_4$ and ~5% $\text{SiO}(\text{OH})_3^-$, the dissociated anion of $\text{Si}(\text{OH})_4$

level responses to climate-induced oceanic changes, it is critical to evaluate the role of diatoms in the marine cycling of Si, the coupling between the Si, C and N cycles, and the processes which link them. This is especially critical in the high-latitude oceans where changes in marine ecosystem from climate variability have already been documented (e.g. Li et al., 2009; Grebmeier, 2012; Ardyna et al., 2014; Blais et al., 2017).

1. The World Ocean Silica Cycle

Si in the oceans is found either in the solid phase as particulate silica (SiO_2), or in solution as Si(OH)_4 . Particulate SiO_2 is composed of biogenic (bSiO_2) and lithogenic (lSiO_2) forms, with bSiO_2 being far more soluble than lSiO_2 (Loucaides *et al.*, 2008). Rivers transport both Si(OH)_4 and particulate SiO_2 to the ocean (Figure 2), and constitute ~78% of the total input of Si to the oceans (Tréguer and De La Rocha, 2013). Submarine groundwater discharge, seafloor weathering, aeolian, and hydrothermal processes contribute the remaining 22% of the total marine Si input. The major Si sink in the ocean is the burial of bSiO_2 exported from surface waters, with a smaller, but significant contribution by SiO_2 -secreting sponge reefs on continental shelves (Tréguer and De La Rocha, 2013). Other minor Si sinks are the abiotic precipitation of lSiO_2 in hydrothermal vent plumes and authigenic lSiO_2 formation in sediments.

The main biogeochemical fluxes internally cycling Si within the oceans are the production, dissolution and export of bSiO_2 and vertical mixing of Si(OH)_4 -rich deep waters (Figure 2). In surface waters, the production of bSiO_2 is mainly attributed to diatoms. Diatoms take up Si(OH)_4 and convert it to bSiO_2 , which is comprised of amorphous SiO_2 ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). The bSiO_2 produced by diatoms forms their siliceous cell walls, known as ‘frustules’. Other siliceous plankton found in marine waters (e.g.

radiolarians and silicoflagellates) also produce bSiO_2 , but are believed to contribute significantly less to bSiO_2 production than diatoms (Tréguer and De La Rocha, 2013). The dissolution of bSiO_2 takes place throughout the water column, but has been found to primarily occur in surface waters and at the sediment/water interface (Tréguer and De La Rocha, 2013).

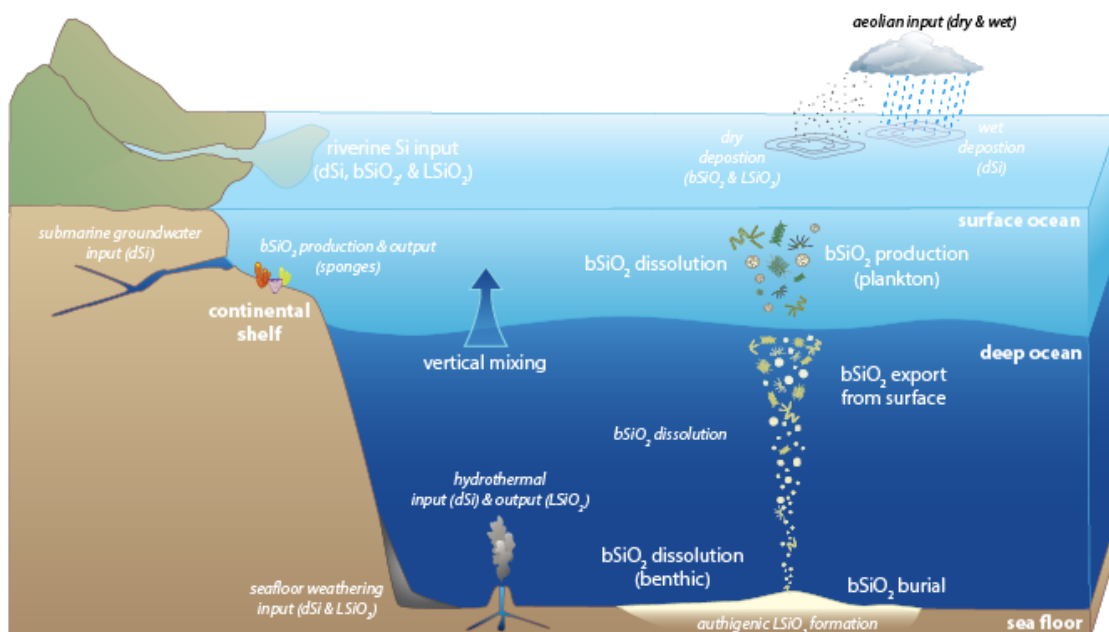


Figure 2. Diagram of the inputs, sinks and fluxes in world ocean silica cycle. Major fluxes are in regular font, and minor fluxes are in italics. dSi = dissolved Si (primarily $\text{Si}(\text{OH})_4$), bSiO_2 = biogenic silica, LSiO_2 = lithogenic silica.

2. Measuring bSiO_2 Production and Dissolution

Few field studies have investigated marine bSiO_2 production rates and even fewer have measured rates of bSiO_2 production and dissolution in conjunction. Conventional methods for measuring bSiO_2 production are either highly labour intensive and involve the use of stable isotopes (e.g. ^{30}Si , Nelson and Goering, 1977), or require the use of relatively large amounts of ^{32}Si (^{32}Si , Brzezinski and Philips, 1997), an expensive radioisotope ($\sim \$1,200/\mu\text{Ci}$). The recent development of a new, more sensitive method to measure bSiO_2 production with ^{32}Si (Krause et al., 2011) has eliminated some of these

complications. With either of these methods, bSiO₂ production is determined by measuring the enrichment of either ³⁰Si or ³²Si in bSiO₂ in the incubated sample.

One method to obtain both bSiO₂ production and dissolution rates from a single sample is also based on ³⁰Si tracer incubations. With this method, bSiO₂ production is determined as described above (i.e., measuring the enrichment of ³⁰Si in bSiO₂), and dissolution by measuring the increase in ²⁸Si of Si(OH)₄ in the incubated sample; however, in spite of recent analytical improvements (Fripiat et al., 2009), this method remains laborious and time consuming. Another, relatively simple, method can estimate the combined bSiO₂ production and dissolution rate (i.e. the ‘net’ production rate of bSiO₂, ΔbSiO₂) by measuring the change in the concentration of bSiO₂. Combining measurements of ΔbSiO₂ and ³²Si-based bSiO₂ production provides an efficient and simple measure of bSiO₂ production and dissolution rates in the water column (e.g. Demarest et al., 2011).

3. Marine bSiO₂ Cycling in the Arctic

While the Arctic is a region historically dominated by diatoms (Gradinger and Baumann, 1991; Booth et al., 1997; Brugel et al., 2009; Wyatt et al., 2013; Crawford et al., 2018), our knowledge of the marine cycling of bSiO₂ in this region is limited. The contribution of the Arctic to the world ocean Si cycle is unknown, though potentially significant, especially considering that the Arctic serves as significant source of North Atlantic Deep Water (Rudels et al., 2000). In addition, while Davis Strait serves as the most important export gateway of nutrients from the Arctic, the most important input of Si to the Arctic is from the nutrient-rich Pacific-origin waters flowing through the Bering Strait (Torres-Valdés et al., 2013). These high-Si Pacific-origin waters are found primarily in the Subarctic and Arctic waters surrounding North America (e.g. Jones et al.,

2003); however, despite the probable importance of these waters to marine Si cycling in the Arctic, only three studies have quantified bSiO₂ production within their flow-path (Fig. 3).

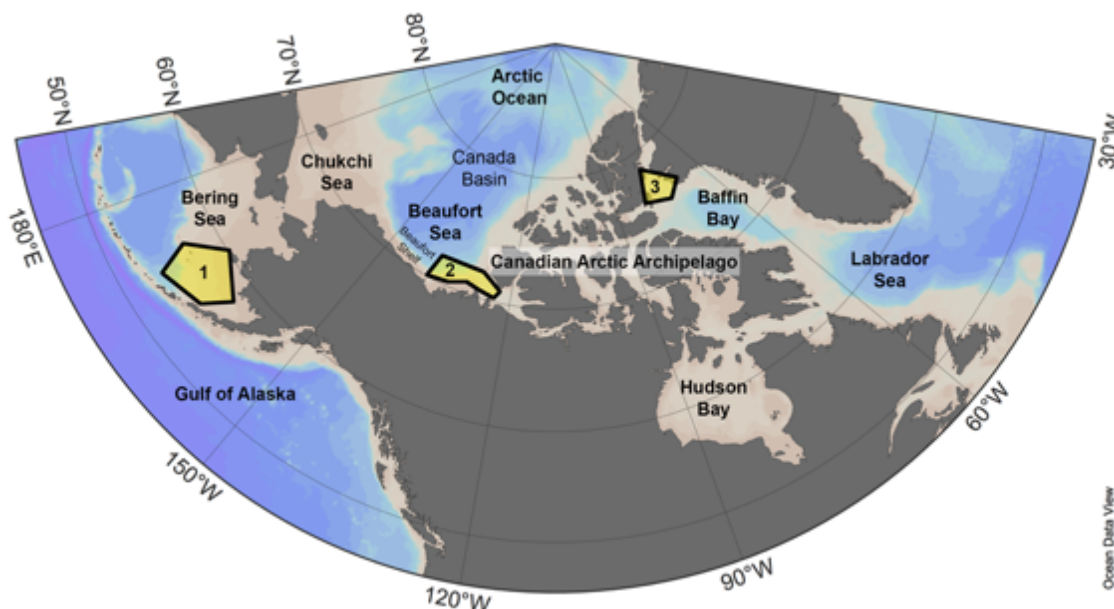


Figure 3. Map of the Subarctic and Arctic waters surrounding North America. The three locations of previous studies estimating bSiO₂ production are highlighted in yellow: 1 – Southeastern Bering Sea (Banahan and Goering, 1986); 2 – Beaufort Shelf (Sampei et al., 2010); 3 – North Water Polynya (Tremblay et al., 2002).

For the southeastern Bering Sea, Banahan and Goering (1986) present the only direct measurements of bSiO₂ production using ³⁰Si tracer incubations. On the Beaufort Shelf, Sampei et al. (2010) estimated bSiO₂ production from an array of sediment traps deployed over an eleven-month period. For the North Water polynya, Tremblay et al. (2002) estimated summertime (May – July) bSiO₂ production from changes in the Si(OH)₄ inventories over a three-month period. There have been no studies with concurrent measurements of bSiO₂ production and dissolution in Arctic waters.

Climate-induced changes may significantly affect the marine cycling of Si in the Arctic. Recent studies have shown shifts in phytoplankton assemblage composition in response to such changes, although whether these changes resulted in an increased or

decreased contribution of diatoms to the phytoplankton assemblage was variable (Li et al., 2009; Blais et al., 2017). In addition, shifts in phytoplankton phenology have also been observed, including an increase in the occurrence of fall blooms being driven by the recent losses in Arctic Ocean sea-ice (Ardyna et al., 2014). These observed changes in phytoplankton assemblage composition and phenology could have far reaching effects on the marine cycling of Si in the Arctic and the world ocean.

4. Climate Change and Phytoplankton Dynamics in the Arctic

The Arctic Ocean is an extremely heterogeneous system with respect to primary productivity (e.g. Gosselin et al., 1997) and it is a region in rapid transition due to climate change. The Arctic has traditionally been thought to be the least productive of all the oceans due to the presence of permanent ice cover over the deep basins, short growing season, and the strong water column stratification that limits nutrient supply from deep waters; however, studies have shown that the annual primary production of the Arctic is much higher than previously estimated (e.g. Sakshaug, 2004; Matrai et al., 2013). The most productive regions of the Arctic are its shelf seas, which account for approximately half of the total area of the Arctic and more than 80% of the total primary production north of 65°N (Sakshaug, 2004). Increased air and sea-surface temperatures in the Arctic (Loeng et al., 2005; Trenberth et al., 2007) have accelerated the loss of multi-year sea-ice (Stroeve et al., 2011) and increased freshwater runoff (Holmes et al., 2012). This in turn has led to changes not only in surface salinity, nutrient concentrations, and stratification, but also in the minimum summer ice extent and length of the phytoplankton-growing season. While the timing of primary production on Arctic shelves is controlled by light availability, primary productivity in these regions is ultimately limited by nutrient supply (Carmack et al., 2006), and both factors are undergoing rapid changes due to shifts in

climate forcing (e.g. Stroeve et al., 2011; Holmes et al., 2012). The anticipated response of Arctic marine ecosystems to climate-induced changes is expected to be complex (Michel et al., 2012), though some changes, such as northward shifts in biodiversity (e.g. Nelson et al., 2009; Grebmeier, 2012) and shifts in phytoplankton assemblage composition and phenology (e.g. Li et al., 2009, Ardyna et al., 2014; Blais et al., 2017; Oziel et al., 2017), are already being observed.

Biological processes such as diatom growth, food web interactions and organic matter export act as links between the marine cycles of Si, C and N. The role of diatoms in organic matter production and export can be estimated by evaluating the contribution of these organisms to primary production and NO_3^- uptake. Changes in environmental (i.e. nutrient and light availability) and biological (i.e. community composition and trophic interactions) forcing may significantly affect the diatom contribution to productivity and carbon export. The warming temperatures, decreasing sea-ice extent and changes in riverine inputs in the Arctic mean that nutrient and light availability are climatically sensitive in this region, as it is climate-induced changes that are driving these trends. The Arctic is a heterogeneous system (Carmack and Wassmann, 2006) where spatial differences in these environmental and biological factors result in large regional variations in primary productivity and phytoplankton assemblage composition (e.g. Booth et al., 1997; Sakshaug, 2004; Varela et al., 2013; Crawford et al., 2018). These variations would affect the contribution of diatoms to productivity and carbon export, though no studies have made concurrent measurements of these processes in the Arctic. Doing so would afford a better understanding of the processes that link the marine cycles of Si, C and N in high-latitude ecosystems.

5. Kinetics of Nutrient Acquisition and Growth in Phytoplankton

One method for investigating how changing nutrient supply affects primary productivity is through field-based nutrient kinetic experiments (e.g. Nelson et al., 2001), which can be used to assess and predict nutrient limitation of phytoplankton communities. Phytoplankton growth requires nutrients such as N and, in the case of diatoms, Si. The transfer of nutrients from the adjacent medium into the cell is biologically mediated and occurs principally through membrane-bound specific transport systems. Nutrient transport across the cell membrane follows Michaelis-Menten enzyme kinetics (Dugdale, 1967), where transport is saturable and the specific rate of nutrient uptake (V) into a cell is dependent on the ambient nutrient concentration ($[\text{nutrient}]$). This relationship is described by:

$$V = \frac{V_{\max} \cdot [\text{nutrient}]}{K_S + [\text{nutrient}]} \quad (1)$$

where $V_{\max}$ represents the maximum uptake rate, or saturable limit of nutrient acquisition when the given nutrient is not limiting, and K_S the half-saturation constant, or the $[\text{nutrient}]$ at which V is equal to $V_{\max}/2$. For Si, diatoms typically reach $V_{\max}$ when the $[\text{Si(OH)}_4]$ is above $0.2 - 8 \mu\text{mol L}^{-1}$, though this depends on the diatom species (Martin-Jézéquel et al., 2000). Measuring the kinetic parameters of nutrient uptake (i.e. $V_{\max}$ and K_S) in the field is a method used for evaluating nutrient limitation in the oceans (e.g. Nelson et al., 2001) and these values can be important component of biogeochemical models (e.g. Moore et al., 2004).

Specific growth rate (μ) also responds to the ambient nutrient concentration, and can be described by a similar equation as shown above, but with V replaced with μ , $V_{\max}$ with $\mu_{\max}$ (the maximum specific growth rate) and K_S with K_{μ} (the $[\text{nutrient}]$ where $\mu =$

$\mu_{\max}/2$). At steady state, these equations are equivalent (i.e. $V = \mu$); however, studies have shown that K_{μ} is often much smaller than K_S , which is a result of acclimation strategies of the organisms. In other words, ambient nutrient concentrations can limit uptake without limiting growth. When uptake is limited, phytoplankton can avoid growth limitation by changing both their internal nutrient quotas and their maximum short-term nutrient uptake rates in response to variability in ambient nutrient concentrations (Morel, 1987). For example, when Si uptake is limiting for diatoms, cells produce less silicified frustules (Harrison et al., 1977; Martin-Jézéquel et al., 2000) and diatom physiological models indicate that diatoms under Si stress may also increase their cellular C quotas, both of which would result in decreased Si:C ratios (Flynn and Martin-Jézéquel, 2000). Given that there is little variation in Si:C ratios among different diatom species (mean of 0.11 ± 0.04 for 47 diatom species; Sarthou et al., 2005), environmentally-driven changes in the Si:C ratio may affect the export efficiency of diatom cells which account for a disproportionate amount of the biological export of carbon (Buesseler, 1998).

Despite regional variations in primary productivity, most of the Arctic is believed to be limited by the availability of NO_3^- (e.g. Tremblay and Gagnon, 2009), though for diatoms, limited availability of Si(OH)_4 may also affect growth (Popova et al., 2012). Both Si and N are required in essentially equimolar amounts in diatoms (Brzezinski et al., 1985), and Si(OH)_4 and NO_3^- are also often found at similar concentrations in seawater because of this. This suggests that co-limitation of diatom growth may occur; however, the effects of these changes may differ significantly, as Si metabolism in diatoms is very different from N metabolism. Si metabolism is closely tied to the regulation of cell growth and division (Martin-Jézéquel et al., 2000), whereas N metabolism is closely

coupled to C metabolism (Mulholland and Lomas, 2008). In addition, the silicification process itself is not energetically expensive (Martin-Jézéquel et al., 2000), while N metabolism relies on C metabolism to provide the significant amount of energy required during NO_3^- assimilation (Mulholland and Lomas, 2008). Si limitation decreases silicification (e.g. Harrison et al., 1977), but likely increases the amount of C in the cell (Flynn and Martin-Jézéquel, 2000). N limitation affects both C and N metabolisms and decreases the cellular N quota, but has little effect on the cellular C or Si quotas (Flynn and Martin-Jézéquel, 2000). Thus, nutrient limitation can have significant, but very different effects on the coupling between the Si, C and N cycles in the oceans. While there have been a number of studies of Si limitation in the world's oceans (e.g. Nelson et al., 2001; Brzezinski et al., 2008; Krause et al., 2012), there has only been one study of Si limitation of diatoms in the Arctic (Krause et al., 2018).

6. Natural Variations in Stable Si Isotopes

During Si uptake, diatoms discriminate against heavier Si isotopes (De La Rocha et al., 1997), leading to variations in the natural abundance of the stable Si isotopes (^{28}Si , ^{29}Si and ^{30}Si) in both bSiO_2 and Si(OH)_4 . Consequently, seawater variations in the Si isotopic composition of bSiO_2 and Si(OH)_4 can be used to investigate marine Si dynamics over broad spatio-temporal scales (e.g. Varela et al., 2004, 2016; Beucher et al., 2008; Pichevin et al., 2009). Si isotope values are commonly expressed relative to the NBS28 quartz sand reference material using delta notation ($\delta^{30}\text{Si}$ in ‰):

$$\delta^{30}\text{Si} = \left(\frac{\left(\frac{{}^{30}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{{}^{30}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{NBS28}}} - 1 \right) \times 1,000 \quad (2)$$

The seawater $\delta^{30}\text{Si}(\text{OH})_4$ in the modern ocean has been used to determine annual marine Si utilization and supply (Fripiat et al., 2011), to estimate the degree of Si isotope discrimination by siliceous organisms (the biological fractionation factor, ϵ) from field data (e.g. Varela et al., 2004; Beucher et al., 2008), and to identify water masses (e.g. de Souza et al., 2012). The $\delta^{30}\text{Si}$ signal in sedimentary $\delta^{30}\text{Si}\text{-bSiO}_2$ has been used to estimate potential C export and nutrient utilization over geological timescales (De La Rocha et al., 1998). One of the main drawbacks in the analysis of Si isotope ratios was the requirement of an extremely hazardous fluorinating gas prior to analysis on an isotope-ratio mass spectrometer (IRMS) (De La Rocha et al., 1996). Recently, safer methods have been developed that no longer require this hazardous step (De La Rocha, 2002; Brzezinski et al., 2006; Georg et al., 2006). These methods use either an IRMS (Brzezinski et al., 2006) or a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; De La Rocha, 2002; Georg et al., 2006) to measure the Si isotope ratios.

The Arctic Ocean is strongly linked to the bordering Subarctic Atlantic and Pacific Oceans, the end members of the global thermohaline circulation (Carmack and McLaughlin, 2011). Pacific inflow waters, having already travelled through the highly productive Bering Sea, enter the Arctic through the Bering Strait, crossing the highly productive Chukchi Sea and splitting to either flow farther northward into the oligotrophic Arctic Ocean (and outflow into the North Atlantic through Fram Strait), or flow into the productive Canadian Arctic shelf regions (Beaufort Shelf, Canadian Arctic Archipelago and Hudson Bay) before finally entering the Labrador Sea, another gateway to the North Atlantic and an area of deep-water formation (Figure 1). The productive shelf regions of the Arctic are diatom dominated (e.g. Gosselin et al., 1997; Wyatt et al., 2013), meaning

bSiO₂ production and dissolution may lead to significant variations in $\delta^{30}\text{Si}$ within the Arctic Ocean and its marginal seas. Varela et al. (2016) was the first study to measure natural variations in $\delta^{30}\text{Si}$ in the Arctic along a transect from the Mackenzie River delta out to the deep Canada Basin. They found that the deep water of the Canada Basin has the heaviest (i.e. largest) ever measured $\delta^{30}\text{Si}(\text{OH})_4$ value of all marine deep waters, a result of the amplification of $\delta^{30}\text{Si}(\text{OH})_4$ in the already heavy Atlantic-origin intermediate waters by the biological pump and restricted exchange of the deep waters of the Canada Basin. They also found evidence that the $\delta^{30}\text{Si}(\text{OH})_4$ signal of the Pacific-origin water mass were significantly altered based on comparison with waters of a similar $[\text{Si}(\text{OH})_4]$ sampled at the nearest station (50°N, 167°W; Reynolds et al., 2006) in the Pacific. No data currently exist for the Pacific inflow waters at Bering Strait to confirm this.

7. Research Objectives and Motivation

The primary goal of this thesis was to improve our understanding of Si cycling in marine Arctic and Subarctic ecosystems by using novel techniques to investigate marine bSiO₂ cycling and the coupling between the marine cycles of Si, C and N over broad spatial and temporal scales. Five specific questions were addressed by this research:

1. What is the contribution of diatoms to marine primary production and NO_3^- uptake in the Arctic?
2. What is the contribution of diatoms to the phytoplankton assemblages?
3. What spatial and temporal variations exist in the bSiO₂ dynamics of Arctic surface waters?
4. To what extent are diatoms limited by the availability of Si in the Arctic?

5. How do $\delta^{30}\text{Si}(\text{OH})_4$ signals change across Arctic ecosystem regimes and how do these variations relate to Si utilization and supply?

To answer these questions, summertime field studies within Subarctic and Arctic waters surrounding North America were conducted over a period of several years, resulting in an unprecedented broad-scale and methodologically consistent dataset of phytoplankton productivity and bSiO_2 dynamics. To summarize these findings, this thesis comprises of five chapters, general conclusions and five appendices.

Chapter 1 examines ten years of phytoplankton biomass, productivity and assemblage composition from July cruises in the Bering and Chukchi Seas, with the primary goal of addressing questions (1) and (2). This work was conducted under the auspices of the DBO with Jackie Grebmeier as the lead PI. Jozef Wiktor analyzed the phytoplankton assemblage samples.

Chapter 2 addresses questions (1) and (3), presenting four years of bSiO_2 production measurements and the diatom contribution to primary productivity and NO_3^- uptake, also from July cruises in the Bering and Chukchi Seas.

Chapter 3 builds upon the dataset presented in Chapter 2 and aims at further answering question (3), summarizing four years of net bSiO_2 production and bSiO_2 dissolution rate measurements in the Bering and Chukchi Seas.

Chapter 4 also addresses questions (1) and (3), although for a different region of the Arctic compared to Chapter 2. In this chapter, measurements of bSiO_2 production and the diatom contribution to primary productivity and NO_3^- uptake collected in July and August 2015 are presented for the Labrador Sea, Baffin Bay and the Canadian Arctic

Archipelago. In addition, this chapter also aims to answer question (4), presenting a series of field-based Si limitation experiments.

To answer question (5), Chapter 5 explores the natural variations in $\delta^{30}\text{Si}(\text{OH})_4$ in Arctic marine waters surrounding northern North America, summarizing a dataset collected on three cruises conducted from July-September 2015 from the Bering to the Labrador Sea.

Finally, the general conclusions from all chapters are presented after Chapter 5.

Additional data is included in the series of five appendices found after the bibliography. These appendices further address questions (1) through (5):

Appendix A also addresses question (4), presenting four years of Si limitation experiments in the Pacific Arctic Region.

Appendix B aims to further answer questions (1) and (2), with measurements of phytoplankton biomass and productivity from the Eastern Canadian Arctic, at the same stations outlined in Chapter 4.

Appendix C details a comparison between storage methods for samples collected for $\text{Si}(\text{OH})_4$ analysis.

Appendix D includes measurements of bSiO_2 dissolution from the same stations sampled for Chapter 4 in Eastern Canadian Arctic, addressing question (3)

Appendix E details an alternative method to calculate the ^{30}Si fractionation factor using data from the Beaufort Sea to Baffin Bay, elaborating on aspects of question (5).

Chapter 1
**A decade of summertime measurements of phytoplankton
biomass, productivity and assemblage composition in the
Pacific Arctic Region from 2006 – 2016**

Citation:

Giesbrecht, K.E., D.E. Varela, J. Wiktor, J.M. Grebmeier, B. Kelly and J.E. Long. (2018)

A decade of summertime measurements of phytoplankton biomass, productivity and
assemblage composition in the Pacific Arctic Region from 2006 – 2016. *Deep-Sea*

Research II. doi: 10.1016/j.dsr2.2018.06.010

1.1 Abstract

We present phytoplankton and nutrient observations from a period of ten years within five biological ‘hotspots’ in the Bering and Chukchi Seas, as identified by the Distributed Biological Observatory (DBO). Nitrate (NO_3^-) and total and size-fractionated ($<$ and $>5 \mu\text{m}$) chlorophyll *a* (Chl *a*) concentrations, and rates of carbon (ρC , ‘primary productivity’) and NO_3^- utilization (ρNO_3) were measured throughout the euphotic zone during eight cruises in July 2006, 2008 and yearly from 2011 to 2016. Samples were collected at one station within each of these five hotspots, which were located south of St. Lawrence Island (DBO1), south of the Bering Strait in the Chirikov Basin (DBO2), in the southeastern (DBO3) and northeastern (DBO4) Chukchi Sea, and in Barrow Canyon (DBO5). Nitrate concentrations averaged over the 10 years increased with depth and euphotic-zone integrated values were highest in the Chirikov Basin. Subsurface maxima in Chl *a* were present at about 30 m depth at most locations, although the maximum ρC and ρNO_3 rates were shallower, within the top 10 m of the water column. The f-ratio (calculated as $\rho\text{NO}_3/\rho\text{C}$) averaged for all DBO regions and for the 10-year study period was 0.41 (± 0.24). Similarly, phytoplankton $>5 \mu\text{m}$ in size accounted for 65 (± 23) % of total Chl *a* for all regions over the 10 years. Taxonomic analysis done in 2013 showed that diatoms were the dominant taxa throughout all of the DBO regions, with the exception of areas influenced by low-nutrient waters on the eastern side of the Chukchi shelf near the Alaska coast. These coastal waters were dominated by coccolithophores and small ($< 7 \mu\text{m}$) flagellates, and had much lower Chl *a* concentrations, ρC and ρNO_3 than farther west. In addition, the proportion of pennate diatoms to total diatom abundance was found to be elevated relative to centric diatoms when sea-ice was present. Our measurements of phytoplankton biomass and ρC indicated that the higher abundance

of pennate diatoms in the euphotic zone was the result of phytoplankton blooms happening below the ice, rather than pennate diatoms being supplied by a sea-ice diatom bloom. The dynamic nature of the Pacific Arctic Region (PAR) resulted in strong interannual variability within each DBO region for all parameters, with no clear increasing or decreasing trends from 2006 to 2016. Spatial variations were more consistent, with the highest rates of ρC and ρNO_3 occurring in the nutrient-rich waters of the southeastern Chukchi Sea (away from shore), and decreasing in regions further north where NO_3^- concentrations were lower. An east-west gradient in phytoplankton biomass and productivity was also observed in the southeastern Chukchi Sea, which can be attributed to differences in the nutrient content of the water masses along the gradient. This study shows that the observed strong interannual variability in phytoplankton biomass and productivity cannot be attributed to differences in methodology or sampling time. It also highlights the need for better temporal and spatial sampling resolution such that the long-term effects of climate-induced changes can be identified against the backdrop of the naturally-strong interannual variability in the PAR.

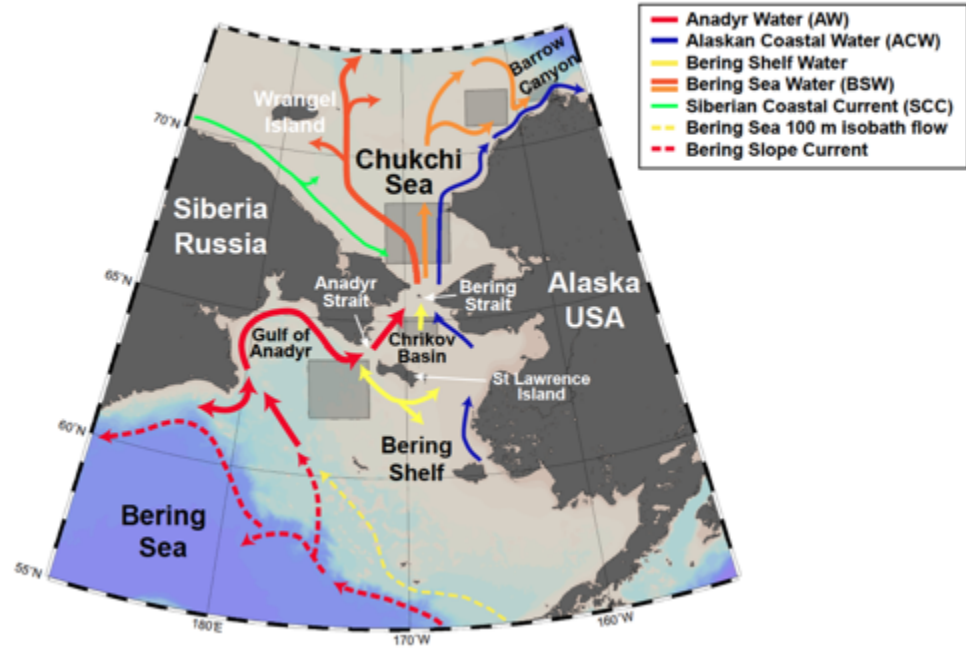
1.2 Introduction

The Pacific Arctic Region (PAR) extends from the northern Bering Sea, through the Chukchi Sea, and into the western Beaufort Sea, and contains some of the most productive waters in the world's oceans (Springer and McRoy, 1993). Biological and physical processes in this region are strongly influenced by the northward advection of Pacific waters that supply nutrients, heat and freshwater to the PAR and subsequently to the Arctic Ocean (Grebmeier et al., 2006a; Serreze et al., 2006; Woodgate et al., 2010). In addition, climate-induced changes such as declining seasonal sea-ice extent and earlier sea-ice retreat (e.g. Frey et al., 2014; 2015; Stroeve et al., 2014) are affecting the

biological state in this region, driving rapid shifts in ecosystem structure and function (e.g. Grebmeier et al., 2012; Nelson et al. 2014).

The flow of Pacific waters from the northern Bering Sea into the Chukchi Sea is primarily driven by a sea-level gradient towards the Chukchi Sea (Coachman and Aagaard, 1966; Stigebrandt, 1984; Woodgate et al., 2005a), with seasonal variability in the strength of the transport as a result of wind-driven forcing. Prevailing winds in this region are opposite to the pressure-driven flow such that the mean northward transport through the Bering Strait is at a maximum in the summer when winds are weaker, and at a minimum in the winter when winds are stronger (Woodgate et al., 2005b, Danielson et al., 2014; Woodgate, 2018). Waters flowing from the northern Bering Sea into the Bering Strait are made up of three major water masses (Figure 1.1a) differentiated primarily by their temperature, salinity and nutrient characteristics: cold, saline, and nutrient-rich Anadyr Water (AW) on the western side; warm, less saline, and nutrient-poor Alaskan Coastal Water (ACW) on the eastern side; and Bering Shelf Water of intermediate characteristics in the middle (Coachman et al., 1975; Walsh et al., 1989). As these waters flow through the Bering Strait, Bering Shelf Water and AW merge into a water mass known as Bering Sea Water (BSW). The southwestern region of the Chukchi Sea is also influenced by nutrient-poor waters from the south-flowing Siberian Coastal Current (SCC), although their contribution to the overall water mass mixture in the Chukchi Sea is small (Weingartner et al., 1999). More than ~80% of the water flowing into the Chukchi Sea through the Bering Strait is composed of nutrient-rich BSW (Coachman et al., 1975), which, in combination with the shallow bathymetry of the Chukchi shelf, support the high productivity observed in the Chukchi region.

a



b

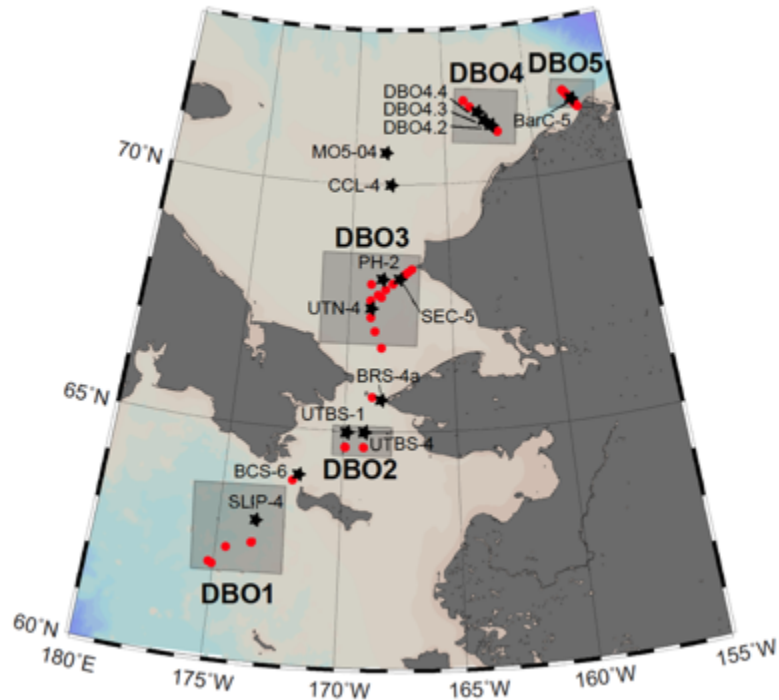


Figure 1.1. (a) Map of the Pacific Arctic Region (PAR) with major geographical features, water mass flow patterns, and DBO region bounding boxes in grey. Adapted from Grebmeier et al. (2015) with updated flow patterns for the Bering Slope Current and Bering Sea 100 m isobath flow from Stabeno et al. (2016). (b) DBO CTD/rosette station locations (red circles) and bounding boxes for each DBO region. Stations where phytoplankton productivity experiments were conducted are marked with a black star.

Quantifying the autotrophic drawdown of nutrients, primary productivity and export of organic matter in the PAR is crucial for understanding the status and health of the local marine ecosystems and of other areas of the Arctic influenced by these waters (Carmack and Wassmann, 2006; Yamamoto-Kawai et al., 2006). Measurements of phytoplankton biomass (as chlorophyll *a*, Chl *a*) and pelagic primary productivity (as utilization rates of ^{13}C or ^{14}C) are standard methods used to assess the biological state of autotrophic organisms in marine environments. However, a broader picture of the ecology of the region can be provided by additional measurements of NO_3^- utilization rates using ^{15}N -labelled NO_3^- , used as an index of new production into a system, and by the assessment of the taxonomic composition of the phytoplankton assemblages. New production is defined as the autotrophic utilization rate of ‘new’ N sources (primarily NO_3^-) to the euphotic zone, which, on an annual basis and at steady state, can be considered equivalent to net community production, or the total amount of C available for export. Measurements of NO_3^- and C utilization rates can also be used to estimate the f-ratio, an index of the proportion of total primary production available for export (Eppley and Peterson, 1979). In addition to evaluating the status of autotrophic organisms, these measurements are powerful tools for assessing the cascading effects that changes at the bottom of marine food webs might have on higher trophic levels.

The high productivity on the continental shelves of the northern Bering and Chukchi Seas (e.g. Sakshaug, 2004; Varela et al., 2013) supports a diverse ecosystem with strong benthic-pelagic coupling (e.g. Grebmeier and McRoy, 1989; Grebmeier et al., 2006a). Measurements of daily C utilization rates on these shelves include some of the highest values ever documented in the ocean ($12 \text{ g C m}^{-2} \text{ d}^{-1}$ from McRoy et al., 1987), and

annual estimates range from 100 – 720 g C m⁻² yr⁻¹ (Sakshaug et al., 2004; Brown et al., 2011; Varela et al., 2013; Hill et al., 2017). Nitrate utilization rates and phytoplankton biomass in these regions are twice as high as in the Beaufort Sea and Canadian Arctic Archipelago, (Varela et al., 2013), and phytoplankton assemblages are generally dominated by diatoms (e.g. Wyatt et al., 2013; Crawford et al., 2018). Shallow water-columns and low zooplankton grazing pressures (e.g. Campbell et al., 2009; Sherr et al. 2009, 2013; Mathis et al., 2014) tightly couple pelagic primary production to the benthos (Grebmeier et al., 2006a), with these productive waters sustaining some of the highest benthic faunal biomass in the world's oceans (Grebmeier and McRoy, 1989; Highsmith and Coyle, 1990; Grebmeier et al., 2015). As a result, the PAR is both ecologically and economically important, supporting a large and diverse populations of fishes, seabirds and marine mammals (e.g. Grebmeier et al., 2006a). It is also one of the fastest changing marine environments, with significant shifts in upper trophic levels in recent decades (e.g. Overland and Stabeno, 2004; Moore et al., 2014, 2016; Divoky et al., 2015).

Due to dramatic climate-induced environmental changes in the PAR (e.g. Stabeno et al., 2007; Woodgate et al., 2012; Jefferies et al., 2013; Wood et al., 2015), there is growing consensus that the Arctic is changing at a rate faster than any marine ecosystem can naturally adapt (Wassmann et al., 2010), and it is therefore reaching a 'tipping' point (Duarte et al., 2012). Some of the most significant changes in the PAR are decreasing sea-ice extent, earlier melting of the seasonal ice pack, and a shift from multi-year ice to thinner, first-year ice (e.g. Jefferies et al., 2013; Stroeve et al., 2014; Frey et al., 2014; 2015); however, these changes are not uniform across the PAR. The Chukchi Sea has experienced some of the fastest declines in sea-ice cover in the Arctic due to significant

year-round warming (e.g. Cavalieri and Parkinson, 2012), whereas changes in the northern Bering Sea have resulted in more complex, multi-year variability in sea-ice cover (Frey et al., 2015). Regardless, these changes can have a major impact on both the timing and magnitude of primary productivity with potential cascading effects on higher trophic levels. However, due to the naturally-high spatial, seasonal, and interannual variability in the PAR, the extent to which these changes can be attributed to bottom-up pressures of climate change is still unclear (Grebmeier et al., 2010).

The Distributed Biological Observatory (DBO) (<http://pmel.noaa.gov/dbo>) was established in 2010 to assess the effects of climate change on the physical and biological state of the PAR (Grebmeier et al., 2010; Moore and Grebmeier, 2018). Sampling for the DBO occurs along a series of five transects that are centered on ‘biological hotspots’, identified by previous studies as locations of elevated productivity, biodiversity and rates of biological change (Figure 1.1b). These five hotspots are located within the influence of the St. Lawrence Island Polynya (DBO1), in the Chirikov Basin between St. Lawrence Island and the Bering Strait (DBO2), in the southeastern (DBO3) and northeastern (DBO4) Chukchi Sea, and in Barrow Canyon (DBO5). Transects have been re-occupied both seasonally and annually by a number of participating international collaborators under the umbrella of DBO since 2010 and other programs prior to 2010 to help elucidate seasonal and interannual variability in the PAR.

Here, we present measurements of NO_3^- concentrations, and phytoplankton biomass, productivity and assemblage composition collected using consistent methodologies within the five DBO regions that span the period from 2006 to 2016. The main objectives of this study were to: (1) quantify a baseline of these measurements for current and future

studies, (2) investigate the extent of the spatial and interannual variability between and, whenever possible, within each DBO region, and (3) elucidate potential environmental controls on this variability to better predict how phytoplankton dynamics might vary under current and predicted climate changes.

1.3 Methods

1.3.1 Sampling Locations

Seawater samples were collected on eight oceanographic cruises onboard the *CCGS Sir Wilfrid Laurier* in July of 2006, 2008 and yearly from 2011 to 2016. Data from stations occupied in 2006 and 2008 are included when these stations were located within (or near) the identified DBO hotspot regions. The cruise conducted in 2006 was part of the Bering Strait Environmental Observatory program, while the cruise in 2008 was part of the International Polar Year Canada's Three Oceans (IPY-C3O) program. The 2008 data presented here represents a subset of the data already published in Varela et al. (2013) (nutrients and productivity) and Wyatt et al. (2013) (size fractionated Chl *a*). We include the 2008 data in this paper to provide a historical context to our data from 2006 and to our DBO dataset from 2011 onwards. A maximum of 54 CTD/rosette stations distributed along 5 transects were occupied on each cruise for water column and sediment studies (red circles in Figure 1.1b; Table 1.1), but primary productivity experiments were only conducted at 1-2 'primary productivity' stations per transect per year (black stars in Figure 1.1b; Table 1.2). The aim was to conduct primary productivity experiments at the same stations within each region every year, although this was not always logistically possible due to ice and weather conditions. In particular, sampling in the eastern sector of DBO3 and in DBO5 occurred on only two out of the eight cruises (Table 1.2). Data from stations in DBO3 are separated into 'eastern' (DBOE, station SEC-5) and 'western'

(DBO3W, stations UTN-4 and PH-2) sectors due to the significant spatial differences in water mass properties across this region.

1.3.2 Seawater Sampling

At every CTD/rosette station (Table 1.1), water column profiles of physical parameters were collected with a CTD profiler (Seabird SB911+) equipped with sensors for salinity (S), temperature (T), pressure, *in vivo* fluorescence, and photosynthetically active radiation. Seawater samples were collected with 10-L Niskin bottles, which were part of the 24-bottle rosette sampling system that included the CTD.

At primary productivity stations (Table 1.2), seawater samples were collected at six depths corresponding to light levels of 100%, 55%, 30%, 15%, 1% and 0.1% of the surface incident irradiance (I_0). Seawater for 100% I_0 was collected at a ‘surface’ depth of 1-2 m. At each light level, we measured dissolved nitrate (NO_3^-), total and size-fractionated phytoplankton biomass (as Chl *a*), and ^{13}C and $^{15}\text{NO}_3^-$ utilization rates (ρC and ρNO_3).

Table 1.1. Summary of the number of CTD/rosette stations, productivity stations and DBO regions sampled on each of the six DBO cruises from 2011 to 2016 and from previous cruises not affiliated with DBO but in the same area (2006 & 2008).

Cruise ID ^a (YEAR-ID)	Cruise Dates	Total number of CTD/rosette stations	Total number of Productivity Stations	DBO regions ^b	CTD/rosette data reference
2006-01 ^c	Jul 1-29	19	4	<i>1, 2, 3, 4</i>	Cooper et al. (2016a)
2008-02 ^d	Jul 3-27	16	5	<i>1, 2, 3, 4, 5</i>	Cooper et al. (2016b)
2011-18	Jul 6-21	37	3	<i>1, 2, 3, 5</i>	Cooper et al. (2016c)
2012-09	Jul 4-22	26	3	<i>1, 2, 3</i>	Cooper et al. (2016d)
2013-05	Jul 4-25	50	4	<i>1, 2, 3, 4, 5</i>	Cooper et al. (2016e)
2014-12	Jul 4-23	47	5	<i>1, 2, 3, 4, 5</i>	Cooper et al. (2016f)
2015-07	Jul 4-25	54	5	<i>1, 2, 3, 4, 5</i>	Cooper et al. (2016g)
2016-17	Jul 2-21	48	4	<i>1, 2, 3, 4, 5</i>	Cooper et al. (2017)

^aCruise IDs were designated by the Department of Fisheries and Oceans Canada

^bBolded and italicized numbers represent regions where productivity experiments were conducted.

^cThis cruise was part of the Bering Strait Environmental Observatory program

^dThis cruise was conducted as part of the International Polar Year – Canada’s Three Oceans project (see Varela et al., 2013 and Wyatt et al., 2013 for further details)

Table 1.2. Locations of primary productivity stations for each of the eight cruises in the Bering and Chukchi Seas from 2006 – 2016.

Cruise ID (YEAR-ID)	Date	Station	Latitude (°N)	Longitude (°W)	Bottom Depth (m)	Euphotic Zone Depth, Z_{eu} ^b (m)	DBO Region
2006-01	13 Jul	BCS-6	64.044	171.841	49	36	1 ^c
	16 Jul	BRS-4a	65.670	168.341	50	40	2 ^c
	18 Jul	PH-2	68.093	168.369	57	27	3W
	19 Jul	M05-04	70.644	168.244	45	30	4 ^c
2008-02	16 Jul	SLIP-4	63.026	173.456	74	59	1
	17 Jul	UTBS-1	64.990	169.140	49	44	2
	19 Jul	UTN-4	67.504	168.903	51	42	3W
	20 Jul	CCL-4	69.991	168.020	50	30	4 ^c
	21 Jul	BC-2	71.414	157.497	127	44	5
2011-18	15 Jul	SLIP-4	63.030	173.460	71	37	1
	16 Jul	UTBS-1	64.990	169.139	48	32	2
	17 Jul	UTN-4	67.500	168.909	49	20	3W
2012-09	14 Jul	SLIP-4	63.030	173.460	73	40	1
	15 Jul	UTBS-4	64.961	169.885	50	30	2
	17 Jul	SEC-5	68.131	167.510	55	30	3E
2013-05	14 Jul	SLIP-4	63.030	173.460	71	48	1
	15 Jul	UTBS-1	64.992	169.139	49	42	2
	19 Jul	UTN-4	67.500	168.943	51	22	3W
	22 Jul	DBO4.4	71.360	163.028	45	22	4
2014-12	15 Jul	SLIP-4	63.030	173.460	71	46	1
	16 Jul	UTBS-1	64.991	169.141	48	38	2
	17 Jul	UTN-4	67.501	168.904	50	36	3W
	18 Jul	SEC-5	68.128	167.495	50	39	3E
	20 Jul	DBO4.3	71.233	162.635	46	37	4
2015-07	15 Jul	SLIP-4	63.030	173.461	74	67	1
	16 Jul	UTBS-1	64.991	169.141	48	25	2
	17 Jul	UTN-4	67.500	168.942	49	26	3W
	19 Jul	DBO4.4	71.362	163.031	44	38	4
	20 Jul	BarC-5	71.410	157.491	125	29	5
2016-17	13 Jul	SLIP-4	63.030	173.461	72	67	1
	14 Jul	UTBS-1	64.991	169.141	49	44	2
	16 Jul	UTN-4	67.500	168.942	50	25	3W
	18 Jul	DBO4.2	71.102	162.275	49	39	4

^aCruise IDs were designated by the Department of Fisheries and Oceans Canada.

^bThe euphotic zone extends from the ocean surface to the 0.1% incident surface irradiance (I_0) level.

Euphotic zone depth (Z_{eu}) corresponds to the 0.1% I_0 depth.

^cIn 2006 and 2008, cruises were not conducted as part of the DBO. Stations where sampling occurred near (but not exactly within) the five DBO regions were included within the closest DBO region.

1.3.3 Dissolved Nutrients

Samples for NO_3^- concentrations were syringe-filtered through pre-combusted $0.7\ \mu\text{m}$ glass fibre filters and collected in acid-washed 30-mL polypropylene bottles. Samples were immediately frozen at -20°C until analysis on shore using an Astoria Nutrient Autoanalyzer and following the protocols of Barwell-Clark and Whitney (1996). Dissolved inorganic carbon (DIC) samples were collected near the surface (5 m) and 5 m from the bottom in 500-mL borosilicate bottles. Samples were preserved with 200 μL of a saturated mercuric chloride solution, stored at 4°C , and analyzed at the Institute of Ocean Sciences (Fisheries and Oceans Canada; Sidney, BC) using a SOMMA-Coulometer system following the methods of Dickson and Goyet (1994). DIC concentrations at the remaining sampling depths were estimated by interpolation using seawater density, and these values were used in the calculation of ρ_C .

1.3.4 Total and Size-Fractionated Phytoplankton Biomass (Chl *a*)

Seawater (0.5 L) was sequentially filtered through $5\ \mu\text{m}$ pore-size polycarbonate filters and $0.7\ \mu\text{m}$ pore-size glass fibre filters for analysis of size-fractionated Chl *a*. Prior to 2013, an additional seawater sample (0.5 L) for total Chl *a* was filtered through a $0.7\ \mu\text{m}$ pore size glass fibre filter. After 2013, total Chl *a* was calculated as the sum of the two size fractions. Samples were stored frozen at -20°C until analysis ashore. The filtered Chl *a* was extracted with 90% acetone at -20°C for 24 hours in the dark, measured on a Turner Designs 10AU fluorometer, and corrected for phaeopigment interference following Parsons et al. (1984).

1.3.5 Phytoplankton Taxonomy

Phytoplankton taxonomic analyses were conducted in 2013. Seawater samples (125 mL) were collected in amber high-density polyethylene bottles at the depth of the Chl *a*

maximum, or near the surface (5 m) if no Chl *a* maximum was evident. Samples were fixed with acidic Lugol's solution, and stored in the dark at room temperature (Parsons et al. 1984) until analysis. Due to logistical constraints, phytoplankton identification in DBO1 and DBO2 was only carried out at stations located near (but not within) these regions (i.e. BCL-6a for DBO1 and BRS-3 for DBO2, see Figure 1.5 for station locations). For DBO3-DBO5, samples were analyzed from both the productivity stations and all other CTD/rosette stations. Prior to microscopic identification, samples were settled for 24 h using 10-mL Utermöhl sedimentation chambers. Phytoplankton cells were enumerated following the Utermöhl (1958) technique and using an inverted microscope equipped with phase and interference (Nomarski) contrasts. Cells were identified to genus/species level, and abundances for each taxon were expressed as number of cells per litre of seawater. The presence or absence of chloroplasts was used to differentiate between autotrophic and heterotrophic cells with the exception of undetermined flagellates, which may include some heterotrophic taxa.

Phytoplankton were further categorized into major taxonomic groups and the total abundance for each group was calculated. These groups are Diatoms (Bacillariophyceae), Dinoflagellates (Dinophyceae), Coccolithophores (Prymnesiophyceae), Phaeocystis (Prymnesiophyceae), Cryptomonads (Cryptophyceae), Chrysophytes (Chrysophyceae), Prasinophytes (Prasinophyceae), Chlorophytes (Chlorophyceae), and undetermined flagellates of likely different taxonomic affinities that were separated into three size classes: $<3\mu\text{m}$, between $3\mu\text{m}$ and $7\mu\text{m}$, and $>7\mu\text{m}$.

1.3.6 Sea-ice concentrations

Sea-ice concentration data, used to interpret phytoplankton taxonomy for July 2013, were retrieved in May 2017 from the Integrated Climate Data Center

(<http://icdc.zmaw.de/>) at the University of Hamburg (Hamburg, Germany). Sea-ice concentrations were calculated by applying the ARTIST sea-ice (ASI) algorithm to brightness temperatures from the Advanced Microwave Scanning Radiometer on board the EOS (AMSR-E) satellite. A three-day mean of sea-ice concentrations (including the entire sampling date and 2 days prior to sampling) was calculated to account for short-term changes in the amount of sea ice.

1.3.7 Carbon and Nitrate Utilization Rates, New Production, and f-ratios

Carbon and NO_3^- utilization rates were measured using a ^{13}C - $^{15}\text{NO}_3^-$ dual tracer method (Dugdale and Goering, 1967; Slawyk et al. 1977). Seawater was collected in 1-L acid-cleaned polycarbonate bottles and enriched with ^{13}C -labeled NaHCO_3 (99 atom % ^{13}C , Cambridge Isotope Laboratories) and ^{15}N -labeled NaNO_3 (98 atom % ^{15}N , Cambridge Isotope Laboratories) as soon as possible after collection. Isotopic ^{13}C and $^{15}\text{NO}_3^-$ additions were made at $\leq 10\%$ of the climatological DIC and NO_3^- concentrations, respectively. Sample bottles were placed in acrylic tubes covered with neutral density and blue-coloured photographic film to simulate the *in situ* irradiance level and wavelengths at the sampling depths. Samples were then incubated for 24 h in on-deck acrylic tanks, which were temperature-controlled by using flowing surface seawater. Experiments were terminated by gentle vacuum filtration onto pre-combusted $0.7\ \mu\text{m}$ glass-fibre filters that were then dried at 60°C and stored in a desiccator until analysis ashore. The total particulate C (PC) and N (PN) and isotopic composition (^{12}C : ^{13}C and ^{14}N : ^{15}N) were measured using an elemental analyzer (Elementar Vario EL Cube) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer at the Stable Isotope Facility at the University of California Davis.

Carbon utilization rates (referred as ‘primary productivity’ in this paper, ρC) were calculated following Hama et al. (1983), while NO_3^- utilization rates (ρNO_3) were calculated using equations (6) and (3) of Dugdale and Wilkerson (1986). When ambient concentrations of NO_3^- were below the detection limit ($0.1 \mu\text{mol L}^{-1}$), a value equal to the NO_3^- detection limit was used to calculate ρNO_3 . Therefore, under those conditions, ρNO_3 represent a potential maximum value of ρNO_3 . We estimated the error associated with our measurements of ρC to be $\pm 20\%$ and with ρNO_3 to be $\pm 18\%$, based on the mean coefficient of variation from triplicate measurements conducted every year from 2011-2016 ($n = 54$).

New primary production in C-based units (New-Prod) was estimated by multiplying ρNO_3 by the ratio of PC:PN measured at the end of the incubation for each sample. The proportion of total primary productivity attributable to new primary production was also calculated using these C-based estimates as the f -ratio = $(\rho \text{NO}_3 \times \text{PC/PN}) / \rho C$.

1.3.8 Data organization and analysis

Primary productivity data were depth-integrated using trapezoidal integration from the surface to the bottom of the euphotic zone (0.1% of surface irradiance). While ρC data from each depth is expressed in molar units, depth-integrated ρC and New-Prod are expressed in units of $\text{g C m}^{-2} \text{ d}^{-1}$ using a conversion of 12 g C mol^{-1} to better compare with published results. Figures 1.1, and 1.5-1.7 were created using Ocean Data View version 4.7.9 (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2012). Matlab R2014b was used to conduct all statistical tests and significance was determined at $\alpha < 0.05$ unless otherwise stated.

1.4 Results

1.4.1 Time-averaged Nitrate concentrations, Phytoplankton Biomass, and Utilization of C and NO_3^-

1.4.1.1 Vertical Distributions

Concentrations of NO_3^- increased with depth in the five DBO regions (Figure 1.2a) from 2006 to 2016, with the exception of DBO3E (station SEC-5). Station SEC-5, located in the eastern sector of DBO3 and close to the Alaska coastline, was characterized by much lower and invariable $[\text{NO}_3^-]$ throughout the water column. The highest $[\text{NO}_3^-]$ in the upper euphotic zone (100, 55 and 30% I_0) occurred in DBO2 and DBO3W. The time-averaged $[\text{NO}_3^-]$ showed less vertical variation in these regions compared to DBO1 and DBO4-5, although there was still a small increase with depth. DBO2 had the broadest range of $[\text{NO}_3^-]$ for the 10-year period, spanning from undetectable to up to $18 \mu\text{mol L}^{-1}$ at the surface, and from 12 to $20 \mu\text{mol L}^{-1}$ at 0.1% I_0 . In DBO1-2 and DBO3W, the bottom of the euphotic zone (0.1% I_0) generally showed the least variability compared to the rest of the euphotic zone. In contrast, $[\text{NO}_3^-]$ in DBO4 and DBO5 were low with reduced interannual variability in the upper euphotic zone (100%, 55% and 30% I_0), and higher and more variable interannually in the lower euphotic zone (15%, 1% and 0.1% I_0).

The 10-yr time-averaged Chl *a* concentrations were lower in the upper euphotic zone (100, 55 and 30% I_0) compared to the lower euphotic zone (15, 1 and 0.1% I_0 ; Figure 1.2b). An exception was DBO3E (Figure 1.2b) that showed low values and little variation with depth, similar to $[\text{NO}_3^-]$ (Figure 1.2a). Subsurface Chl *a* maxima were observed in DBO1, DBO3W, DBO4 and DBO5. These subsurface maxima typically occurred at either 15 or 1% I_0 and corresponded to an increase in $[\text{NO}_3^-]$.

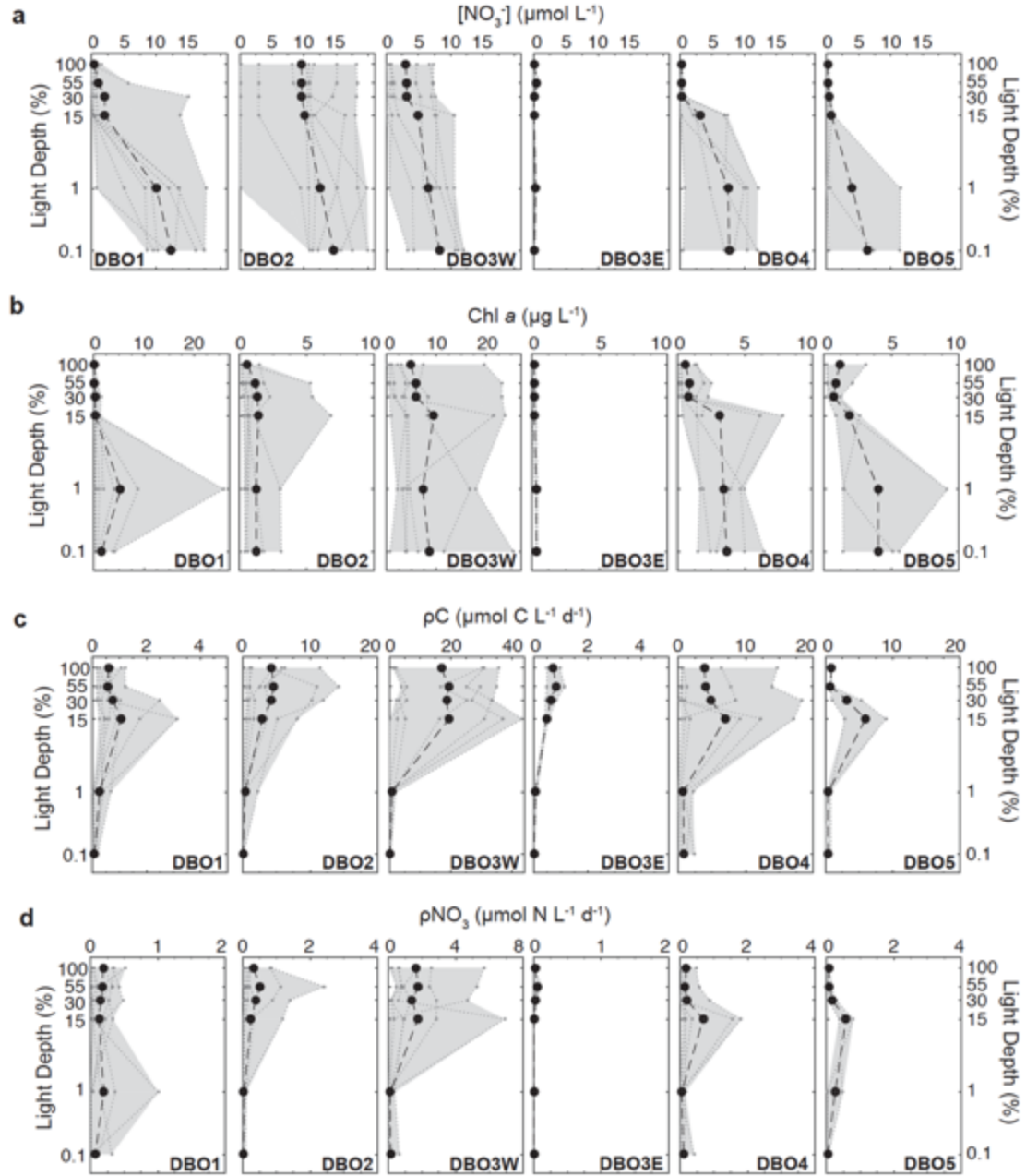


Figure 1.2. Time-averaged vertical profiles of (a) NO_3^- concentration, (b) total Chl *a* concentration, (c) C utilization rate, pC , and (d) NO_3^- utilization rate, $p\text{NO}_3$, over the 2006-2016 period for each DBO region. Data are plotted against light depths (i.e. percentage of incident surface irradiance, I_0) to account for differences in depths sampled among years. The y-axis depth scale is logarithmic to reflect the exponential attenuation of irradiance in the water column. Filled black dots and black dashed lines represent the time-averaged vertical profiles, calculated as the average of all years sampled for each light depth. Smaller grey dots and grey dotted lines represent vertical profiles from each year sampled. Note that DBO3E and DBO5 were only sampled on two out of the eight cruises. Shaded grey areas indicate the range of values (maximum and minimum) for each parameter in each region. Profiles from the DBO3 region are separated into west and east sectors (DBO3W and DBO3E, respectively), which are influenced by different water masses (DBO3W = nutrient rich AW/BSW; DBO3E = nutrient poor ACW). Note the different horizontal scales (x-axis) among DBO regions in panels b to d.

DBO3W exhibited the highest Chl *a* of all regions, as well as the most interannual variability, while DBO3E showed the lowest Chl *a* and least variability. Chl *a* in DBO1 also showed relatively low interannual variability at all light depths except at 1% I_0 . At this depth, Chl *a* was at least 2-3 times higher and showed much more interannual variability ($0.25 - 25.8 \mu\text{g L}^{-1}$) than the other depths.

Vertical profiles of ρC (Figure 1.2c) and ρNO_3 (Figure 1.2d) averaged over the 10-yr study exhibited similar spatial trends for the five DBO regions. Both ρC and ρNO_3 were much lower in DBO1 (note different scale for DBO1 for Figure 1.2c-d) and in DBO3E compared to the other regions. DBO3E exhibited the lowest ρC and ρNO_3 for the entire DBO region, while ρC and ρNO_3 in DBO3W were the highest (note different scale for DBO3W for Figure 1.2c-d). In all regions, ρC decreased to $<1 \mu\text{mol C L}^{-1} \text{ d}^{-1}$ ($<12 \text{ mg C m}^{-3} \text{ d}^{-1}$), and ρNO_3 decreased to $<0.2 \mu\text{mol N L}^{-1} \text{ d}^{-1}$ below 15% I_0 . Both ρC and ρNO_3 exhibited higher interannual variability at depths above 1% I_0 for all regions except for DBO1 and DBO3E. In DBO1, ρNO_3 showed slightly more interannual variability at 1% I_0 , as it was also observed for Chl *a*.

1.4.1.2 Depth-integrated Distributions

The high spatial and temporal variabilities observed in the vertical profiles were also reflected in the depth-integrated distributions of $[\text{NO}_3^-]$, Chl *a*, ρC and ρNO_3 . Depth-integrated $[\text{NO}_3^-]$ were generally highest in DBO1 and DBO2, lowest in DBO3E, and intermediate in DBO3W, DBO4 and DBO5 (Table 1.3; Figure 1.3a). There were no obvious temporal trends for $[\text{NO}_3^-]$ in any of the DBO regions (Table 1.3). Depth integrated $[\text{NO}_3^-]$ in DBO3E was relatively invariable between years, while interannual variability in $[\text{NO}_3^-]$ was much higher for the other DBO regions (Table 1.3, Figure 1.3a).

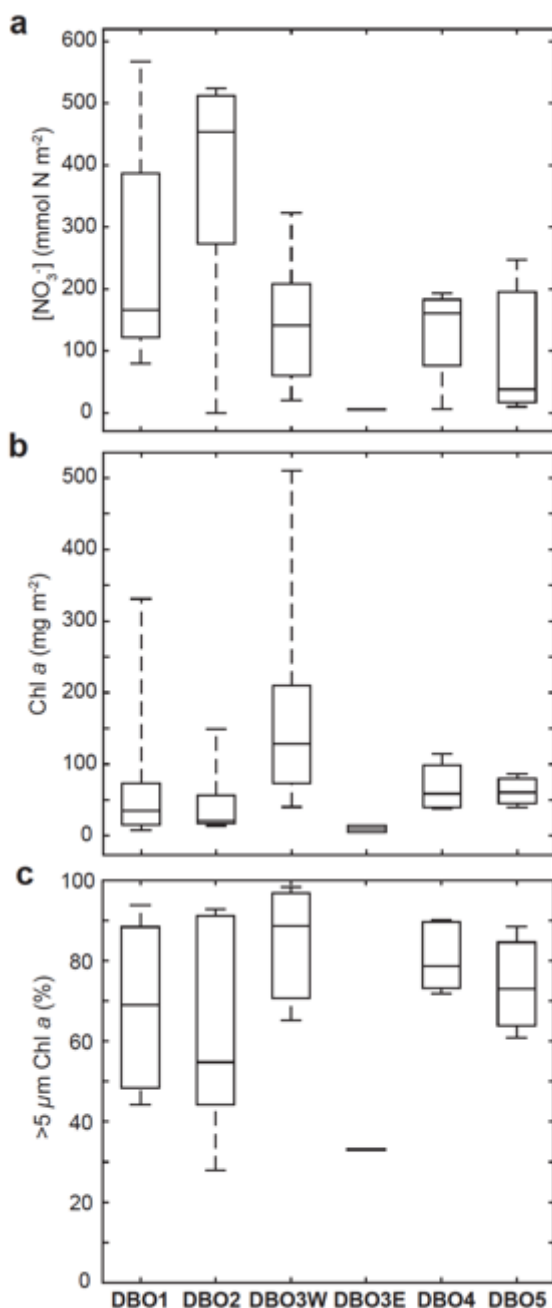


Figure 1.3. Box plots of time-averaged depth-integrated (a) NO_3^- concentration, (b) total Chl *a* concentration, and (c) percent contribution of $>5 \mu\text{m}$ Chl *a* to total Chl *a* for each DBO region from 2006 to 2016. Depth integrations were done from the ocean surface to the $0.1\% I_0$ depth. The horizontal line in the middle of each box represents the median, and the top and bottom of the boxes represents the 25th and 75th percentiles, respectively. The whiskers extending above and below each box extend to the maximum and minimum measured values, respectively. Data from the DBO3 region are separated into west (DBO3W) and east (DBO3E) as in Figure 2

Table 1.3. Depth-integrated measurements of nitrate (NO_3^-) and chlorophyll *a* (Chl *a*) concentrations, the percent contribution of $>5 \mu\text{m}$ Chl *a*, primary productivity (ρC), nitrate utilization rates (ρNO_3), new production and *f*-ratios for the five DBO regions in the Bering and Chukchi Seas in July from 2006-2016. Data from DBO3 is split longitudinally into the western (DBO3W) and eastern (DBO3E) sectors due to differences in the water mass composition (AW/BSW and ACW, respectively). Depth integrations were done from the ocean surface to the 0.1% I_0 depth. (-) indicates that no data is available. Values listed as $<1.6 \text{ mmol m}^{-2}$ for $[\text{NO}_3^-]$ represent stations where $[\text{NO}_3^-]$ at all depths sampled were below the analytical detection limit ($<0.1 \mu\text{mol L}^{-1}$).

Region	Year	$[\text{NO}_3^-]$ (mmol m^{-2})	Chl <i>a</i> (mg m^{-2})	Chl <i>a</i> $> 5 \mu\text{m}$ (%)	ρC ($\text{g C m}^{-2} \text{ d}^{-1}$)	ρNO_3 ($\text{mmol N m}^{-2} \text{ d}^{-1}$)	New-Prod ($\text{g C m}^{-2} \text{ d}^{-1}$)	<i>f</i> -ratio
<i>Northern Bering Shelf</i>								
DBO1	2006	437	46.1	-	0.65	5.37	0.44	0.67
	2008	568	17.6	44.3	0.17	7.37	0.45	>1
	2011	79.8	23.5	-	0.19	6.41	0.53	>1
	2012	153	98.7	88.4	0.13	3.01	0.21	>1
	2013	168	331	68.1	0.44	10.4	0.97	>1
	2014	91.1	47.4	76.6	0.66	14.9	0.87	>1
	2015	165	7.4	61.3	0.25	0.97	0.09	0.35
	2016	337	13.3	32.0	0.21	1.94	0.18	0.57
Mean ($\pm\text{SE}$)		250 ± 62.9	73.1 ± 38.3	61.8 ± 8.5	0.34 ± 0.08	6.30 ± 1.64	0.47 ± 0.11	0.53 ± 0.09^a
DBO2	2006	<1.6	17.2	-	0.17	0.40	0.03	0.18
	2008	502	21.4	47.5	0.97	2.96	0.15	0.18
	2011	144	149	-	2.19	28.9	2.09	0.99
	2012	524	31.0	92.9	0.23	4.89	0.29	>1
	2013	501	14.0	61.8	0.24	1.45	0.11	0.45
	2014	522	81.4	91.2	2.74	15.3	0.97	0.38
	2015	403	17.8	27.9	0.63	1.6	0.12	0.19
	2016	406	19.7	43.5	0.83	1.98	0.13	0.19
Mean ($\pm\text{SE}$)		429 ± 51.3	43.9 ± 16.9	60.8 ± 10.8	1.00 ± 0.34	7.19 ± 3.53	0.49 ± 0.25	0.37 ± 0.11
<i>Southeastern Chukchi Sea</i>								
DBO3W	2006	39.6	77.2	-	0.44	1.58	0.12	0.26
	2008	323	40.2	72.5	1.03	95.5	5.27	>1
	2011	141	141	-	4.46	35.3	4.70	0.88
	2012	-	-	-	-	-	-	-
	2013	123	233	95.7	3.66	17.7	0.82	0.40
	2014	157	128	88.6	1.32	7.85	0.65	0.48
	2015	226	71.8	65.2	4.96	36.7	3.25	0.64
	2016	19.9	510	90.2	7.94	13.5	1.56	0.21
Mean ($\pm\text{SE}$)		147 ± 39.5	172 ± 61.2	82.4 ± 5.79	3.40 ± 1.01	29.7 ± 12.0	2.34 ± 0.78	0.48 ± 0.10

Region	Year	[NO ₃ ⁻] (mmol m ⁻²)	Chl <i>a</i> (mg m ⁻²)	Chl <i>a</i> > 5μm (%)	ρC (g C m ⁻² d ⁻¹)	ρNO ₃ (mmol N m ⁻² d ⁻¹)	New-Prod (g C m ⁻² d ⁻¹)	<i>f</i> -ratio
DBO3E	2006	-	-	-	-	-	-	-
	2008	-	-	-	-	-	-	-
	2011	-	-	-	-	-	-	-
	2012	5.00	5.01	33.3	0.07	0.08	0.01	0.08
	2013	-	-	-	-	-	-	-
	2014	6.38	14.0	32.9	0.22	0.54	0.04	0.23
	2015	-	-	-	-	-	-	-
	2016	-	-	-	-	-	-	-
	Mean (±SE)	5.69 ± 0.69	9.51 ± 4.50	33.1 ± 0.20	0.15 ± 0.08	0.31 ± 0.23	0.03 ± 0.02	0.16 ± 0.08
<i>Northeastern Chukchi Sea</i>								
DBO4	2006	76.9	114		0.95	4.32	0.40	0.40
	2008	172	54.4	89.5	1.15	27.9	2.33	>1
	2011	-	-	-	-	-	-	-
	2012	-	-	-	-	-	-	-
	2013	6.29	63.2	61.2	2.87	3.45	0.17	0.17
	2014	183	39.9	73.7	0.31	3.58	0.27	>1
	2015	194	98.6	90.2	1.44	12.5	1.09	0.75
	2016	149	38.2	67.9	0.32	1.29	0.11	0.33
	Mean (±SE)	130 ± 30.1	68.1 ± 12.8	76.5 ± 5.80	1.17 ± 0.39	8.84 ± 4.13	0.73 ± 0.35	0.41 ± 0.12
DBO5	2006	-	-	-	-	-	-	-
	2008	248	60.7	88.5	1.58	11.1	0.85	0.50
	2011	-	-	-	-	-	-	-
	2012	-	-	-	-	-	-	-
	2013	-	-	-	-	-	-	-
	2014	-	-	-	-	-	-	-
	2015	37.9	40	73.0	0.40	6	0.54	>1
	2016	-	-	-	-	-	-	-
	Mean (±SE)	143 ± 105	50.4 ± 10.4	80.8 ± 7.75	0.99 ± 0.59	8.55 ± 2.55	0.70 ± 0.16	0.50

^a the mean *f*-ratio was only calculated from years where the *f*-ratio was <1

Depth-integrated Chl *a* distributions and the percent contribution of $>5\ \mu\text{m}$ Chl *a* to total Chl *a* were generally highest in DBO3W, lowest in DBO3E, and in between these two extremes for the other DBO regions (Table 1.3; Figure 1.3b-c). Chl *a* $>5\ \mu\text{m}$ contributed more than 40% to total Chl *a* in all regions, except for DBO3E where it accounted for only $\sim 30\%$ of total Chl *a* (Table 1.3, Figure 1.3c). Higher total Chl *a* in DBO3W coincided with a greater contribution of the $>5\ \mu\text{m}$ size fraction ($r = 0.56$, $p < 0.003$). Interannual variability was highest in DBO1-2 and DBO3W for total Chl *a*, and there were no clear year-to-year trends in any of the DBO regions. The same was true for the percent contribution of $>5\ \mu\text{m}$ cells to total Chl *a* in all DBO regions except for DBO1, where a significant decreasing trend ($r = -0.94$, $p < 0.02$) was calculated from 2012 to 2016 (Table 1.3).

Depth-integrated ρC and ρNO_3 exhibited similar spatial variations to Chl *a*, with the highest and lowest values occurring in DBO3W and DBO3E, respectively, while values for the other DBO regions fell between those in DBO3W and E (Table 1.3; Figure 1.4a-b). There were no consistent trends with time anywhere, but DBO1, DBO3E and DBO5 were less variable than the other regions (Table 1.3). Although ρC showed similar spatial variations to ρNO_3 , ρNO_3 and ρC were only weakly correlated with each other ($r = 0.33$, $p < 0.10$).

1.4.1.3 New primary production and f-ratios

Depth-integrated New-Prod followed similar spatial trends to Chl *a*, ρC and ρNO_3 , with rates being highest in DBO3W, lowest in DBO3E and intermediate for the other DBO regions (Table 1.3; Figure 1.4c). Rates of New-Prod were highly variable between years in DBO1-2, DBO3W and DBO4, with no consistent trends with time (Table 1.3). Depth

integrated f -ratios were highly variable from year to year, while, when averaged over the entire study period, f -ratios were similar for all DBO regions except for DBO3E (Table 1.3; Figure 1.4d). In addition, little can be said for the f -ratios in the DBO1 region, as values were often greater than 1. An f -ratio >1 is not realistic given that 1 represents 100% of the productivity resulting from NO_3^- utilization and potentially available for export. These high f -ratios are likely a result of calculation artefacts by using the ratio of ρNO_3 to ρC , rather than a more accurate f -ratio of N-based utilization rates (i.e. $\rho\text{NO}_3/(\rho\text{NH}_4 + \rho\text{Urea} + \rho\text{NO}_3)$). Therefore, the f -ratios presented for DBO1 in Table 1.3 and Figure 1.4d should be interpreted with caution.

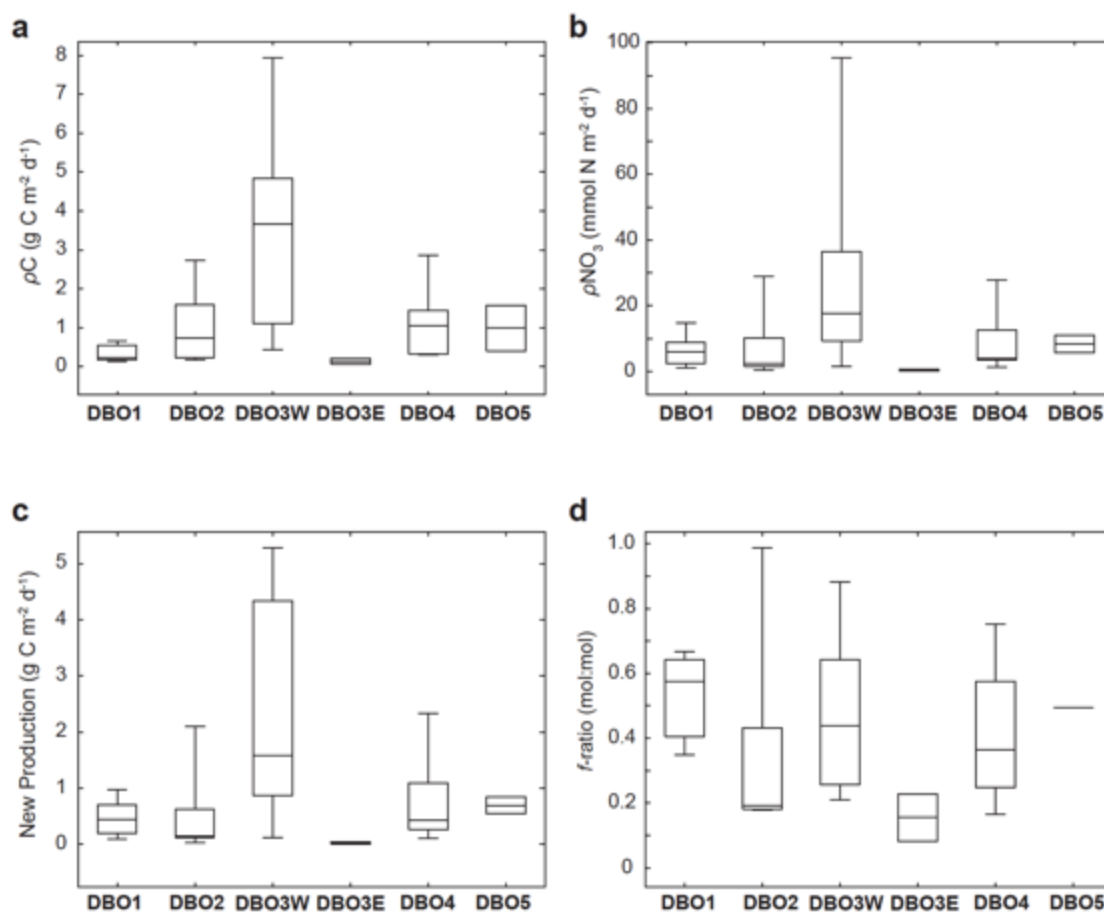


Figure 1.4. Box plots of time-averaged depth-integrated (a) C utilization rate, ρC , (b) NO_3^- utilization rate, ρNO_3 (c) new production (New-Prod), and (d) f -ratios for each DBO region from 2006 to 2016 as in Figure 3. Note that f -ratio values >1 are not included in the box plot for DBO1.

1.4.1.4 Statistical comparisons among DBO regions and years sampled

Statistical differences in depth-integrated $[\text{NO}_3^-]$, Chl a , ρC , ρNO_3 , New-Prod and f -ratios grouped either by region or by year were determined using a nonparametric Kruskal-Wallis test with post hoc comparison (at $p < 0.05$). When data were grouped by DBO region, significant differences were observed between DBO3W and E for depth-integrated Chl a , ρC , ρNO_3 and New-Prod, and between DBO1 and DBO3W for depth-integrated ρC . No significant differences occurred between any of the combinations of DBO2, DBO4 or DBO5 for any of the parameters measured. If data were grouped geographically into either the Bering Sea (DBO1 and DBO2) or the Chukchi Sea (DBO3 to 5), significant differences occurred between the Bering and Chukchi Seas for depth-integrated $[\text{NO}_3^-]$, Chl a , ρC and New-Prod. With the exception of New-Prod, the differences between the Bering and Chukchi Seas remained significant regardless of whether or not the data from DBO3E were included in the Chukchi Sea group. When data were instead grouped by year, no significant differences between years occurred regardless of how the data were grouped, i.e. by station, by DBO region, by water mass (i.e. separating DBO3 into east and west) or by geography (i.e. Bering Sea or Chukchi Sea). It is possible that the lack of significant yearly differences results from a low ratio of observational frequency to natural variability.

1.4.1.5 Correlation analysis between physical and biological parameters in the Bering and Chukchi Seas

To identify potential environmental controls on phytoplankton biomass and productivity, we conducted a correlation analysis between euphotic-zone integrated $[\text{NO}_3^-]$, phytoplankton biomass, primary productivity, and several physical parameters (Table 1.4).

Table 1.4. Correlation matrix among physical, chemical and biological parameters for the Bering and Chukchi Seas from 2006 to 2016. Physical data (temperature and salinity) is presented for surface and bottom depths, and biological and chemical data are presented as depth-integrated values from the ocean surface to the 0.1% I_0 depth. Significant relationships at $p < 0.05$ and $p < 0.01$ are in bold. Significant relationships at $p < 0.10$ are in italics. Surf = surface (1-2 m), Bot = bottom (2-5 m) from the seafloor, T = temperature, S = salinity, Z_{eu} = euphotic zone depth.

	Surf T	Bot T	Surf S	Bot S	Z_{eu} (m)	$[NO_3^-]$	Chl a	Chl a >5 μ m	Chl a <5 μ m	ρC	ρNO_3	New- Prod
<i>Bering Sea (DBO1, DBO2)</i>												
Surface T												
Bottom T	-0.56**											
Surface S	-0.73*	0.22										
Bottom S	0.00	-0.07	0.37									
Z_{eu} (m)	0.41	-0.66*	-0.06	-0.18								
$[NO_3^-]$	-0.41	0.18	0.56**	0.64*	-0.05							
Chl a	0.18	-0.25	-0.27	-0.08	-0.09	-0.28						
Chl a >5 μ m	0.31	-0.30	-0.53 [†]	-0.13	-0.06	-0.39	0.998*					
Chl a <5 μ m	0.37	-0.06	-0.34	0.13	-0.17	-0.31	0.75*	0.72*				
ρC	-0.24	0.43	0.15	0.09	-0.32	0.17	0.23	0.06	0.04			
ρNO_3	-0.02	-0.03	-0.06	0.01	-0.24	-0.18	0.49 [†]	0.44	0.34	0.72*		
New-Prod	0.01	-0.05	-0.13	-0.03	-0.24	-0.23	0.59**	0.66**	0.49	0.68*	0.98*	
f -ratio	0.21	-0.31	-0.37	0.00	-0.05	-0.15	0.74**	0.13	-0.71 [†]	0.36	0.74**	0.78*
<i>Chukchi Sea (DBO3, DBO4, DBO5)</i>												
Surface T												
Bottom T	0.65*											
Surface S	0.65*	0.78*										
Bottom S	-0.41 [†]	-0.52**	-0.24									
Z_{eu} (m)	0.03	-0.20	-0.24	-0.21								
$[NO_3^-]$	-0.02	0.01	0.01	0.21	0.50**							
Chl a	0.01	0.23	0.34	0.05	-0.42	-0.20						
Chl a >5 μ m	0.02	0.25	0.39	0.04	-0.40	-0.19	0.99*					
Chl a <5 μ m	-0.32	0.02	-0.01	0.25	-0.41	0.16	-0.12	-0.14				
ρC	0.18	0.41 [†]	0.40	0.22	-0.57**	-0.03	0.83*	0.83*	0.29			
ρNO_3	0.22	0.34	0.37	0.04	0.11	0.69*	0.00	-0.03	0.20	0.20		
New-Prod	0.28	0.43	0.41	0.20	-0.22	0.59**	0.12	0.07	0.40	0.46 [†]	0.91*	
f -ratio	0.24	0.16	0.09	0.13	0.00	0.77*	-0.02	-0.04	0.37	0.22	0.76*	0.75*

* $p < 0.01$, ** $p < 0.05$, [†] $p < 0.10$

Data were grouped into either Bering Sea (DBO1-DBO2) or Chukchi Sea (DBO3-DBO5) regions, and a separate analysis was conducted for each of the two regions (Bering and Chukchi). Significant ($p < 0.05$) correlations between parameters were found in both the Bering and Chukchi Seas.

In the Bering Sea, only the depth of the euphotic zone (Z_{eu}) and $[NO_3^-]$ showed any correlation with physical parameters, with Z_{eu} being negatively correlated with bottom temperature (i.e. Z_{eu} was deeper when bottom temperatures were lower/colder), and $[NO_3^-]$ being positively correlated with both surface and bottom salinity. In contrast, a number of biological parameters were significantly correlated with each other. Total Chl a was positively correlated with the $>5 \mu m$ and $<5 \mu m$ Chl a size fractions, as well as with New-Prod and the f -ratio, while Chl $a > 5 \mu m$ was positively correlated with New-Prod. In addition, ρC was positively correlated with ρNO_3 and New-Prod, while ρNO_3 , New-Prod and the f -ratio were all positively correlated with each other.

In the Chukchi Sea, no significant correlations were found between any biological and physical parameters; however, like for the Bering Sea, a number of significant correlations were found between biological parameters. For example, $[NO_3^-]$ was positively correlated with Z_{eu} , ρNO_3 , New-Prod and the f -ratio. Total Chl a and Chl $a > 5 \mu m$ were positively correlated with each other and with ρC , while ρC was also negatively correlated with Z_{eu} . Similar to the Bering Sea, ρNO_3 , New-Prod and the f -ratio in the Chukchi Sea were all positively correlated with each other.

1.4.2 Phytoplankton assemblage composition

Phytoplankton taxonomic analysis was only conducted in 2013 at the depth of the Chl a maximum (or at 5 m if no Chl a maximum was identified) (Figures 1.5 and 1.6). For each DBO region, with the exception of DBO3, the average proportion of cell numbers

from each taxonomic group was calculated using data from all CTD/rosette and primary productivity stations within each region (Figure 1.5a). In DBO3, stations were further separated into DBO3E (SEC-5 to SEC-8) and DBO3W (UTN-1 to UTN-7, and SEC-1 to SEC-2) (Figure 1.5a). Diatoms dominated the phytoplankton assemblages in all of the DBO regions with the exception of DBO3E where coccolithophores and small ($<7\ \mu\text{m}$) flagellates were dominant (Figure 1.5b).

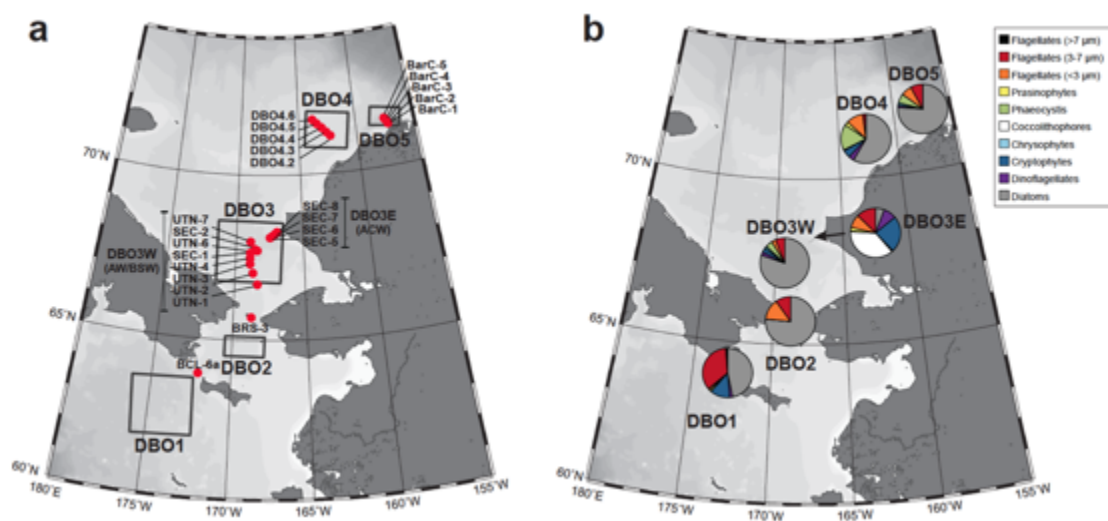


Figure 1.5. Station locations and DBO averages for phytoplankton assemblage composition in July 2013. (a) Map of DBO region bounding boxes and station locations where phytoplankton taxonomic identification was conducted at the depth of the chlorophyll maximum (or 5 m depth if maximum was not identified). AW/BSW and ACW refer to the dominant water masses in DBO3W and DBO3E, respectively (Figure 1a). (b) Proportion of cell numbers from each taxonomic group to total phytoplankton cell numbers averaged for each DBO region. The three size classes of flagellates ($<3\ \mu\text{m}$, $3-7\ \mu\text{m}$ and $>7\ \mu\text{m}$) were undetermined species of likely different taxonomic affinities. Data from the DBO3 region are separated into west (DBO3W) and east (DBO3E) as in previous figures. Due to logistical constraints, only samples from stations near (but not within) DBO1 (BCL-6a) and DBO2 (BRS-3) were analyzed for phytoplankton taxonomy.

Spatial variations in total phytoplankton abundance were primarily driven by the contribution of diatoms ($r = 0.92$, $p < 0.01$), but also correlated with the amount of sea ice cover ($r = 0.65$, $p < 0.01$; Figure 1.6a-b). The highest total cell abundance ($\sim 4 \times 10^6$ cells L^{-1}) was measured in DBO4 and corresponded to an increase in sea ice cover (Figure 1.6a-b). This region also exhibited the largest diversity in phytoplankton assemblage composition, although diatoms were still the most abundant. *Phaeocystis* spp. reached up

to $\sim 1.3 \times 10^6$ cells L^{-1} at DBO4.3, and was also present at some stations in the DBO3 and DBO5 regions, but was not observed in DBO1 or DBO2. Flagellates were present at all stations, but their abundance was spatially variable.

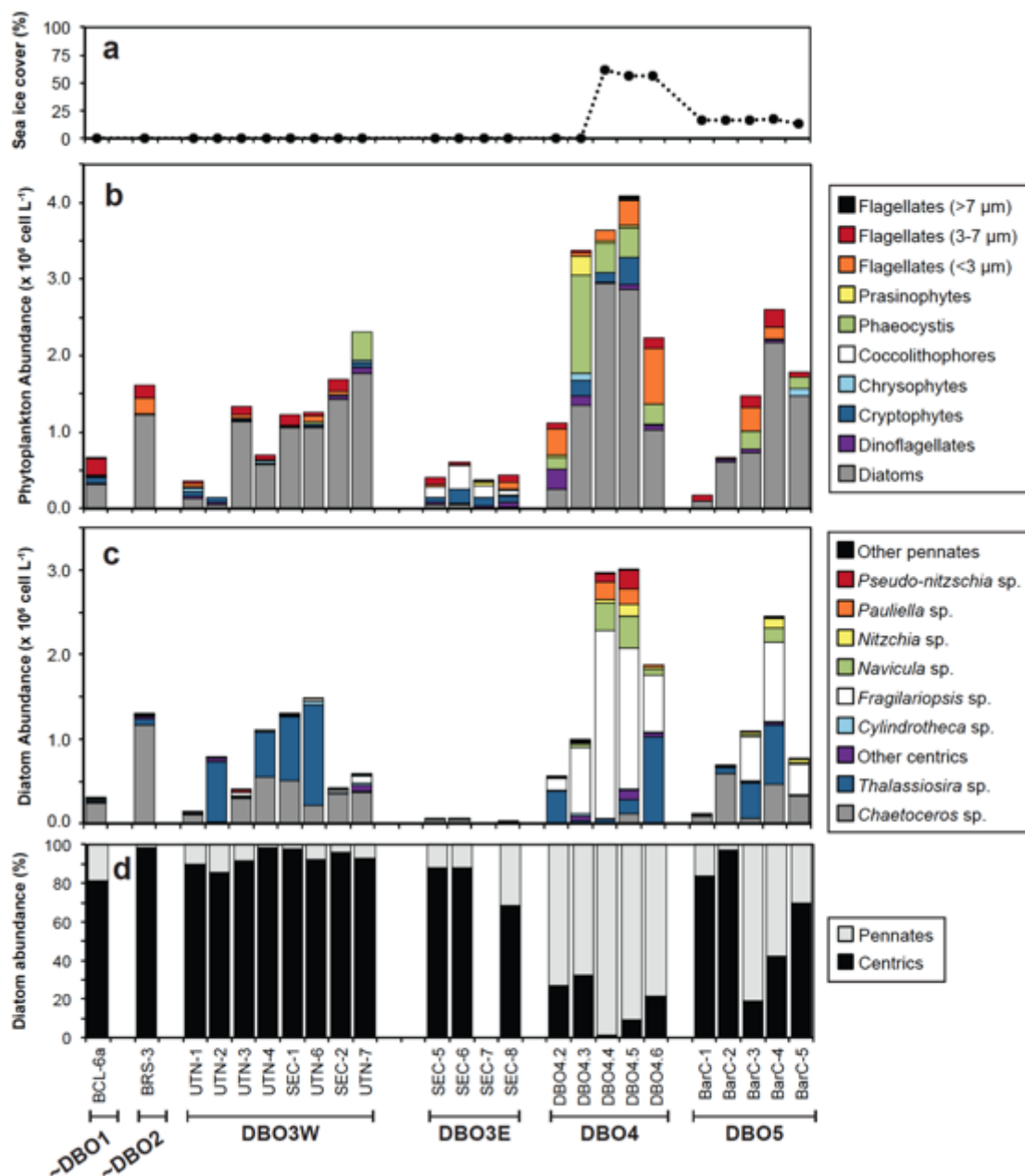


Figure 1.6. Sea-ice concentration and phytoplankton assemblage composition for each station in July 2013. (a) Three-day mean of sea-ice concentration (%). (b) Cell abundance of major phytoplankton taxonomic groups. (c) Abundance of the prominent diatom taxa. (d) Relative abundance of centric versus pennate diatoms. Taxonomic data presented in panels b to d is derived from samples collected at the depth of the chlorophyll maximum (or at 5 m depth if maximum was not identified). The three size classes of flagellates ($<3 \mu m$, $3-7 \mu m$ and $>7 \mu m$) were undetermined species of likely different taxonomic affinities. Data from the DBO3 region are separated into west (DBO3W) and east (DBO3E) as in previous figures.

Larger ($>7\mu\text{m}$) unidentified flagellates were most abundant in DBO4 (Figure 1.6b), while smaller ($3\text{--}7\mu\text{m}$) unidentified flagellates did not exhibit much spatial variability, with an average abundance of $\sim 0.08 \times 10^6 \text{ cells L}^{-1}$ for all stations. The lowest total phytoplankton abundance of $\sim 0.15 \times 10^6 \text{ cells L}^{-1}$ was observed at stations near the southernmost edge of DBO3 (UTN-1 and UTN-2) and at BarC-1 in DBO5, although diatoms were still the dominant group at these stations. Coccolithophores were present in the highest numbers at stations with relatively low total abundance ($\sim 0.46 \times 10^6 \text{ cells L}^{-1}$) in the eastern sector of DBO3 (SEC-5 to SEC-8) near the Alaska coast, reaching a maximum of $0.32 \times 10^6 \text{ cells L}^{-1}$ at SEC-6 (Figure 1.6b). Autotrophic dinoflagellates were present in consistently low numbers throughout the DBO regions ($0.002 - 0.27 \times 10^6 \text{ cells L}^{-1}$) with relatively little spatial variation, except for a slight increase at DBO4. The centric diatoms *Chaetoceros* sp. and *Thalassiosira* sp. were the most abundant in all of the DBO regions except for DBO4, where *Fragilariopsis* sp. and other pennate diatom species dominated the assemblages (Figure 1.6c-d).

The most commonly observed phytoplankton taxa (i.e. those taxa that were present at 10 or more stations) were small ($<7\mu\text{m}$) flagellates, cryptophytes, prymnesiophytes and diatoms (Table 1.5). Small ($<7\mu\text{m}$) flagellates, and the diatom *Cylindrotheca closterium* were the only phytoplankton present in all DBO regions, although *Chaetoceros socialis* and *Chaetoceros furcellatus* were observed in all regions except DBO3E and DBO4 respectively. *Cryptomonas* spp. and *Phaeocystis pouchetii* were only found north of the Bering Strait (DBO3-DBO5), although *Cryptomonas* spp. was not found in DBO5. *Phaeocystis pouchetii* was only observed as single cells, not in colonies. Diatoms were the most abundant and diverse in the entire DBO region, with *Thalassiosira*

nordenskioeldii, *Fragilariopsis oceanica*, *Cylindrotheca closterium* and spores of

Chaetoceros furcellatus present at 14-23 of the 24 stations analyzed.

Table 1.5. Phytoplankton taxa present at 10 or more stations in the PAR in 2013. Data are summarized for the entire PAR and by DBO region. The total number of stations where phytoplankton taxonomic analysis was conducted within each region is listed in parentheses below the region.

Group	Taxa present at 10 or more stations	Number of stations where taxa present						
		Total (24)	DBO1 (1)	DBO2 (1)	DBO3W (8)	DBO3E (4)	DBO4 (5)	DBO5 (5)
Flagellates <7µm	Flagellates <3µm	19	1	1	6	4	3	5
	Flagellates 3-7µm	20	1	1	6	4	5	2
Cryptomonads (Cryptophyceae)	<i>Cryptomonas</i> sp.	10	0	0	4	4	2	0
Prymnesiophyceae	<i>Phaeocystis pouchetii</i> *	11	0	0	3	1	5	2
Diatoms (Bacillariophyceae)	<i>Chaetoceros convolutus</i>	10	1	1	7	0	0	1
	<i>Chaetoceros furcellatus</i> , resting spores	14	1	1	7	2	0	3
	<i>Chaetoceros furcellatus</i>	11	1	1	6	1	0	2
	<i>Chaetoceros socialis</i>	11	1	1	6	0	1	2
	<i>Cylindrotheca closterium</i>	23	1	1	8	3	5	5
	<i>Fragilariopsis cylindrus</i>	10	0	0	3	0	4	3
	<i>Fragilariopsis oceanica</i>	14	0	1	5	0	4	4
	<i>Thalassiosira</i> >30µm	11	0	1	4	0	3	3
	<i>Thalassiosira antarctica</i> v. <i>borealis</i>	12	0	0	4	0	5	3
	<i>Thalassiosira nordenskioeldii</i>	14	0	1	5	0	4	4

* single cells

1.5 Discussion

1.5.1 Regional patterns of summertime nutrient and phytoplankton dynamics in the Pacific Arctic Region from 2006-2016

1.5.1.1 Nutrient and Phytoplankton Biomass

Our measurements of euphotic zone $[\text{NO}_3^-]$ and Chl *a* fell within the range of published summertime values and followed similar spatial trends (e.g. Hansell and Goering, 1990; Springer and McRoy, 1993; Lee et al., 2007; 2012; 2013a; Varela et al., 2013; Danielson et al., 2017). In the Chukchi Sea regions (DBO3-5), both $[\text{NO}_3^-]$ and Chl *a* exhibited depth profiles often observed in Arctic marine waters (e.g. Martin et al., 2012; Brown et al., 2015), with $[\text{NO}_3^-]$ depleted at the surface and a subsurface Chl *a* maxima (SCM) occurring at the depth where $[\text{NO}_3^-]$ increases (with DBO3E as an exception; Figure 1.2a-b). Nitrate concentrations increased with depth in all regions except in the eastern sector

of DBO3, but the increase was most pronounced in regions farther away from the Bering Strait (i.e. DBO1, DBO4 and DBO5). Similarly, although SCM were generally observed in all regions, this feature was least apparent in DBO2 (near the Bering Strait) and in the eastern sector of DBO3.

The highest $[\text{NO}_3^-]$ were usually observed in DBO2 in the Chirikov Basin (Table 1.3; Figure 1.3a), where turbulent mixing brings nutrient-rich bottom waters to the surface (Walsh et al., 1989). Chl *a* concentrations in DBO2 were low and invariant throughout the water column, which could be a reflection of our time of sampling given that the seasonal bloom in DBO2 typically occurs when the sea ice retreats earlier in the year (e.g. Springer and McRoy, 1993; Brown et al., 2011). However, given the high $[\text{NO}_3^-]$ throughout the water column, the low Chl *a* could be due to turbulent vertical mixing of the water (occurring after sea-ice melt) to below the critical depth. DBO2 had a relatively low stratification index ($\sim 0.5 \text{ kg m}^{-3}$, calculated as the difference between densities at the surface and bottom depths) compared to DBO1, DBO4 and DBO5 (1.7 to 3.3 kg m^{-3}), which confirms that the water column in DBO2 is well mixed. However, while DBO3W had a stratification index the same as that of DBO2 ($\sim 0.5 \text{ kg m}^{-3}$) and similarly high water-column $[\text{NO}_3^-]$, the time-averaged Chl *a* in DBO3W was 5-8 times higher throughout the water column compared to DBO2 (Figure 1.2b). These results suggest that bottom-up controls, such as mixing alone, cannot explain the low biomass in DBO2. Another possibility is top-down controls, such as grazing by zooplankton. While zooplankton grazing rates are generally low in the PAR compared to other Arctic and global ecosystems (e.g. Campbell et al. 2009; Sherr et al., 2009), grazing by microzooplankton in the Bering Sea has been shown to limit biomass accumulation in the

later stages of phytoplankton blooms (Sherr et al., 2013). The differences we observe between DBO2 and DBO3W could also reflect a difference in bloom timing between these regions, with the seasonal bloom in DBO3W occurring later (and thus closer to our sampling time), leaving less time for the zooplankton in this region to respond to the increasing phytoplankton biomass.

While $[\text{NO}_3^-]$ was detectable throughout the water column in DBO3W, it was almost undetectable in DBO3E. Chl *a* showed a similar trend, with values significantly lower in the eastern sector of DBO3 compared to the west. This east-west gradient is consistent with previous studies (e.g. Walsh et al., 1989; Cooper et al., 2012; Danielson et al., 2017) and is discussed in more detail in section 1.4.2.2. In DBO4 and DBO5, $[\text{NO}_3^-]$ and Chl *a* were usually minimal in the upper euphotic zone (100, 55 and 30% I_0) compared to the lower euphotic zone (15, 1 and 0.1% I_0). This is indicative of biological utilization of NO_3^- as the waters transit northwards and is reflected in the decreasing euphotic-zone $[\text{NO}_3^-]$ throughout the PAR, with $[\text{NO}_3^-]$ in the Chukchi Sea regions (DBO3 to DBO5) being about half of those in the northern Bering Sea regions (DBO1 and DBO2).

1.5.1.2 Primary productivity and nitrate utilization rates

The magnitude of our productivity estimates (ρC and ρNO_3) agreed with those in published studies (Table 1.6), except for ρNO_3 in the entire DBO3 region (DBO3E and W combined), where our measurements were 2-4 times higher than those reported previously (Lee et al., 2007, 2013a; Codispoti et al., 2013). This discrepancy is likely because of later sampling times (August) for the Lee et al. (2007; 2013a) studies. The discrepancy with Codispoti et al. (2013) may be driven by the assumed length of the growing season, given that they estimate the length of growing season in the southern Chukchi Sea to range from 40-86 days. The value of ρNO_3 for the Codispoti et al. study

listed in Table 1.6 is based on an 86-day growing season. Recalculating their estimate of ρNO_3 using a shorter, 40-day growing season increases this value from 10.3 to 22.1 $\text{mmol N m}^{-2} \text{ d}^{-1}$, which is then in good agreement with our own estimate of ρNO_3 for DBO3 (Table 1.6).

Spatial trends were similar for ρC , ρNO_3 and New-Prod. The similarity between ρNO_3 and New-Prod was primarily due to the relatively consistent PC:PN ratio, which is used for the conversion of ρNO_3 to units of C, throughout the study area and period (average $\pm$ SD = 6.8 ± 1.4 mol:mol). Distinct subsurface maxima were observed in DBO1 for ρC , and in DBO4 and DBO5 for ρC and ρNO_3 . With the exception of DBO1, profiles of ρC and ρNO_3 exhibited similar trends within each region, which suggests that NO_3^- utilization drives primary productivity in these regions. Despite generally high $[\text{NO}_3^-]$, productivity was almost undetectable at 1 and 0.1% I_0 in all DBO regions, which suggests that light is the limiting factor at these depths. It is possible that the relatively high ammonium concentrations ($[\text{NH}_4^+]$) of $\sim 1\text{--}3 \mu\text{mol L}^{-1}$ typically found below ~ 25 m (i.e. 1 and 0.1% I_0) in the PAR (e.g. Lee et al., 2012; 2013a; Danielson et al., 2017) may inhibit ρNO_3 at these depths (e.g. Dortch, 1990, Lomas and Gilbert, 1999); however, the fact that ρC is also low suggests that another factor (most likely light), rather than nutrients, may be responsible for the low productivity at 1 and 0.1% I_0 .

Latitudinal patterns of primary productivity reflected differences in the timing of the seasonal bloom, which are, in turn, tied to the timing of the annual sea-ice retreat (Brown et al., 2011; 2013). Sea-ice retreat begins in early May in DBO1 and continues northward as the season progresses (Brown et al., 2011; Frey et al., 2015).

Table 1.6. Depth-integrated primary productivity (ρC), nitrate utilization rates (ρNO_3) and f -ratios (mean $\pm$ SE) within or near the five DBO hotspot regions in the Bering and Chukchi Seas for June-August from 1954 to 2016. Data from DBO3 is split longitudinally into the western (DBO3W, influenced by the AW/BSW water mass) and eastern (DBO3E, influenced by the ACW water mass) sectors. Bold indicates data from this study and (-) indicates that no data are available. The number in parenthesis after the standard error (SE) indicates the number of samples. ICESCAPE stands for the ‘Impacts of Climate on the Eco-Systems and Chemistry of the Arctic Pacific Environment’ project.

Region	Date (Month, Year)	ρC (g C m ⁻² d ⁻¹)	ρNO_3 (mmol N m ⁻² d ⁻¹)	f -ratio	Data source
<i>Northern Bering Shelf</i>					
DBO1	Jul 2006-2016	0.34 $\pm$ 0.08 (8)	6.30 $\pm$ 1.64 (8)	0.53 $\pm$ 0.09 (3)	This study and Varela et al. (2013)
	Aug 1988	3.8 $\pm$ (-)	–	–	Springer and McRoy (1993)
	May-Jun 2007	0.99 $\pm$ 0.23 (12)	7.81 $\pm$ 1.28 (12)	0.76 $\pm$ 0.03 (12)	Lee et al. (2012)
DBO2	Jul 2007	0.17 $\pm$ 0.07 (2)	5.31 $\pm$ 3.36 (15) ^a	0.43 $\pm$ 0.16 (3)	Lee et al. (2013a)
	Jul 2006-2016	1.00 $\pm$ 0.34 (8)	7.19 $\pm$ 3.53 (8)	0.37 $\pm$ 0.11 (7)	This study and Varela et al. (2013)
	Jun-Sep 1969-1983	2.7 $\pm$ (-)	17.6 $\pm$ (-)	0.55 $\pm$ (n.d.)	Sambrotto et al. (1984)
	Jul-Sep 1987	–	8.0 $\pm$ 0.7 (15)	0.30 $\pm$ (n.d.)	Hansell and Goering (1990)
	Aug 1988	4.0 $\pm$ (-)	–	–	Springer and McRoy (1993)
	May-Jun 2007	1.03 $\pm$ 0.04 (3)	11.1 $\pm$ 3.2 (3)	0.83 $\pm$ 0.05 (3)	Lee et al. (2012)
Entire region (DBO1-DBO2)					
	Jul 2006-2016	0.67 $\pm$ 0.19 (16)	6.74 $\pm$ 1.88 (16)	0.42 $\pm$ 0.08 (10)	This study and Varela et al. (2013)
	Jul 1950-2012	1.8 $\pm$ 0.26 (68)	–	–	Hill et al. (2017)
	May-Sep 1954-2007	–	8.41 $\pm$ (-) ^c	0.4	Codispoti et al. (2013)
<i>Southeastern Chukchi Sea</i>					
DBO3W	Jul 2006-2016	3.40 $\pm$ 1.01 (7)	29.7 $\pm$ 12.0 (7)	0.48 $\pm$ 0.10 (6)	This study and Varela et al. (2013)
	Jul-Sep 1987	–	45.6 $\pm$ 0.7(2) ^b	0.50 $\pm$ (n.d.)	Hansell and Goering (1990)
	Jun-Aug 2002-2004	1.44 $\pm$ 0.66 (5)	10.0 $\pm$ 4.6 (5) ^b	0.41 $\pm$ 0.20 (5)	Lee et al. (2007)
DBO3E	Jul 2006-2016	0.15 $\pm$ 0.08 (2)	0.31 $\pm$ 0.23 (2)	0.16 $\pm$ 0.08 (2)	This study and Varela et al. (2013)
	Jul-Sep 1987	–	2.30 $\pm$ 0.54 (3) ^b	0.15 $\pm$ (-)	Hansell and Goering (1990)
	Jun-Aug 2002-2004	0.14 $\pm$ 0.04 (2)	1.02 $\pm$ 0.25 (2) ^b	0.19 $\pm$ 0.09 (2)	Lee et al. (2007)
Entire region (DBO3, all water masses)					
	Jul 2006-2016	2.68 $\pm$ 0.91 (9)	23.2 $\pm$ 10.2 (9)	0.40 $\pm$ 0.09 (9)	This study and Varela et al. (2013)
	Jul 1950-2012	3.02 $\pm$ 0.18 (22)	–	–	Hill et al. (2017)
	May-Sep 1954-2007	–	10.3 $\pm$ (n.d.) ^{c,d}	0.3 ^d	Codispoti et al. (2013)
	Jul 1974	1.3 $\pm$ 1.1 (3)	–	–	Hameedi (1978)
	Aug 1988	4.7 $\pm$ (-)	–	–	Springer and McRoy (1993)
	Jun-Aug 2002-2004	1.07 $\pm$ 0.56 (7)	8.22 $\pm$ 4.16 (7) ^b	0.35 $\pm$ 0.18 (7)	Lee et al. (2007)
	Aug 2007	1.61 $\pm$ 0.56 (4)	5.31 $\pm$ 3.36 (15) ^a	0.72 $\pm$ 0.11 (2)	Lee et al. (2013a)
	Jun 2010-2011	12.90 $\pm$ 3.25 (2)	–	–	Arrigo ICESCAPE unpubl. data*

Region	Date (Month, Year)	ρC (g C m ⁻² d ⁻¹)	ρNO_3 (mmol N m ⁻² d ⁻¹)	<i>f</i> -ratio	Data source
Northeastern Chukchi Sea					
DBO4	Jul 2006-2016	1.17 ± 0.39 (6)	8.84 ± 4.13 (6)	0.41 ± 0.12 (5)	This study and Varela et al. (2013)
	Jul 1974	1.3 ± 1.0 (3)	—	—	Hameedi (1978)
	Aug 1993	0.49 ± 0.17 (3)	1.11 ± 0.48 (3) ^c	0.17 ± 0.12 (3)	Cota et al. (1996)
	Jul-Aug 2002/2004	0.67 ± 0.06 (2)	—	—	Hill and Cota (2005)
	Aug 2007	0.18 ± 0.03 (6)	5.31 ± 3.36 (15) ^a	—	Lee et al. (2013a)
	Jul 2010-2011	0.67 ± 0.06 (2)	—	—	Arrigo ICESCAPE unpubl. data*
DBO5	July 2008/2015	0.99 ± 0.59 (2)	8.55 ± 2.55 (2)	0.50 (1)	This study and Varela et al. (2013)
	Jul 2002	~2	—	—	Hill and Cota (2005)
Entire region (DBO4-DBO5)					
	Jul 2006-2016	1.13 ± 0.33 (8)	8.77 ± 3.31 (8)	0.43 ± 0.12 (6)	This study and Varela et al. (2013)
	Jul 1950-2012	2.02 ± 0.47 (33)	—	—	Hill et al. (2017)
	May-Sep 1954-2007	—	5.89 ± (-) ^{c,d}	0.3 ^c	Codispoti et al. (2013)
	Aug 2008	1.38 ± 0.49 (11)	—	—	Coupel et al. (2015)

^aAverage rates for Northern Bering Sea to Northern Chukchi Sea.

^bAverage daily rates were calculated from hourly rates assuming a 15-h photoperiod (Hansell and Goering, 1990)

^cAverage daily rates were calculated from annual net community production (NCP), derived from *in situ* changes in [NO₃⁻] and [PO₄³⁻], assuming an 86-day productive season and a C:N ratio of 6.6 (Tables 3 and 5 in Codispoti et al., 2013)

^dSouthern Chukchi Sea from Codispoti et al (2013) covers DBO3-5.

^eAverage daily rates were calculated from daily primary production (based on ¹³C utilization rates) and % new production based on ¹⁵NO₃⁻ utilization rates and assuming a C:N ratio of 6.6 (Cota et al., 1996, Table 2)

* from Grebmeier et al. (2015)

By the time of our July sampling in DBO1, the seasonal bloom would have already passed, depleting nutrients in surface waters and resulting in a SCM below the nutricline (e.g. Cooper et al., 2012; Figure 1.2a-b). This agrees with our observations of a subsurface Chl *a* maximum generally at 1% I_0 (Figure 1.2b), with corresponding, but shallower maximum in ρC at 15% I_0 . A subsurface productivity maximum found at shallower depths than the SCM is consistent with previous observations in the PAR (Brown et al., 2015). This difference between the depths of the SCM and productivity maximum could be driven by an adaptation of phytoplankton to lower light levels through an increase in chlorophyll content. This would lead to a decrease in C:Chl *a* ratios with depth, consistent with that observed in this study (data not shown) and previously (e.g. Beardall and Morris, 1976; Falkowski et al., 1985). It is also possible that the high phytoplankton biomass observed below the ρC maximum in DBO1 could have been formed farther south, given that waters near the lower limit of the euphotic zone (15-0.1% surface irradiance) in this region also carry the temperature and salinity signature of the cold and saline waters flowing out of the Gulf of Anadyr. These waters transport both nutrients and organic matter northwards from the Pacific, and thus could have contributed to the high biomass concentrations we observe (e.g. Hansell et al., 1989). Nevertheless, it is most likely that the high phytoplankton biomass observed at 1% I_0 in DBO1 was produced locally given that both ρC and ρNO_3 were detectable at this depth. Furthermore, years with high euphotic-zone integrated Chl *a* generally also had high euphotic-zone integrated ρC and ρNO_3 (Table 1.3). This also suggests that high biomass we observed in DBO1 would have been produced locally and not advected into the region.

In contrast to the presence of a subsurface ρC maximum at 15% I_0 , ρNO_3 was relatively low and invariant throughout the water column at DBO1, which also supports the assertion that DBO1 was in a post-bloom condition at the time of our sampling.

Differences in the shape of the vertical profiles of ρNO_3 and ρC suggest that phytoplankton growth may have been supported by other, likely regenerated, N sources such as NH_4^+ , at least at the depth of the ρC maximum. Ammonium concentrations in the upper (100-30% I_0) and lower (15-0.1% I_0) euphotic zone in DBO1 were $\sim 0.5 \mu mol L^{-1}$ and $1-3 \mu mol L^{-1}$ respectively for our sampling period (Cooper et al., 2016a-g; 2017).

The low $[NO_3^-]$ in the upper euphotic zone could explain the low ρNO_3 observed at these depths; however, the low ρNO_3 in the lower euphotic zone despite high $[NO_3^-]$ could be due to inhibition of ρNO_3 by NH_4^+ given the higher $[NH_4^+]$ observed at these depths (Dortch, 1990; Lomas and Gilbert, 1999; Varela and Harrison, 1999). Previous work further supports that NH_4^+ may be responsible for reduced ρNO_3 , since Lee et al. (2013a) observed high $[NH_4^+]$ and ρNH_4 , and low ρNO_3 despite high $[NO_3^-]$ in the lower euphotic zone in late July in this region, only two weeks after our sampling time.

Primary productivity in DBO2 was relatively low given the high $[NO_3^-]$ in surface waters. This result could be tied to the timing of the seasonal phytoplankton bloom and grazing by zooplankton. Campbell et al. (2009) found that grazing rates by mesozooplankton doubled in summer compared to spring in the Chukchi Sea, with mesozooplankton consuming $\sim 28\%$ of primary productivity per day in summer. A concurrent study by Sherr et al. (2009) indicated that grazing by microzooplankton can also be an important process limiting phytoplankton biomass during the later stages of a bloom. However, combined microzooplankton-mesozooplankton grazing was found to

only consume a total of ~44% of primary productivity per day, which is still much lower than in other polar marine ecosystems such as the Barents Sea or the Southern Ocean (e.g. Table 4 in Sherr et al., 2009 and references therein).

Zooplankton may have also indirectly affected phytoplankton productivity in DBO2 through increased NH_4^+ release from excretion and nutrient regeneration into the water column (e.g. Steinberg and Saba, 2008), which, in turn, could inhibit ρNO_3 by phytoplankton as indicated for DBO1 above. This grazing-associated increase in $[\text{NH}_4^+]$ could limit the accumulation of Chl *a* and drive the system into a steady-state based on the use of regenerated nitrogen. The range of $[\text{NH}_4^+]$ observed in DBO2 during our sampling time was similar to that in DBO1 (i.e. $\sim 0.5 \mu\text{mol L}^{-1}$ and $1\text{--}3 \mu\text{mol L}^{-1}$ in the upper and lower euphotic zone, respectively; data from Cooper et al., 2016a-g; 2017). In both DBO regions, $[\text{NH}_4^+]$ were higher than those observed earlier in the season (e.g. Lee et al., 2012), indicating that NH_4^+ accumulated in the water column through the growing season up to levels that could be inhibiting ρNO_3 for some phytoplankton. However, diatoms, which are the dominant phytoplankton taxon throughout the nutrient rich waters of the Pacific Arctic (Figures 1.5-1.6), have higher half-inhibition constants for NO_3^- utilization by NH_4^+ ($K_i = \sim 2.7 \mu\text{mol L}^{-1}$ from Lomas and Gilbert, 1999) compared to other phytoplankton (e.g. $K_i = 0.24 \mu\text{mol L}^{-1}$ for the coccolithophore *Emiliana huxleyi* from Varela and Harrison, 1999), meaning that diatom utilization of NO_3^- is inhibited at higher $[\text{NH}_4^+]$ compared to other phytoplankton. Furthermore, while $[\text{NH}_4^+]$ in the upper euphotic zone was below the K_i threshold for diatoms in both DBO1 and DBO2, $[\text{NO}_3^-]$ was much higher in the upper euphotic zone of DBO2 compared to DBO1, which may

explain the higher productivity in DBO2 as there was simply more NO_3^- available to support phytoplankton growth.

The highest ρC and ρNO_3 in the PAR were generally found in the western sector of DBO3, likely the result of turbulent vertical mixing in the Chirikov Basin and Bering Strait providing nutrients to surface waters. Similar to $[\text{NO}_3^-]$ and Chl *a* distributions, east to west gradients in ρC and ρNO_3 were observed in DBO3, with the highest ρC and ρNO_3 in the western sector (i.e. station UTN-4), and lowest in the eastern sector (i.e. station SEC-5). Primary productivity and ρNO_3 continued to decrease northwards from DBO3 to DBO5 as $[\text{NO}_3^-]$ in surface waters decreased, likely a result of the intense productivity occurring in the southeastern Chukchi Sea (DBO3), and the lack of replenishment of nutrients as the waters travel north.

1.5.1.3 *f*-ratios and C export

The average *f*-ratio for all DBO regions was 0.41 ± 0.24 , which agrees well with previous results (Table 1.6). Some spatial variability was observed among DBO regions, with *f*-ratios being higher closer to the shelf edges (DBO1, DBO4 and DBO5), although differences were not significant. The effect of water mass differences in DBO3 was also evident in *f*-ratios, which were higher in the western sector (0.37) than in the eastern sector (0.15), as also seen in previous studies (Hansell and Goering, 1990; Lee et al. 2007).

On an annual basis and assuming steady-state, New-Prod can be considered equivalent to the amount of C available for export or net community production (NCP) in most marine systems (e.g. Platt et al., 1989). However, due to the high interannual variability of the PAR and limited temporal sampling of our study, it is challenging to use our one-time, short-term measurements to make such estimates. New-Prod in the Bering and

Chukchi Seas was calculated in previous studies from the seasonal drawdown of $[\text{NO}_3^-]$ (e.g. Sambrotto et al., 1984; Hansell et al. 1993), which may better reflect seasonal variations in primary productivity. Despite our New-Prod measurements only representing a snapshot of the growing season, our average daily New-Prod in the nutrient-rich waters of DBO3W ($2.34 \pm 0.78 \text{ g C m}^{-2} \text{ d}^{-1}$; Table 1.3) is remarkably close to the estimate based on the seasonal $[\text{NO}_3^-]$ drawdown given by Hansell et al (1993) for the same location ($2.4 \text{ g C m}^{-2} \text{ d}^{-1}$). While this agreement may suggest that our results could be extended to longer temporal and spatial scales, our estimates of daily New-Prod in the regions south of the Bering Strait ($0.48 \pm 0.13 \text{ g C m}^{-2} \text{ d}^{-1}$ for DBO1-2; Table 1.3) were much lower than the value reported by Hansell et al. (1993) for the same area ($3.1 \text{ g C m}^{-2} \text{ d}^{-1}$). This difference between our estimate and that of Hansell et al. (1993) for DBO1-2 could reflect the timing of our sampling with respect to the peak of the seasonal bloom in these regions (e.g. Cooper et al., 2012), since a lower New Prod estimate would be expected under post-bloom conditions. However, this difference could also reflect a longer-term (yearly) decrease in productivity, which is consistent with previously documented declines in primary productivity (Lee et al., 2012) and benthic biomass (Grebmeier et al., 2006b) in the region. Nevertheless, these comparisons highlight the importance of accounting for time and seasonal scales when attempting to equate New-Prod (estimated from short-term measurements of ρNO_3) to annual C export.

1.5.1.4 Phytoplankton Assemblages

The Bering and Chukchi Seas are dominated by diatoms, as shown by our 2013 phytoplankton composition data and previous studies (e.g. Gosselin et al., 1997; Booth et al., 1997; Hill and Cota, 2005; Sukhanova et al. 2009; Poulin et al., 2010; Coupel et al., 2012; Joo et al., 2012; Lee et al., 2012; Wyatt et al., 2013; Crawford et al., 2018).

Diatoms accounted for $65 \pm 21\%$ of the total phytoplankton assemblage, on average, for all DBO regions, with the exception of four stations in the eastern sector of DBO3 (SEC5 to SEC8). In DBO3E, the assemblage was primarily composed of coccolithophores and small ($<7\mu\text{m}$) unidentified flagellates. The presence of small non-diatom phytoplankton can be explained by the differences in water mass composition and lower nutrient content in the eastern sector of DBO3 in comparison to the western sector (see section 1.4.2.2).

Diatom abundance increased slightly towards the north (Figure 1.6b), likely due to the timing of the seasonal retreat of sea-ice and the northward propagation of the seasonal bloom (i.e. earlier stages of a bloom would be expected to have a larger diatom presence).

In DBO4, an increase in the abundance of pennate diatoms (primarily *Fragilariopsis* spp.) was associated with the presence of sea-ice (Figure 1.6). It is possible that the increased abundance of this diatom in the water column was due to sea-ice algae being released from sea-ice algal blooms, given that *Fragilariopsis* spp. are commonly found in sea ice (e.g. Booth et al., 1997; Lundholm and Hasle, 2010). However, our 2013 observations of very high ρC and ρNO_3 at 7-10 m depth combined with extremely low $[\text{NO}_3^-]$ in the euphotic zone (range: $0 - 0.7 \mu\text{mol L}^{-1}$) in DBO4 are indicative of an actively growing phytoplankton community below the ice. Several studies have reported the existence of diatom blooms near or below the ice in the Chukchi Sea (e.g. Booth et al., 1997; Coupel et al., 2012; Arrigo et al., 2014), although typically the assemblage composition is dominated by centric diatoms, such as *Chaetoceros* spp. and *Thalassiosira* spp., that are generally associated with the late stage of a pelagic bloom. Arrigo et al. (2014) also found *Fragilariopsis* species in an under-ice bloom and argued that these were pelagic species and not the remnant of a sea-ice bloom. Similar to Arrigo et al.

(2014), we cannot rule out that the diatoms present in the under-ice bloom were seeded from the sea-ice, even if our results suggest that they were part of a pelagic bloom.

Similar to diatoms, small ($<7\ \mu\text{m}$) flagellates were also present in all of the DBO regions during 2013, and slightly increased in abundance northwards. These flagellates were shown to dominate the phytoplankton assemblages in the oligotrophic waters of the Canada Basin (Crawford et al, 2018), but were also present on the Chukchi Shelf (e.g. Gosselin et al., 1997; Coupel et al., 2012; Crawford et al., 2018). Small flagellate plankton $<7\ \mu\text{m}$ are usually present throughout the global oceans under a variety of nutrient and light conditions (e.g. Chisholm, 1992); however, they typically only dominate the assemblage composition under low nutrient concentrations, which are less favourable to the growth of other phytoplankton (e.g. Pasciak and Gavis, 1974; Chisholm, 1992). Single cells of the small, flagellated species *Phaeocystis pouchetii* were present in the Chukchi Sea and were most abundant in DBO4, where total phytoplankton abundance was high. This species is often observed after the late stages of the seasonal bloom in polar waters (e.g. Sakshaug, 2004), or co-occurring with diatoms (e.g. Wassman et al. 1999; Olli et al., 2002), and can be a significant contributor to the vertical flux of C (Smith et al., 1991). The presence or absence of *Phaeocystis pouchetii* colonies can serve as an indicator of the stage of a phytoplankton bloom, with colonies disappearing toward the later stages of a bloom (e.g. Estep et al., 1990). The high abundance of both diatoms and single cells of *Phaeocystis pouchetii* in DBO4, but the lack of colonies of *Phaeocystis pouchetii*, suggest that our sampling may have occurred after the peak of the seasonal phytoplankton bloom.

Size fractionated measurements of Chl *a* are a relatively simple way to assess the size structure of phytoplankton assemblages. While no taxonomic data can be obtained from these measurements, this information is still important especially given that different size classes tend to dominate under different environmental conditions (Chisholm, 1992) and that zooplankton grazing rates depend on the phytoplankton size structure (Zurek and Bucka, 1994). The average contribution of the $>5\ \mu\text{m}$ Chl *a* to total Chl *a* for all productivity stations in 2013 was $77 \pm 13\%$ ($\pm\text{SD}$), and for the entire study period (2006-2016) it was $65 \pm 23\%$. Neither of these values are significantly different from the percent contribution of diatoms to total cell numbers in 2013, which suggests that the $>5\ \mu\text{m}$ Chl *a* size fraction could be used as a proxy for diatom biomass in this region. Furthermore, Wyatt et al. (2013) found a significant positive correlation between diatom abundance and the contribution of the $>5\ \mu\text{m}$ Chl *a* size fraction in marine waters throughout the Arctic. Thus, while the taxonomy of phytoplankton assemblages is only presented for 2013, size-fractionated Chl *a* data show evidence of spatial and interannual differences in the structure of phytoplankton assemblages between the Bering Sea (DBO1 and DBO2) and the Chukchi Sea (DBO3 to DBO5) during the 10-year period (Table 1.3; Figure 1.3c).

1.5.2 Drivers of regional differences in phytoplankton biomass and productivity in the Pacific Arctic Region

1.5.2.1 Environmental controls

The correlation analysis between euphotic-zone integrated biological parameters and several physical parameters indicated that there were geographical differences in bottom-up controls on phytoplankton biomass and productivity between the Bering Sea (DBO1, DBO2) and Chukchi Sea regions (DBO3-DBO5) (Table 1.4).

In the Bering Sea, $[\text{NO}_3^-]$ was positively correlated with surface and bottom S, which likely reflects the influence of the saline and nutrient-rich AW. The negative correlation between Z_{eu} and bottom T could be the result of earlier sea-ice retreat from 2012 to 2016 causing increased water column stratification and an earlier shift in the seasonal bloom (Grebmeier et al., 2018; Frey et al., this issue). Bottom water temperatures in DBO1 are relatively low in summer, experiencing only limited warming from their winter values as a result of persistent water column stratification (e.g. Cooper et al., 2012; Grebmeier et al., 2015). Earlier sea-ice melt could result in an even greater degree of stratification due to low-salinity surface waters having more time to warm, thus further limiting mixing of the water column and resulting in bottom water temperatures even closer to their very low winter values (Cooper et al., 2012). Earlier sea-ice retreat also results in an earlier onset of the seasonal bloom (Brown et al., 2013), meaning that by the time of our sampling each year, we are sampling later and later into the seasonal bloom, resulting in changes in phytoplankton phenology from year-to-year (see section 1.4.2.3). Changes in the abundance and type of phytoplankton present in the euphotic zone could allow light to penetrate deeper into the water column, and thus for the euphotic zone depth to increase. The positive correlations between ρC and both ρNO_3 and New-Prod indicate that NO_3^- was responsible for the high rates of primary production in the Bering Sea. Furthermore, the positive correlation between Chl a $>5 \mu\text{m}$ and New-Prod indicates that larger phytoplankton were the primary drivers of new production. The lack of a correlation between ρNO_3 and $[\text{NO}_3^-]$ may indicate that phytoplankton were not limited by the availability of NO_3^- in the Bering Sea. This is consistent with results from Lee et al. (2013a), who found that light, rather than NO_3^- , had a larger influence on ρC in marine

Arctic regions. In addition to light, our study suggests that bloom timing and zooplankton grazing could also influence rates of primary productivity in July (see section 1.4.1.2).

In the Chukchi Sea, no significant correlations were found between biological and physical water-column parameters, but it is highly unlikely that there were no physical controls on primary productivity during July. Alternatively, it is possible that other parameters, not considered in this study, may have affected productivity more strongly during this period. The lack of significant correlations may have also resulted from high interannual variability in the T-S properties of the different water masses (e.g. Coachman, 1975; Woodgate et al., 2005b), which could have confounded the correlations if the drivers of the physical variability did affect the biology in a similar way. Our statistical analyses suggest that phytoplankton $>5\ \mu\text{m}$ were the major contributors to total Chl *a* and primary productivity in the Chukchi Sea. Contrary to the situation in the Bering Sea, ρNO_3 and $[\text{NO}_3^-]$ were positively correlated in the Chukchi Sea, potentially due to a broader range of values for ρNO_3 and $[\text{NO}_3^-]$ strengthening the correlations. This result indicates that $[\text{NO}_3^-]$ exerted a stronger control on productivity towards the northern regions of DBO during July.

In summary, our correlation analysis indicates that phytoplankton were not limited by NO_3^- availability on the Northern Bering Sea and that NO_3^- utilization by phytoplankton $>5\ \mu\text{m}$ in size (primarily diatoms) drove the high rates of primary productivity throughout both the Northern Bering Sea and Chukchi Sea. This analysis also suggests that light, bloom timing, and zooplankton grazing could have a significant influence on primary productivity during July.

1.5.2.2 Water mass effects on phytoplankton assemblage composition and productivity

In 2013, a direct east-west comparison of the phytoplankton assemblage composition was conducted at all CTD/rosette stations in the southern Chukchi Sea. A similar direct comparison of euphotic zone $[\text{NO}_3^-]$, Chl *a*, ρC and ρNO_3 was conducted at the productivity stations UTN-4 (DBO3W) and SEC-5 (DBO3E) in 2014. A strong east-west gradient in $[\text{NO}_3^-]$, and phytoplankton biomass, productivity and assemblage composition was found in the DBO3 region (Figures 1.2-1.6, Table 1.3). The values of these biological parameters were up to two orders of magnitude lower on DBO3E compared to DBO3W, and these differences coincided with changes in T, S and $[\text{NO}_3^-]$ measured at all CTD/rosette stations in DBO3 (Figure 1.7; data from Cooper et al. 2016e).

The T, S and $[\text{NO}_3^-]$ data we present in Figure 1.7 are only for 2013 so that the spatial trends in these parameters are directly comparable with the phytoplankton assemblage data show in Figure 1.6; however, similar spatial differences between W and E for T, S and $[\text{NO}_3^-]$ were observed during other years, including 2014 (Figures 1.2-1.3, Table 1.3; Cooper et al., 2016a-g; 2017). Abundant phytoplankton assemblages in DBO3W were dominated by diatoms, in contrast to the flagellate- and coccolithophore-dominated assemblages of DBO3E. Previous studies in nearby areas of the northern Bering and Chukchi Seas have also shown an east-west gradient in nutrients, Chl *a* and the size structure of phytoplankton assemblages (e.g. Walsh et al., 1989; Cooper et al., 2012; Danielson et al., 2017), and primary productivity (Lee et al., 2007), likely driven by the presence of different waters masses on each side of the transect. The nutrient poor waters of ACW on DBO3E cannot support the high rates of primary production and high diatom abundance characteristic of DBO3W and the other DBO regions.

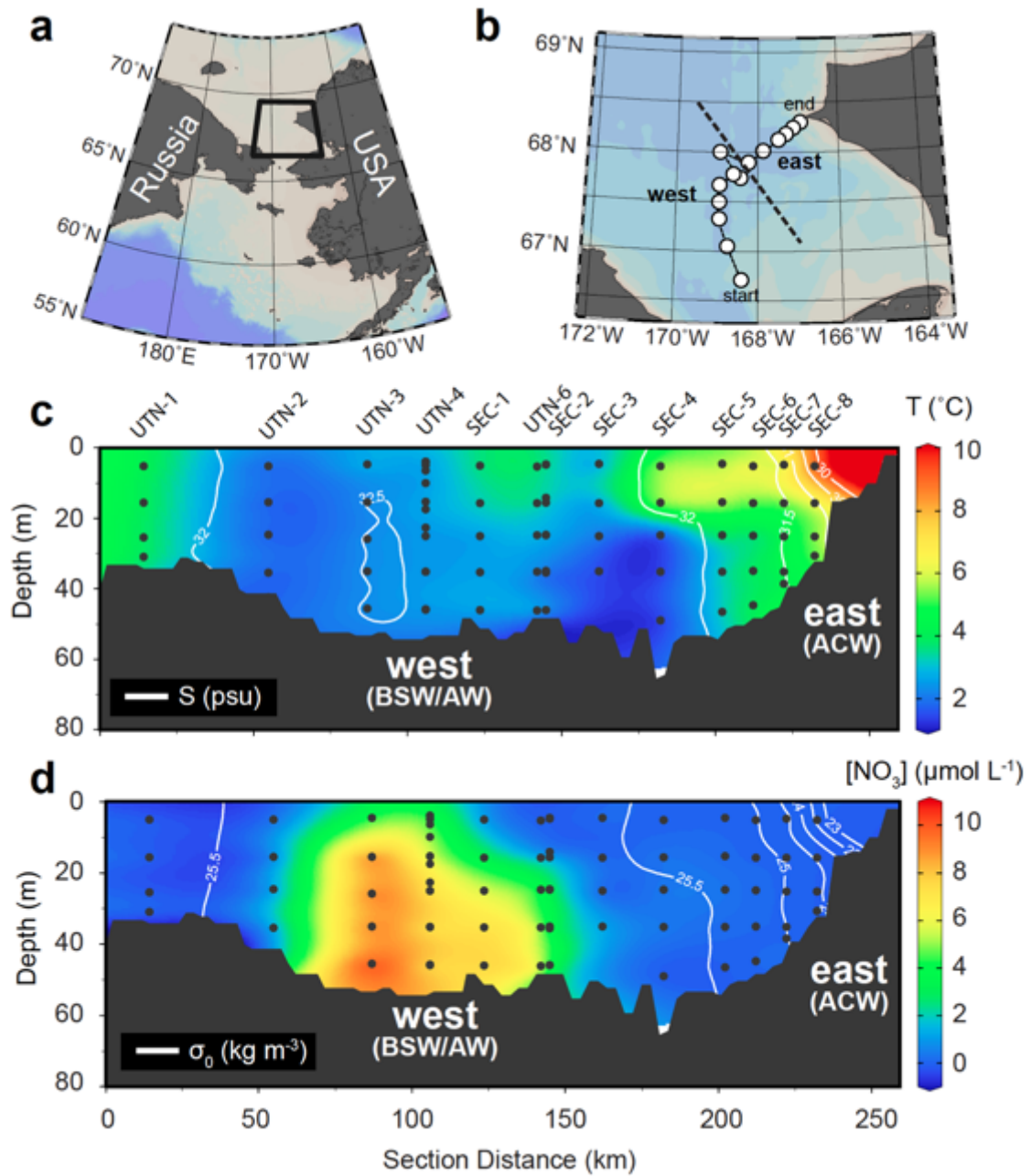


Figure 1.7. Physico-chemical differences between the Alaska Coastal Water (ACW) in the east and Bering Shelf Water (BSW/AW) in the west, along the DBO3 transect in the southeastern Chukchi Sea in July 2013. (a) Map of the PAR, with the black box denoting the bounding coordinates for panel b. (b) Map of the transect line. (c) Vertical section of temperature (T) with contours of salinity (S) superimposed in white. (d) Vertical section of NO_3^- concentration with contours of potential density (σ_0) superimposed in white. T-S data for all stations, and $[\text{NO}_3^-]$ data from CTD/rosette stations are from Cooper et al., 2016e.

In contrast, coccolithophores and other small phytoplankton are better adapted to the low nutrient conditions of DBO3E given their higher surface area to volume ratios and typically lower nutrient half-saturation constants (K_s) than diatoms (e.g. Eppley et al., 1974). The presence of coccolithophores in the PAR is not unprecedented (e.g. Napp and Hunt, 2001; Stockwell et al., 2001). A sustained bloom that lasted >2-3 months was first observed in the Bering Sea in 1996 using satellite ocean color (Merico et al., 2003); however, there has been some indication that coccolithophore abundance in the Bering Sea has decreased in recent years (Iida et al., 2012) due to reduced surface stratification.

Although DBO focuses on biological hotspots, the east-west gradient observed in DBO3 suggests that large spatial variability in water-column physical, chemical and biological parameters could still exist within each of the DBO regions. Furthermore, these spatial variations in water mass composition and properties coincide with changes in benthic ecosystems in DBO3 (e.g. Grebmeier et al., 2015). Given that diatoms are the major contributor to phytoplankton biomass and productivity in the nutrient-rich waters that overlay benthic hotspots, it is important to consider how climate-induced changes can impact diatom dynamics and how this may cascade up the food web and affect pelagic-benthic coupling. Increasing temperatures and changing sea-ice cover may result in summertime conditions that are unfavourable to diatoms, but instead support the growth of coccolithophores and other small phytoplankton, as seen in the oligotrophic Arctic basin (Li et al., 2009) and in DBO3E (this study). Climatic changes throughout the PAR could also lead to variations in plankton phenology, including a shorter period of sea-ice algal production and a longer period of pelagic production. Changes in phenology could ultimately result in a shift from benthic to pelagic-dominated marine ecosystems

(e.g. Grebmeier et al. 2006; Moore and Stabeno, 2015). These effects could be further exacerbated if the contribution of nutrient-rich AW to the Chukchi Sea decreased, or if there were changes to the T-S properties of waters flowing through the Bering Strait. Previous studies documented decreases in the volume and distribution of AW into the region that contributed to significant decreases in primary productivity and the contribution of larger ($>5\ \mu\text{m}$) cells to the phytoplankton assemblage (Lee et al., 2013b; Yun et al., 2014). However, these biological changes could have also been driven by variations in phytoplankton phenology due to increased temperatures and decreased salinities of the Bering Strait inflow (Woodgate et al., 2018). Ultimately, a negative impact to the base of the regional food web could result in the loss of the DBO benthic hotspots and, furthermore, they could have far reaching consequences for biogeochemical fluxes and climate feedbacks in the region and further into the Arctic.

1.5.2.3 Temporal trends and interannual variability in the Bering and Chukchi Seas

We compared historical measurements of phytoplankton productivity with our own findings for the five DBO regions (Table 1.6). While there is fairly good agreement between this and past studies, it is unclear whether any differences are indicative of year-to-year productivity changes in the region, or simply the result of differences in the time of sampling (i.e. earlier vs. later in the growing season), in methodology (i.e. productivity method, incubation time), in sampling location, and, most importantly, whether the changes are due to the lack of comprehensive spatial and temporal coverage. Therefore, it is difficult to draw any significant conclusions regarding changes prior to 2006.

Our sampling occurred at the same time (mid-July) and used consistent methodology every year from 2006 to 2016 to allow for valid comparisons. We observed large interannual variations in all parameters, with almost no consistent year-to-year trends

throughout the 10-yr period (i.e. see Table 1.3 and Figures 1.4-1.6). These results exemplify the difficulties in identifying long-term trends in this region. One exception was a significant decreasing trend in the contribution of the $>5 \mu\text{m}$ Chl *a* to total Chl *a* in DBO1 from 2012 to 2016. This trend could have been the result of a shift in the timing of the spring bloom from later to earlier in the growing season, meaning that with each passing year we sampled later stages of the phytoplankton spring bloom. Brown et al. (2013) showed that the timing of the spring bloom on the Bering Sea shelf was dependent on the timing of the seasonal sea-ice breakup. Although decadal changes in the mean timing of sea-ice breakup were not observed in DBO1 from 1978-2012 (Grebmeier et al., 2015), this timing did decrease over the shorter 2012-2016 period (Grebmeier et al., 2018; Frey et al., this issue), which suggests that spring blooms could have happened earlier with the passing years from 2012 to 2016. While the decrease in the proportion of $>5 \mu\text{m}$ Chl *a* over this period indicates that phytoplankton phenology responds to short-term environmental changes, it is difficult to know whether or not such changes to the ecosystem can be sustained throughout a longer period given the naturally high interannual variability of the region. These results further highlight the need for long-term and consistent monitoring programs, like DBO, to better understand present and future climate-induced changes on the productive ecosystems of the PAR.

1.6 Conclusions

We present here a decade of information on phytoplankton and nutrient dynamics during summer for five biological ‘hotspots’ in the northern Bering and Chukchi Seas. Although interannual variability was high for all measured parameters, we consistently found that diatoms dominated the phytoplankton assemblages throughout most of the DBO regions, and phytoplankton biomass and productivity were high under the influence

of the nutrient rich AW. In contrast, the coastal region of the southeastern Chukchi Sea was dominated by coccolithophores and flagellated plankton and characterized by low euphotic zone $[\text{NO}_3^-]$, and low phytoplankton biomass and productivity. These contrasting results demonstrate the presence of an east to west gradient in phytoplankton assemblage composition, biomass, and productivity in the southeastern Chukchi Sea that could be attributed to differences in the nutrient content of the water masses affecting these locations. Another highlight of this study is the finding that the presence or absence of sea-ice can impact the composition of phytoplankton assemblages. In the northern Chukchi Sea, pennate diatoms have higher abundances than centric diatoms when sea-ice was present. The low $[\text{NO}_3^-]$, but high ρC and ρNO_3 throughout the euphotic zone of this northern region suggest that the abundance of pennate diatoms is the result of a pelagic boom rather than them being supplied by a sea-ice bloom. Finally, our results suggest that, because of the generally high $[\text{NO}_3^-]$ within the euphotic zone throughout most DBO regions, light and/or grazing may exert a greater control on phytoplankton productivity than $[\text{NO}_3^-]$ during July.

An important aspect of this work was the consistency in methodologies, and sampling time and locations throughout the 10 years that allowed for rigorous comparisons both temporally and spatially. Results from this study emphasize the significant interannual variability in phytoplankton biomass and productivity that cannot be attributed to differences in methodology. However, the highly dynamic nature of the PAR may be responsible for such large interannual variations and can complicate the identification of long-term trends.

This study contributes to our knowledge of temporal and spatial variations in summertime productivity for this region, but also illustrates the need for a better understanding of the long-term temporal variability that will likely only be revealed by increased sampling resolution, both seasonally and annually. The PAR is an important gateway for nutrients and biomass to the Arctic Ocean. Improving our ability to constrain climate-induced changes against the backdrop of natural interannual variability will greatly enhance our ability to predict how future environmental change will affect this ecologically and economically important region.

Chapter 2
**A decade of diatoms: summertime silica dynamics in the
Pacific Arctic Region from 2006 to 2016**

2.1 Abstract

We present a decade of dissolved and particulate silica concentrations within five biological ‘hotspots’ in the Pacific Arctic Region (PAR), composed of the Bering and Chukchi Seas, and the first measurements of biogenic silica production rates from a period of four years at the same sites. Our results confirm that diatoms are responsible for most of the high primary productivity in this region and that phytoplankton phenology is responding to short-term climatic changes. The ‘hotspots’ sampled were identified as part of the Distributed Biological Observatory (DBO), and were located south of St. Lawrence Island (DBO1), south of the Bering Strait in the Chirikov Basin (DBO2), in the southeastern (DBO3) and northeastern (DBO4) Chukchi Sea, and in Barrow Canyon (DBO5). Silicic acid ($\text{Si}(\text{OH})_4$), and biogenic (bSiO_2) and lithogenic silica (lSiO_2) concentrations were measured in the euphotic zone during eight cruises in July 2006, 2008, and yearly from 2011 to 2016. Rates of bSiO_2 production (ρSi) were measured in the euphotic zone from 2013 to 2016. Average $\text{Si}(\text{OH})_4$ and bSiO_2 concentrations increased with depth and euphotic-zone integrated values were similar in all regions with the exception of lower $\text{Si}(\text{OH})_4$ and higher bSiO_2 in the southeastern Chukchi Sea. Rates of bSiO_2 production were high throughout the PAR, with the highest values in the southeastern Chukchi Sea. Both $[\text{bSiO}_2]$ and ρSi were comparable to previous measurements in the Southeastern Bering Sea. In the southeastern Chukchi Sea, we observed an east to west gradient in biogenic silica concentrations and production rates that could have been driven by differences in NO_3^- rather than $\text{Si}(\text{OH})_4$. Diatoms contributed an average of 62% to primary productivity and 87% to NO_3^- utilization for the entire region from 2013-2016, confirming that diatom utilization of NO_3^- is responsible for the high rates of productivity observed. Irradiance and $\text{Si}(\text{OH})_4$ exhibited

both separate and interactive effects on bSiO_2 production, with irradiance modulating both the magnitude of bSiO_2 production and the response of diatoms to changes in Si(OH)_4 . Despite the dynamic nature of the PAR driving strong interannual variability within each DBO region, we observed some temporal trends indicating that phytoplankton phenology is responding to short-term climatic changes. Such changes may have far reaching effects on other regions of the Arctic influenced by the Pacific-origin waters flowing through this important gateway to the Arctic.

2.2 Introduction

Diatoms dominate the highly productive waters of the Pacific Arctic Region (PAR) that extends from the northern Bering Sea to the Beaufort Sea (e.g. Gosselin et al., 1997; Varela et al., 2013; Crawford et al., 2018; Chapter 1). Accounting for approximately 40% of the total annual marine primary production (Nelson et al., 1995; Smetacek, 1999; Tréguer and Pondaven, 2000), diatoms are unique among phytoplankton in that they have an obligate requirement for Si. Diatoms take up dissolved Si from the water column in the form of silicic acid (Si(OH)_4) and convert it to biogenic silica (bSiO_2) to form their siliceous cell walls (frustules). Ballasted by their relatively heavy silica frustules, these unicellular organisms are not only a major contributor to the biological carbon pump (Buesseler, 1998), but also to the downward fluxes of bSiO_2 and particulate N. Thus, diatoms can significantly affect the biogeochemical cycling of Si, C, and N through both the photosynthetic process and their subsequent export. In order to better understand ecosystem-level responses to climate-induced oceanic changes, it is critical to evaluate the role of diatoms in the marine cycling of C, N, and Si and the coupling between these cycles. This is especially true in the high-latitude oceans where changes in marine

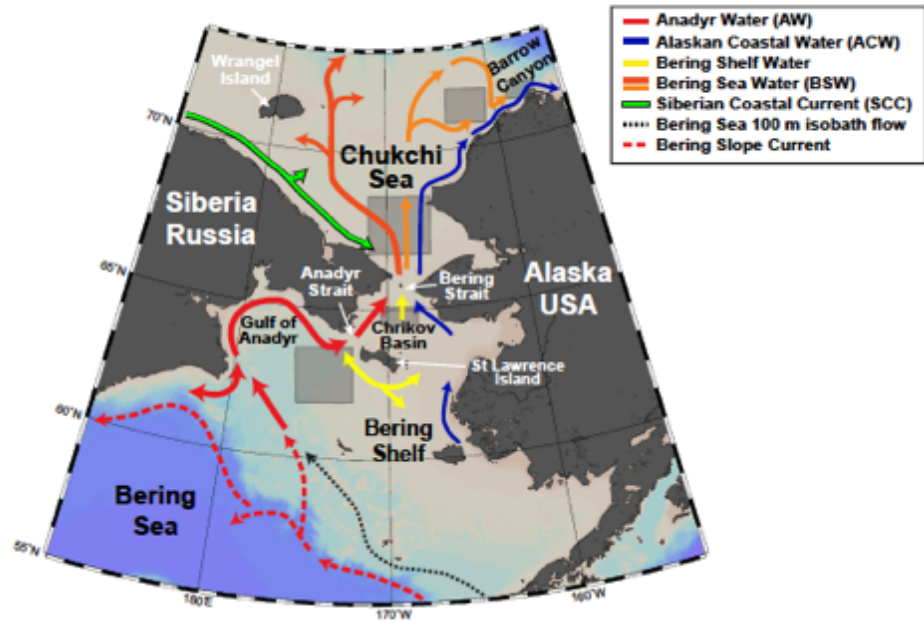
ecosystem from climatic variability have already been documented (e.g. Li et al., 2009; Grebmeier et al., 2012; 2015).

Encompassing areas influenced by the advection of Pacific waters into the Arctic, the PAR is undergoing rapid shifts in ecosystem structure and function driven by climate-induced changes (e.g. Overland and Stabeno, 2004; Grebmeier et al., 2012; 2015; Moore et al., 2014; 2015; Nelson et al. 2014). The highly-productive continental shelves of the northern Bering and Chukchi seas sustain some of the highest benthic macrofaunal biomass in the world's oceans (Grebmeier and McRoy, 1989; Highsmith and Coyle, 1990). This is primarily as a result of the shallow water-columns and low zooplankton grazing pressures that tightly couple the diatom-dominated pelagic primary production to the benthos (Campbell et al., 2009; Sherr et al., 2009; 2013; Grebmeier et al., 2006a; 2015; Mathis et al., 2014). While biological and physical processes in the region are strongly impacted by the inflow of nutrients, heat and freshwater from Pacific waters (Grebmeier et al., 2006a; Serreze et al., 2006; Woodgate et al., 2010), declining sea ice extent and earlier sea ice retreat, along with increasing ocean temperatures and decreasing salinity are also affecting the biological state in this region, making it one of the fastest changing marine environments (e.g. Stabeno et al., 2007; Woodgate et al., 2012; Jeffries et al., 2013; Frey et al., 2014; 2015; Stroeve et al., 2014; Wood et al., 2015). These climate-induced changes have a major impact on both the timing and magnitude of the seasonal phytoplankton bloom, with potential cascading effects on the marine food web (e.g. Brown et al., 2013; Grebmeier et al., 2015).

The northward flow of Pacific waters into the Arctic is driven by a sea level gradient towards the Chukchi Sea, despite prevailing winds being opposite to this pressure-driven

flow (Coachman and Aagaard, 1966; Stigebrandt, 1984; Woodgate et al., 2005a,b). Three major water masses make up the waters that flow from the northern Bering Sea into the Bering Strait (Figure 2.1a): Anadyr Water (AW) on the western side, Alaskan Coastal Water (ACW) on the eastern side, and Bering Shelf Water in the middle. These water masses are primarily differentiated by their temperature, salinity and nutrient characteristics, with AW being cold, saline and nutrient-rich, ACW warm, less saline and nutrient-poor, and BSW falling in between (Coachman et al., 1975; Walsh et al., 1989). Through the Bering Strait, AW and Bering Shelf Water combine into Bering Sea Water (BSW). The BSW splits into three main pathways that follow the local bathymetry, which contributes to a west-to-east nutrient gradient, with the highest nutrient concentrations occurring in the western Chukchi Sea where the contribution of AW to BSW is highest (Figure 2.1a; Coachman et al., 1975; Walsh et al., 1989; Woodgate et al., 2010). The nutrient-poor waters of the ACW on the far eastern side of the Chukchi Sea also contribute to this nutrient gradient, which in turn drives significant west-to-east gradients in Chl *a*, phytoplankton assemblages and PP, with diatom-dominated phytoplankton assemblages and much higher biomass and phytoplankton productivity occurring in the nutrient rich waters of the BSW (e.g. Walsh et al., 1989; Lee et al., 2007; Cooper et al., 2012; Danielson et al., 2017; Chapter 1). While low nutrient waters from the south-flowing Siberian Coastal Current (SCC) are also found on the far western side of the Chukchi Sea, waters from the SCC only contribute a small portion to the overall water mass mixture in the Chukchi Sea (Weingartner et al., 1999). Overall, BSW makes up more than ~80% of the waters flowing into the Chukchi Sea from the Bering Strait.

a



b

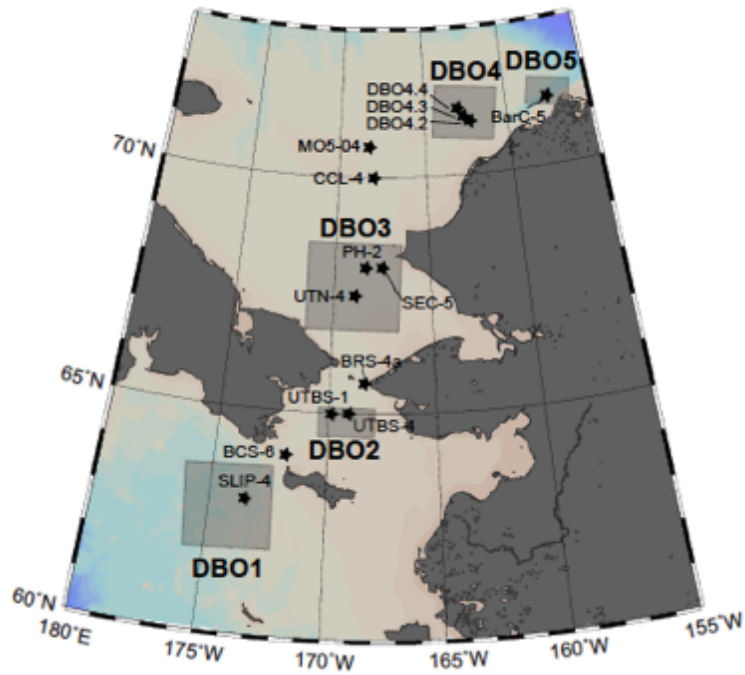


Figure 2.1. (a) Map of the PAR with major geographical features, water mass flow patterns, and DBO region bounding boxes in grey. Adapted from Grebmeier et al. (2015) with updated flow patterns for the Bering Slope Current and Bering Sea 100 m isobath flow from Stabeno et al. (2016). (b) Diatom productivity station locations (black stars) bounding boxes for each DBO region.

It is the nutrient-rich AW and BSW, along with the shallow bathymetry of the Bering and Chukchi shelves that fuels the high rates of primary production observed in these regions.

The naturally strong spatial, seasonal and interannual variability in the PAR make it difficult to constrain the extent to which physical and biological changes can be attributed to the bottom-up pressures of climate change. In an effort to address how climate change is affecting the ecosystem in the PAR, the Distributed Biological Observatory (DBO) was established in 2010 (Grebmeier et al., 2010; Moore and Grebmeier, 2018). As part of the DBO, a series of five transects centered on ‘biological hotspots’ in the PAR are re-occupied both seasonally and annually by a number of participating international collaborators (Figure 2.1b). The five DBO regions are located within the influence of the St. Lawrence Island Polynya (DBO1), in the Chirikov Basin between St. Lawrence Island and the Bering Strait (DBO2), in the southeastern (DBO3) and northeastern (DBO4) Chukchi Sea, and in Barrow Canyon (DBO5).

Our knowledge of the marine cycling of bSiO_2 in the PAR is minimal. Astakhov et al. (2015) showed that the fine-grained sediments in the southeastern Chukchi Sea have a high content of biogenic silica composed primarily of diatoms. Wyatt et al. (2013) looked at the distribution of water column bSiO_2 concentrations within a number of regions along the path of Pacific-origin waters through the Arctic, showing that $[\text{bSiO}_2]$ were the highest in the PAR; however, there was no detail on the more localized spatial variability within the PAR. Several studies have shown that phytoplankton $>5 \mu\text{m}$ contribute the most to primary and new production in the region (Lee et al., 2012; 2013; Varela et al., 2013), with the $>5 \mu\text{m}$ phytoplankton fraction generally believed to be composed of

mainly diatoms (e.g. Wyatt et al., 2013; Crawford et al., 2018; Chapter 1). Only one study in the southeastern Bering Sea directly measured bSiO_2 production (Banahan and Goering, 1986), and showed generally high rates in the region, with values increasing from the Bering Sea basin onto the shelf. Despite all of these studies indicating that diatoms dominate productivity in the PAR, there have been no direct measurements of bSiO_2 production in the northern Bering and Chukchi Seas.

Here, we present measurements of dissolved and particulate SiO_2 concentrations from 2006 to 2016 within the five DBO regions, and the first measurements of bSiO_2 production rates from 2013 to 2016 at the same sites. Our primary objectives were to quantify a baseline for bSiO_2 production and evaluate the spatial and interannual variability among DBO regions. Furthermore, we wanted to confirm suggestions from previous studies that diatoms are the major contributors to primary and new production in the nutrient-rich waters of the PAR. Finally, we sought to elucidate potential environmental controls on this variability to better predict how marine bSiO_2 dynamics might vary under current or predicted climatic changes.

2.3 Methods

2.3.1 Sampling Locations and Seawater Sampling

Sampling was conducted within (or near) the five DBO hotspot regions in the northern Bering and Chukchi Seas in July of 2006, 2008 and yearly from 2011 to 2016 (Figure 2.1). Cruises from 2011-2016 were part of the DBO. The cruise conducted in 2006 was part of the Bering Strait Environmental Observatory program, while the cruise in 2008 was part of the International Polar Year Canada's Three Oceans (IPY-C3O) program. The $[\text{Si}(\text{OH})_4]$ and $[\text{bSiO}_2]$ measurements from 2008 presented here represent a subset of the data already published in Varela et al. (2013) and Wyatt et al. (2013), respectively.

We include the 2008 data in this paper to provide a historical context to our data from 2006 and to our DBO dataset from 2011 onwards.

We present dissolved and particulate SiO_2 concentrations and bSiO_2 production rates from the same ‘primary productivity’ stations as those described in Chapter 1, which we refer to as ‘diatom productivity’ stations in this Chapter (black stars in Figure 2.1b; Table 2.1). For these stations, the aim was to conduct experiments at the same stations every year, although this was not always logistically possible due to ice and weather conditions. Data from stations in DBO3 are separated into ‘eastern’ and ‘western’ sectors (DBO3E and DBO3W) due to the significant spatial differences in water mass properties across this region. Stations UTN-4 and PH-2 were considered to be on the ‘western’ side, while station SEC-5 was considered to be on the ‘eastern’ side.

Seawater samples were collected at six depths corresponding to light levels of 100%, 55%, 30%, 15%, 1% and 0.1% of the surface incident irradiance (I_0). Seawater from 100% I_0 were collected at a ‘surface’ depth of 1-2 m. At each light level, we measured the concentrations of silicic acid ($\text{Si}(\text{OH})_4$) and particulate silica (bSiO_2 and lSiO_2) from 2006 to 2016. From 2013-2016, we added measurements of bSiO_2 production rates (ρSi) using the radioisotope ^{32}Si . The precision of all analytical techniques was determined from triplicate subsamples collected at one or more depths at each station every year from 2013-2016. Seawater samples for phytoplankton biomass (as Chl *a*) and primary productivity and nitrate uptake experiments were also collected simultaneously from the same water samples and have been presented in Chapter 1.

2.3.2 Dissolved silica concentrations

Samples for $[\text{Si}(\text{OH})_4]$ were syringe-filtered through pre-combusted $0.7\ \mu\text{m}$ glass fibre filters and collected in acid-washed 30-mL polypropylene bottles. Samples were

immediately frozen at -20°C ($[\text{Si}(\text{OH})_4]_{\text{frozen}}$) until analysis on shore using an Astoria

Nutrient Autoanalyzer and following the protocols of Barwell-Clark and Whitney (1996).

Table 2.1. Sampling locations for each of the eight cruises in the Bering and Chukchi Seas from 2006 – 2016. Stations from DBO3 are split into the western (DBO3W) and eastern (DBO3E) sectors due to differences in water mass composition (AW/BSW and ACW, respectively). Note that DBO3E was only sampled in 2012 and 2014, while DBO3W was sampled on every cruise except in 2012.

Cruise ID (YEAR-ID)	Date	Station	Latitude (°N)	Longitude (°W)	Bottom Depth (m)	Euphotic Zone Depth, Z_{eu} ^b (m)	DBO Region
2006-01	13 Jul	BCS-6	64.044	171.841	49	36	1 ^c
	16 Jul	BRS-4a	65.670	168.341	50	40	2 ^c
	18 Jul	PH-2	68.093	168.369	57	27	3W
	19 Jul	M05-04	70.644	168.244	45	30	4 ^c
2008-02	16 Jul	SLIP-4	63.026	173.456	74	59	1
	17 Jul	UTBS-1	64.990	169.140	49	44	2
	19 Jul	UTN-4	67.504	168.903	51	42	3W
	20 Jul	CCL-4	69.991	168.020	50	30	4 ^c
2011-18	21 Jul	BC-2	71.414	157.497	127	44	5
	15 Jul	SLIP-4	63.030	173.460	71	37	1
	16 Jul	UTBS-1	64.990	169.139	48	32	2
	17 Jul	UTN-4	67.500	168.909	49	20	3W
2012-09	14 Jul	SLIP-4	63.030	173.460	73	40	1
	15 Jul	UTBS-4	64.961	169.885	50	30	2
	17 Jul	SEC-5	68.131	167.510	55	30	3E
2013-05	14 Jul	SLIP-4	63.030	173.460	71	48	1
	15 Jul	UTBS-1	64.992	169.139	49	42	2
	19 Jul	UTN-4	67.500	168.943	51	22	3W
	22 Jul	DBO4.4	71.360	163.028	45	22	4
	23 Jul	BarC-5	71.410	157.491	125	24	5
2014-12	15 Jul	SLIP-4	63.030	173.460	71	46	1
	16 Jul	UTBS-1	64.991	169.141	48	38	2
	17 Jul	UTN-4	67.501	168.904	50	36	3W
	18 Jul	SEC-5	68.128	167.495	50	39	3E
	20 Jul	DBO4.3	71.233	162.635	46	37	4
2015-07	15 Jul	SLIP-4	63.030	173.461	74	67	1
	16 Jul	UTBS-1	64.991	169.141	48	25	2
	17 Jul	UTN-4	67.500	168.942	49	26	3W
	19 Jul	DBO4.4	71.362	163.031	44	38	4
	20 Jul	BarC-5	71.410	157.491	125	29	5
2016-17	13 Jul	SLIP-4	63.030	173.461	72	67	1
	14 Jul	UTBS-1	64.991	169.141	49	44	2
	16 Jul	UTN-4	67.500	168.942	50	25	3W
	18 Jul	DBO4.2	71.102	162.275	49	39	4

^a Cruise IDs were designated by the Department of Fisheries and Oceans Canada

^b Euphotic zone depth extends from the surface to the 0.1% incident surface irradiance (I_0) level. Euphotic zone depth (Z_{eu}) corresponds to the 0.1% I_0 depth.

^c In 2006 and 2008, cruises were not conducted as part of the DBO program, therefore sampling stations were not always located within each specified DBO region. Stations where sampling occurred near (but not within) the five DBO regions were included within the closest DBO region.

Starting in 2014, additional replicate samples for $[\text{Si}(\text{OH})_4]$ were syringed-filtered through $0.6\ \mu\text{m}$ PC filters and stored at 4°C ($[\text{Si}(\text{OH})_4]_{\text{cold}}$) until analysis on shore to

evaluate potential methodological biases in our original $[\text{Si}(\text{OH})_4]$ collection and storage protocol. The results of this analysis showed that $[\text{Si}(\text{OH})_4]_{\text{cold}}$ had a lower median coefficient of variation ($\text{CV}_{\text{cold}} = 8\%$) compared to $[\text{Si}(\text{OH})_4]_{\text{frozen}}$ ($\text{CV}_{\text{frozen}} = 16\%$), and that $[\text{Si}(\text{OH})_4]_{\text{frozen}}$ was $16 \pm 3\%$ (mean $\pm$ SE, $n = 29$) lower than $[\text{Si}(\text{OH})_4]_{\text{cold}}$ when $[\text{Si}(\text{OH})_4]_{\text{cold}} > 15 \mu\text{mol L}^{-1}$ (Appendix C). Correcting $[\text{Si}(\text{OH})_4]$ from 2006 – 2013 for this offset would have corresponded to marginal increases in depth-integrated $[\text{Si}(\text{OH})_4]$ (mean: 4.5%, range: 0 – 21%) and biogenic silica production rates (ρSi) (mean: 5%, range: 0 – 7.4%). Thus, considering that (1) these increases in $[\text{Si}(\text{OH})_4]$ and ρSi are less than the median CV for these parameters (8% and 11% respectively), and (2) there is considerable spread in $[\text{Si}(\text{OH})_4]_{\text{frozen}}$ compared to $[\text{Si}(\text{OH})_4]_{\text{cold}}$ above $15 \mu\text{mol L}^{-1}$, the $[\text{Si}(\text{OH})_4]$ data from 2006 – 2013 were not corrected.

2.3.3 Particulate silica concentrations

Seawater samples (0.5 – 2.3L) for particulate SiO_2 were filtered through $0.6 \mu\text{m}$ pore-size PC filters. To minimize systematic errors from bSiO_2 adsorption to bottle walls (e.g. Krause et al. 2010), samples bottles were rinsed three times with $0.6 \mu\text{m}$ filtered seawater. Filters were dried for 48 h at $\sim 60^\circ\text{C}$ and then stored in a desiccator at room temperature until further analysis. A serial NaOH/HF digestion procedure as described by Brzezinski and Nelson (1995) was used to measure bSiO_2 and lSiO_2 concentrations. The concentration of $\text{Si}(\text{OH})_4$ from each digestion was measured with a Beckman DU 530 UV/Vis spectrophotometer using a reverse-order reagent blank (Brzezinski and Nelson, 1986). Samples were digested for 1 h in NaOH prior to subsampling to determine $[\text{bSiO}_2]$ and for 48 h in HF for $[\text{lSiO}_2]$. Median CV values were 12% for $[\text{bSiO}_2]$ and 11% for $[\text{lSiO}_2]$, with average SDs of $0.42 \mu\text{mol L}^{-1}$ and $0.34 \mu\text{mol L}^{-1}$ respectively ($n = 51$). Note that the digestion of bSiO_2 with NaOH can result in the digestion of 10-15% of the lSiO_2

present in the sample (e.g. Ragueneu and Treguer, 1994). At the $\text{[SiO}_2\text{]}$ concentrations observed in this study, this results in an average bias of $<0.5 \mu\text{mol Si L}^{-1}$, which translates to $<12\%$ of the average ambient $\text{[bSiO}_2\text{]}$ and within the median error of our $\text{[bSiO}_2\text{]}$ measurement.

2.3.4 Rates of biogenic silica production

Biogenic silica production rates (ρSi) were measured using ^{32}Si and following the method of Brzezinski and Phillips (1997), with adaptations for gas-flow proportional counting as outlined in Krause et al. (2011). Seawater (0.3 L) was collected in acid-cleaned polycarbonate bottles and 100 μL of a 3700 Bq mL^{-1} solution of high specific activity $^{32}\text{Si}(\text{OH})_4$ ($\sim 25,000 \text{ MBq } \mu\text{mol Si}^{-1}$) was added as soon as possible after collection. Sample bottles were placed in acrylic tubes covered with neutral density and blue-coloured photographic film to simulate the *in-situ* irradiance level and wavelengths at the sampling depths. Samples in the tubes were incubated for 24 h in on-desk acrylic tanks, which were temperature-controlled using flowing surface seawater. Incubations were terminated by gentle vacuum filtration ($<27 \text{ kPa}$) onto 0.6 μm PC filters. Filters were rinsed with 0.6 μm filtered seawater to remove excess ^{32}Si tracer not incorporated into particles. Filters were mounted on nylon discs and dried at room temperature. Once dry, samples were covered with Mylar film and stored until ^{32}Si and its daughter isotope ^{32}P were at secular equilibrium (~ 120 days). The activity of ^{32}Si in the sample was determined by gas-flow proportional counting at secular equilibrium using a Risø 25-5 low-level beta GM multiscaler (Krause et al., 2011). Biogenic silica production rates (ρSi , $\mu\text{mol L}^{-1} \text{ d}^{-1}$) and the specific rate of biogenic silica production (V_{Si} , d^{-1}) were calculated as in Brzezinski and Phillips (1997). Median CV values were 11% for ρSi and 14% for V_{Si} , with average SDs of $0.05 \mu\text{mol L}^{-1} \text{ d}^{-1}$ and 0.017 d^{-1} respectively ($n = 21$).

Note that deck-board incubations can introduce a bias (i.e. overestimation) in ρSi and V_{Si} . This is because bSiO_2 production is temperature sensitive, and the flowing seawater used during incubation originates from the sea surface, which is typically warmer than waters deeper in the euphotic zone. Regardless, rates presented in this Chapter were not corrected so as to maintain consistency with other published ρSi and V_{Si} in the world's oceans, as these measurements are typically not corrected for differences between *in situ* and incubation temperatures in the literature.

2.3.5 Time course of biogenic silica production

A time-course experiment to investigate short-term differences (<24 h) in ρSi was conducted at station DBO4.3 in 2014. Seawater (3L) was collected near the surface (~2 m) and distributed into ten 250-mL polycarbonate bottles. Samples were treated as described above for ρSi , but with incubation times of 4, 8, 12, 16, 20 and 24-h. Triplicate samples were analyzed at the 12 and 24-h time points. Incident surface irradiance data ($\mu\text{E m}^{-2} \text{s}^{-1}$) were continuously logged on board the ship during the experiment using a LI-COR LI-190 Quantum Sensor.

2.3.6 Data organization and analysis

Data from diatom productivity stations were depth-integrated using trapezoidal integration from the surface to the bottom of the euphotic zone (0.1% of surface irradiance). The mean V_{Si} for the euphotic zone (V_{AVE}) was calculated by trapezoidally integrating V_{Si} measurements as above, and dividing the integrated value by the depth of the euphotic zone (Z_{eu}). Given that sampling in DBO3E occurred in only 2 out of the 8 cruises, only data from DBO3W is included in the time-averaged results and discussion. The differences between DBO3W and E are discussed in section 2.4.2.2. Time-averaged data presented in Figures 2.2 and 2.3 are calculated as the average of all years sampled

for each light depth. Figures 2.1 and 2.7 were created using Ocean Data View version 4.7.10 (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2012). Unless otherwise stated, linear relationships were determined using Pearson linear correlation tests, significant differences between measured parameters were determined using student's t-tests, and $\alpha < 0.05$ was used to determine significance. Matlab R2014b was used to conduct all statistical tests.

2.4 Results

2.4.1 Time-averaged dissolved and particulate silica concentrations, and biogenic silica production rates

2.4.1.1 Vertical distributions

Concentrations of dissolved and particulate SiO_2 concentrations increased with depth in all five DBO regions (Figure 2.2). Vertical profiles of ρ_{Si} and V_{Si} averaged over the 10-yr study period exhibited vertical trends that varied between regions, and vertical profiles of ρ_{Si} and V_{Si} within each region did not always exhibit the same trends (Figure 2.3). In DBO1, DBO4 and DBO5, ρ_{Si} was highest in the lower euphotic zone (15, 1 and 0.1% I_0), whereas in DBO2, ρ_{Si} was highest in the upper euphotic zone (100, 55, and 30% I_0). In DBO1-2, vertical trends for V_{Si} were similar to those observed for ρ_{Si} . Although vertical trends for V_{Si} were relatively similar to ρ_{Si} in DBO4-5, differences were observed in the near surface waters, where, unlike ρ_{Si} , V_{Si} was elevated at 100% I_0 in DBO4 and at 100% and 55% I_0 in DBO5. The time-averaged profile of ρ_{Si} in DBO3W was relatively invariable with depth, which was mainly driven by differences in the shapes of the depth profiles between years (see grey dashed lines in Figure 2.3a). In contrast, V_{Si} was higher in the upper euphotic zone compared to the lower in DBO3W. The highest ρ_{Si} and V_{Si} were observed in DBO3W (note different scales for DBO3W in Figure 2.3). Interannual variability in ρ_{Si} and V_{Si} was similar for DBO1-2 and DBO4,

with variability tending to be highest at the depths where rates were the highest. DBO3W exhibited the most interannual variability, while DBO5 was relatively invariable between years.

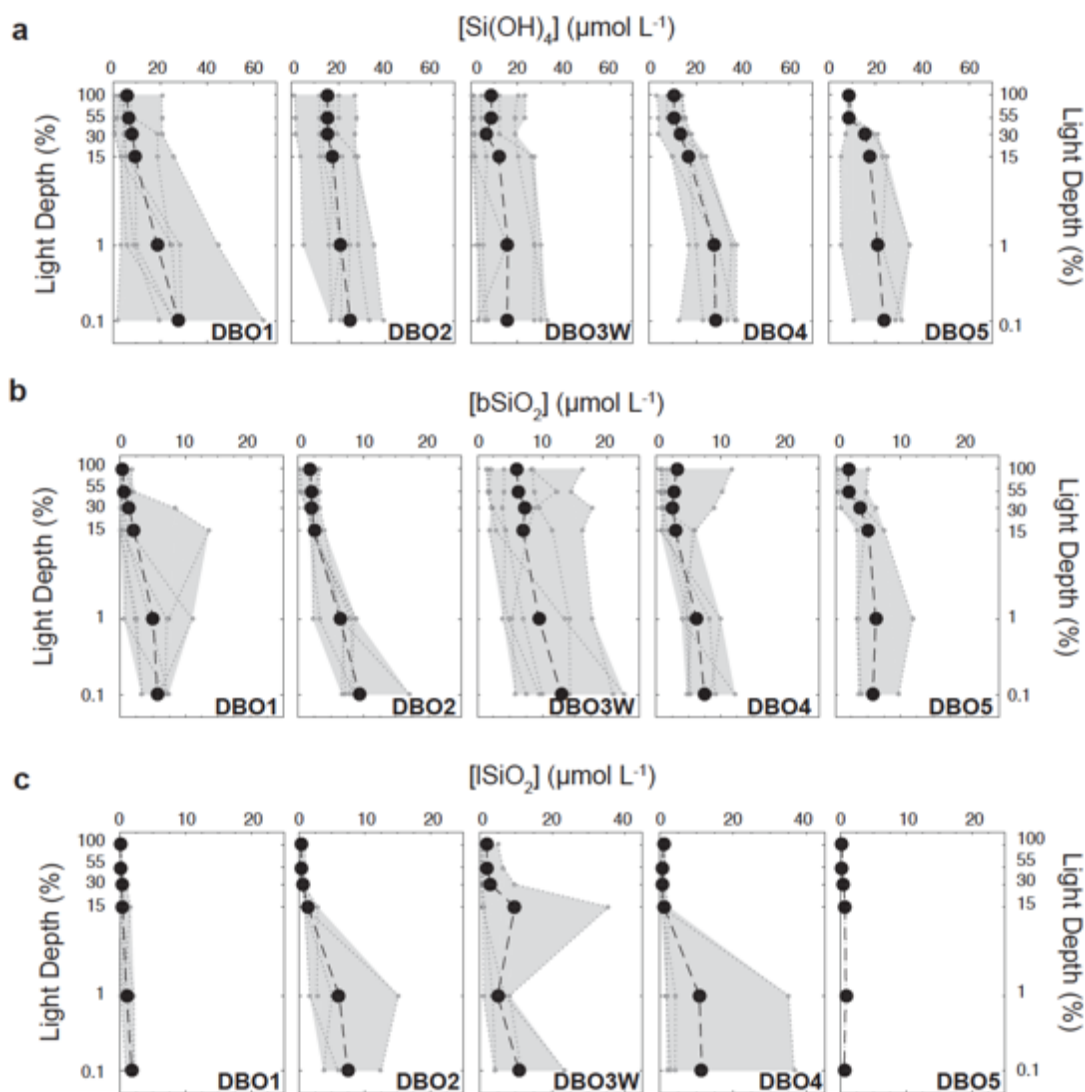


Figure 2.2. Time-averaged vertical profiles of (a) Si(OH)_4 , (b) bSiO_2 , and (c) lSiO_2 concentrations for the 2006-2016 period for each DBO region. Data are plotted using light depths (i.e. percentage of incident surface irradiance, I_0) to account for differences in depths sampled among years. The depth scale is logarithmic to reflect the exponential attenuation of irradiance in the water column. Filled black dots and black dashed lines signify the time-averaged vertical profiles, calculated as the average of all years sampled for each light depth. Smaller grey dots and grey dashed lines represent vertical profiles from each year sampled. Shaded grey areas indicate the range of values (maximum and minimum) for each parameter in each region. Note the different horizontal scales among DBO regions in panels c.

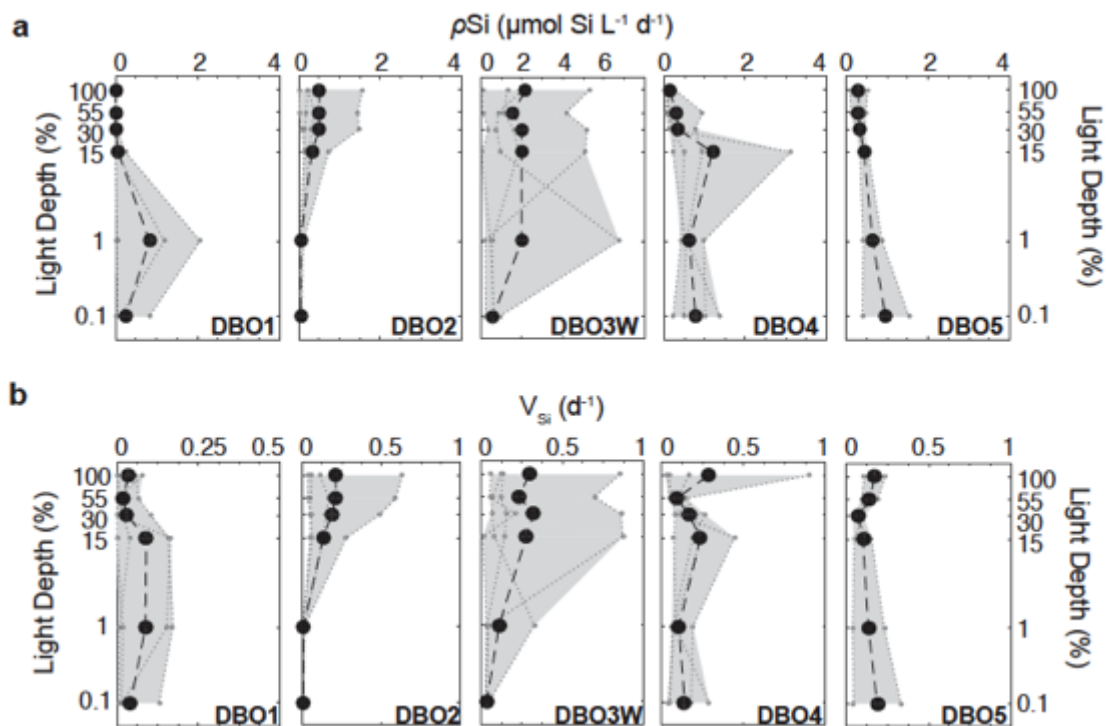


Figure 2.3. Time-averaged vertical profiles of (a) bSiO₂ production, ρ_{Si} , and (b) specific bSiO₂ production, V_{Si} , rates over the 2013-2016 period for each DBO region as in Figure 2. Note the different horizontal scales among DBO regions.

2.4.1.2 Depth-integrated Distributions

Depth-integrated distributions of dissolved and particulate SiO₂ concentrations and bSiO₂ production were variable between DBO regions. Depth-integrated [Si(OH)₄] were the lowest in DBO3W (Table 2.2; Figure 2.4a). No obvious year-to-year trends were observed for [Si(OH)₄] in any of the DBO regions and interannual variability was high for all regions (Table 2.2; Figure 2.4). Depth-integrated [bSiO₂] and [lSiO₂] were highest in DBO3W and lowest in DBO1, although [lSiO₂] was also low in DBO5 (Table 2.2; Figure 2.4b-c). Depth-integrated [lSiO₂] contributed an average of 37% to the depth-integrated total particulate SiO₂ concentration. Interannual variability in [bSiO₂] was higher for DBO1-2 and DBO3W compared to DBO4-5 while [lSiO₂] was more interannually variable in DBO3W and DBO4 compared to DBO1-2. No clear year-to-year trends were observed for either [bSiO₂] or [lSiO₂].

Table 2.2. Depth-integrated measurements of silicic acid ($\text{Si}(\text{OH})_4$), biogenic silica (bSiO_2) and lithogenic silica (lSiO_2) concentrations for the five DBO regions from July 2006-2016. Data from DBO3 is split into the western (DBO3W) and eastern (DBO3E) sectors due to differences in water mass composition (AW/BSW and ACW, respectively). Only data from DBO3W are presented in this table as DBO3E was only sampled on 2 out of the 8 cruises. Depth integrations were done from the ocean surface to the 0.1% I_0 depth. (-) indicates no data is available.

Region	Year	[Si(OH) ₄] (mmol m ⁻²)	[bSiO ₂] (mmol m ⁻²)	[lSiO ₂] (mmol m ⁻²)
<i>Northern Bering Shelf</i>				
DBO1	2006	594	296	32.4
	2008	2448	155	-
	2011	424	1.51	-
	2012	137	75.4	-
	2013	359	180	-
	2014	171	98.3	6.03
	2015	779	52.7	46.5
	2016	711	71.1	36.9
	Mean (±SE)	703 ± 263	116 ± 32.4	30.5 ± 8.66
DBO2	2006	113	64.0	59.1
	2008	999	219	-
	2011	396	125	-
	2012	465	230	-
	2013	670	181	-
	2014	901	177	88.4
	2015	803	92.7	53.4
	2016	726	105	158
	Mean (±SE)	634 ± 103	149 ± 21.6	89.7 ± 24.0
<i>Southeastern Chukchi Sea</i>				
DBO3W	2006	54.1	126	52.6
	2008	1172	185	-
	2011	404	121	-
	2012	-	-	-
	2013	121	255	-
	2014	38.1	265	166
	2015	521	117	38.1
	2016	41.2	393	330
	Mean (±SE)	336 ± 157	209 ± 38.6	147 ± 67.5
<i>Northeastern Chukchi Sea</i>				
DBO4	2006	286	126	53.8
	2008	669	125	-
	2011	-	-	-
	2012	-	-	-
	2013	380	167	-
	2014	921	105	78.5
	2015	882	128	43.3
	2016	824	154	566
	Mean (±SE)	660 ± 110	134 ± 9.19	185 ± 127
DBO5	2006	-	-	-
	2008	1086	121	-
	2011	-	-	-
	2012	-	-	-
	2013	168	168	-
	2014	-	-	-
	2015	597	96.9	14.4
	2016	-	-	-
	Mean (±SE)	617 ± 265	128 ± 20.8	14.4

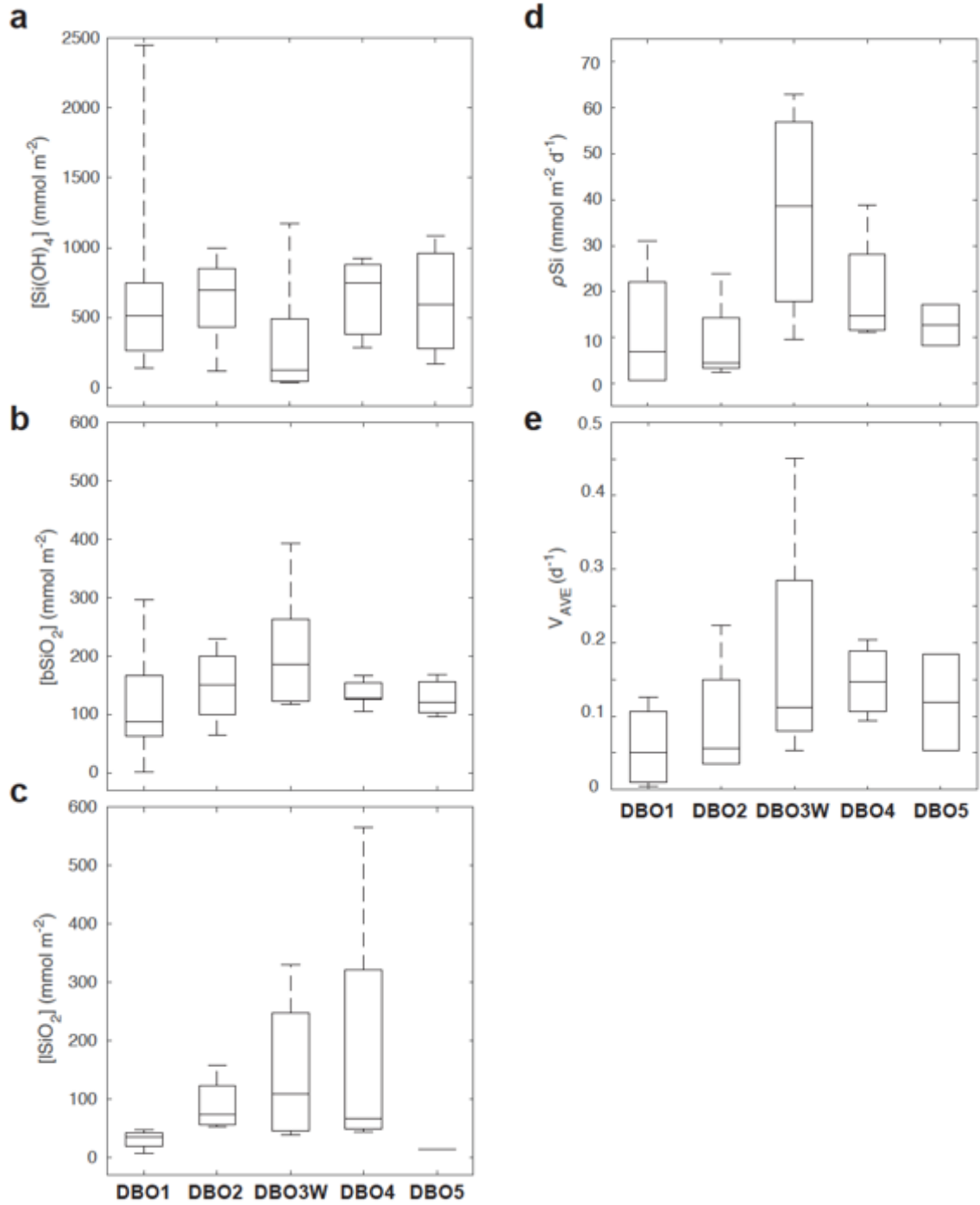


Figure 2.4. Box plots of time-averaged depth-integrated (a) Si(OH)_4 , (b) bSiO_2 , and (c) lSiO_2 concentrations, (d) bSiO_2 production rate, ρSi , and (e) euphotic-zone averaged specific bSiO_2 production rate, V_{AVE} , for each DBO region from 2006 to 2016. Depth integrations were done from the ocean surface to the 0.1% I_0 depth. The horizontal line in the middle of each box represents the median, and the top and bottom of the boxes represents the 25th and 75th percentiles, respectively. The whiskers extending above and below each box extend to the maximum and minimum measured values, respectively.

Depth-integrated ρSi was highest in DBO3W and lowest in DBO1-2 (Table 2.3; Figure 2.4d). A decrease in ρSi from 2013 to 2016 was observed in DBO1 (Table 2.3), although there were no other consistent changes with time in any of the regions. Interannual variability in ρSi was highest in DBO3W and similar between DBO1-2 and DBO4.

Table 2.3. Depth-integrated measurements of absolute (ρSi) and specific (V_{AVE}) rates of Si utilization, and the diatom contribution to primary production (PP) and ρNO_3 for the five DBO regions in the Bering and Chukchi Seas in July from 2013-2016. V_{AVE} represents the depth-weighted mean V_{Si} for the euphotic zone. Data for concurrent measurements of PP and ρNO_3 used in the calculation of % diatom PP and % diatom ρNO_3 are from Chapter 1. Data from DBO3 is presented as for Table 2. Depth integrations were done from the ocean surface to the 0.1% I_0 depth. (-) indicates no data is available.

Region	Year	ρSi (mmol m ⁻² d ⁻¹)	V_{AVE} (d ⁻¹)	% diatom PP*	% diatom ρNO_3 *
<i>Northern Bering Shelf</i>					
DBO1	2013	31.1	0.127	100%	100%
	2014	13.1	0.086	89%	55%
	2015	0.84	0.005	16%	47%
	2016	0.66	0.016	12%	15%
	Mean ($\pm\text{SE}$)	11.4 $\pm$ 7.18	0.059 $\pm$ 0.029	54% $\pm$ 23%	54% $\pm$ 18%
DBO2	2013	4.65	0.035	100%	100%
	2014	23.9	0.224	50%	100%
	2015	4.31	0.076	40%	100%
	2016	2.50	0.037	15%	82%
	Mean ($\pm\text{SE}$)	8.83 $\pm$ 5.03	0.093 $\pm$ 0.045	51% $\pm$ 18%	95% $\pm$ 5%
<i>Southeastern Chukchi Sea</i>					
DBO3W (AW/BSW)	2013	26.1	0.104	42%	100%
	2014	9.66	0.054	41%	87%
	2015	62.9	0.280	83%	100%
	2016	51.0	0.120	37%	100%
	Mean ($\pm\text{SE}$)	37.4 $\pm$ 12.0	0.140 $\pm$ 0.049	51% $\pm$ 11%	97% $\pm$ 3%
<i>Northeastern Chukchi Sea</i>					
DBO4	2013	17.3	0.094	36%	100%
	2014	11.2	0.174	100%	100%
	2015	38.8	0.204	100%	100%
	2016	12.1	0.120	100%	100%
	Mean ($\pm\text{SE}$)	19.9 $\pm$ 6.44	0.148 $\pm$ 0.025	84% $\pm$ 16%	100% $\pm$ 0%
DBO5	2013	8.26	0.054	-	-
	2014	-	-	-	-
	2015	17.1	0.185	100%	100%
	2016	-	-	-	-
	Mean ($\pm\text{SE}$)	12.7 $\pm$ 4.44	0.119 $\pm$ 0.065	100%	100%

* PP and ρNO_3 data from Chapter 1

Spatial patterns in V_{AVE} were not exactly the same as those observed for ρSi (Table 2.3; Figure 2.4e). The highest V_{AVE} occurred in DBO4, although rates were also high in

DBO3W and DBO5. Similar to ρSi , V_{AVE} were low in DBO1-2, and DBO3W exhibited the most interannual variability. In addition, a similar decreasing trend with time was observed for V_{AVE} in DBO1 (Table 2.3).

2.4.2 Time-course of biogenic silica production

Short-term bSiO_2 production rates showed some variation that may be related to changes in light during the 24-h time-course experiment (Figure 2.5).

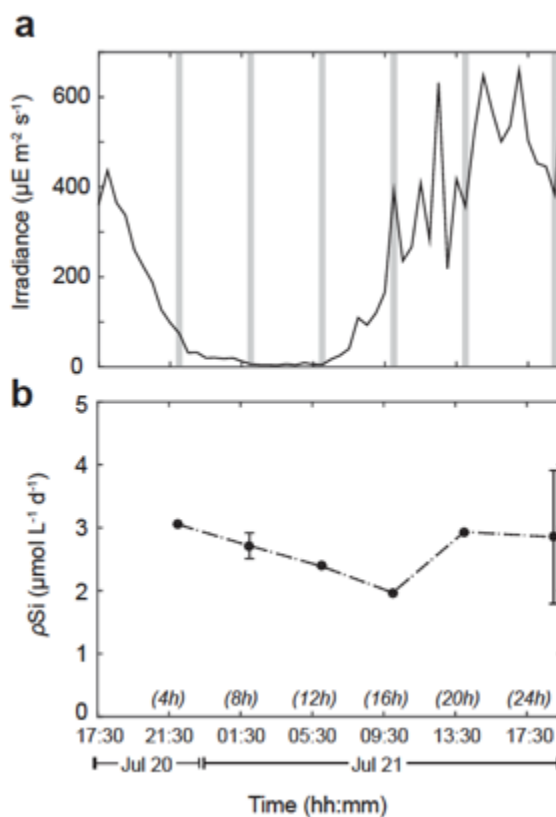


Figure 2.5. Time-series of irradiance and bSiO_2 production over a 24-h period from July 20-21, 2014 at station DBO4.3. (a) irradiance ($\mu\text{mol photons m}^{-2} \text{ s}^{-1}$), and (b) hourly bSiO_2 production rate, ρSi ($\mu\text{mol L}^{-1} \text{ d}^{-1}$). The bottom axis has units of time (UTC-7) in four-hour intervals. Given that the experiment spanned over a period of two days, the date is indicated beneath the times. In addition, incremental time points in units of hours from the starting point of the experiment (i.e. from 0h to 24h) are listed in parentheses. Samples were collected in triplicate for the 8h and 24h time points. For these times, data points and error bars represent the mean $\pm$ standard error (SE) of the replicates.

The irradiance during the time course experiment showed a dark period of ~ 8 -h, spanning from approximately 21:30 to 05:30 (UTC-7), which corresponded to the 4-h to 12-h time points during the experiment (Figure 2.5a). From evening until mid-morning

(i.e. from the 4-h to 16-h time points), ρSi exhibited a significant decreasing trend (Figure 2.5b; $r = -0.998$, $p < 0.002$). Rates then increased in the afternoon and early evening (20-h and 24-h time points) to values similar to those observed in the evening the previous day (i.e. at the 4-h and 8-h time points).

2.4.3 Statistical comparisons among DBO regions and years sampled

Statistical differences in depth-integrated $[\text{Si}(\text{OH})_4]$, $[\text{bSiO}_2]$, $[\text{lSiO}_2]$, ρSi , and V_{AVE} grouped either by region, year or geographic location (i.e. into either the Bering Sea or Chukchi Sea regions) were determined by a nonparametric Kruskal-Wallis test with post hoc comparison (at $p < 0.05$). The only significant difference observed was for ρSi , and only when data were grouped geographically into the Bering Sea (DBO1-2) or Chukchi Sea (DBO3-5) regions. The lack of significant differences may result from the low ratio of observational frequency to natural variability.

2.4.4 Correlation analysis between physical and biological parameters in the Bering and Chukchi Seas

To identify potential environmental influences on siliceous biomass and productivity, a correlation analysis was conducted between several biological and physical parameters and the euphotic zone integrated Si-based parameters of $[\text{Si}(\text{OH})_4]$, particulate SiO_2 concentrations, and bSiO_2 rate measurements (Table 2.4). Biological data for euphotic-zone integrated $[\text{NO}_3^-]$, phytoplankton biomass and primary productivity are from Chapter 1. All data were grouped geographically into either Bering Sea (DBO1-2) or Chukchi Sea (DBO3-5) regions, and a separate analysis was conducted for each. Significant correlations were found in both the Bering and Chukchi Seas; however, note that a multiple hypothesis correction was not applied. This means that at $\alpha = 0.05$, up to

5% of the significant correlations found may be due to random sampling error, rather than attributable to a true relationship between the parameters.

In the Bering Sea, no significant correlations were found between any physical parameters and dissolved or particulate SiO_2 concentrations, or between the physical parameters and bSiO_2 rate measurements. In contrast, there were a number of biological parameters that were significantly correlated with the Si-based measurements (Table 2.4). Euphotic-zone integrated $[\text{Si}(\text{OH})_4]$ and $[\text{bSiO}_2]$ were positively correlated with $[\text{NO}_3^-]$, while $[\text{bSiO}_2]$ was also positively correlated with the percent contribution of phytoplankton $> 5 \mu\text{m}$ to Chl a (% Chl $a > 5 \mu\text{m}$) and with ρSi . In addition, ρSi and V_{AVE} were positively correlated with each other, and with ρC and ρNO_3 , and ρSi was also positively correlated with total Chl a , and the % Chl $a > 5 \mu\text{m}$.

In the Chukchi Sea, $[\text{Si}(\text{OH})_4]$ was negatively correlated to bottom T and positively correlated to surface S, although these relationships were only statistically significant at $p < 0.10$. Similar to the Bering Sea, a number of biological parameters were significantly correlated with each other. For the Si-based parameters, $[\text{Si}(\text{OH})_4]$ was positively correlated with the depth of the euphotic zone (Z_{eu}) and $[\text{NO}_3^-]$, while $[\text{bSiO}_2]$ was positively correlated with Chl a , % Chl $a > 5 \mu\text{m}$, and ρC . Similar to the Bering Sea, ρSi and V_{Si} were positively correlated with each other, and with ρNO_3 . In addition, ρSi was positively correlated with ρC .

Table 2.4. Correlation matrix between physical, chemical and biological parameters for the Bering and Chukchi Seas for 2006-2016. Physical data is presented for surface and bottom depths, and biological and chemical data are presented as depth-integrated values from the ocean surface to the 0.1% I_0 depth. Data for concurrent measurements of T and S (surf and bot), $[\text{NO}_3^-]$, Chl a , % Chl $a > 5 \mu\text{m}$, ρC and ρNO_3 are from Chapter 1. Significant relationships at $p < 0.05$ and $p < 0.01$ are in bold. Significant relationships at $p < 0.10$ are in italics. Surf = surface (1-2m), Bot = bottom (2-5m) from the seafloor, T = temperature, S = salinity, Z_{eu} = euphotic zone depth.

	Surf T	Bot T	Surf S	Bot S	Z_{eu}	$[\text{NO}_3^-]$	$[\text{Si}(\text{OH})_4]$	Chl a	% Chl $a > 5 \mu\text{m}$	$[\text{bSiO}_2]$	ρC	ρNO_3	ρSi
Bering Sea (DBO1, DBO2)													
Surface T													
Bottom T	-0.56*												
Surface S	-0.73**	0.22											
Bottom S	0.00	-0.07	0.37										
Z_{eu} (m)	0.41	-0.66**	-0.06	-0.18									
$[\text{NO}_3^-]$	-0.41	0.18	0.56*	0.64**	-0.05								
$[\text{Si}(\text{OH})_4]$	-0.12	-0.12	0.38	0.40	0.38	0.68**							
Chl a	0.18	-0.25	-0.27	-0.08	-0.09	-0.28	-0.25						
% Chl $a > 5 \mu\text{m}$	-0.28	-0.01	-0.09	0.20	-0.41	0.12	-0.28	0.59*					
$[\text{bSiO}_2]$	-0.18	0.15	0.07	0.39	-0.26	0.67**	0.27	0.18	0.63*				
ρC	-0.24	0.43	0.15	0.09	-0.32	0.17	0.03	0.23	0.21	0.23			
ρNO_3	-0.02	-0.03	-0.06	0.01	-0.24	-0.18	-0.08	<i>0.49†</i>	0.35	0.10	0.72*		
ρSi	0.20	-0.09	-0.45	0.31	-0.26	-0.15	-0.38	0.87**	0.87**	0.71*	0.49	0.80*	
V_{AVE}	0.01	0.31	-0.04	<i>0.64†</i>	-0.49	0.20	-0.02	0.50	<i>0.71†</i>	0.62	0.85**	0.83*	0.84**
Chukchi Sea (DBO3, DBO4, DBO5)													
Surface T													
Bottom T	0.65**												
Surface S	0.65**	0.78**											
Bottom S	<i>-0.41†</i>	-0.52*	-0.24										
Z_{eu} (m)	0.03	-0.20	-0.24	-0.21									
$[\text{NO}_3^-]$	-0.02	0.01	0.01	0.21	0.50*								
$[\text{Si}(\text{OH})_4]$	-0.12	<i>-0.42†</i>	<i>-0.40†</i>	0.27	0.60**	0.77**							
Chl a	0.01	0.23	0.34	0.05	<i>-0.42†</i>	-0.20	-0.39						
% Chl $a > 5 \mu\text{m}$	-0.23	-0.18	0.01	<i>0.50†</i>	-0.14	0.36	0.20	0.55*					
$[\text{bSiO}_2]$	-0.11	0.22	0.29	0.04	-0.22	-0.06	-0.34	0.88**	0.59*				
ρC	0.18	<i>0.41†</i>	0.40	0.22	-0.57*	-0.03	-0.26	0.83**	<i>0.46†</i>	0.67**			
ρNO_3	0.22	0.34	0.37	0.04	0.11	0.69**	<i>0.46†</i>	0.00	0.21	0.11	0.20		
ρSi	0.47	0.36	0.46	0.30	-0.37	0.34	0.08	0.47	0.36	0.27	0.78**	0.89**	
V_{AVE}	0.41	0.18	0.16	0.23	-0.13	<i>0.60†</i>	0.47	-0.10	0.04	-0.27	0.30	0.81**	0.81**

* $p < 0.01$, ** $p < 0.05$, † $p < 0.10$

2.5 Discussion

2.5.1 Regional patterns of silica and diatom bloom dynamics in the Pacific Arctic Region from 2006-2016

2.5.1.1 Dissolved and particulate silica concentrations

Our measurements of euphotic-zone $[\text{Si}(\text{OH})_4]$ and $[\text{bSiO}_2]$ were comparable to published summertime measurements in the PAR (Walsh et al., 1989; Cooper et al., 1997; Varela et al., 2013; Wyatt et al., 2013; Danielson et al., 2017). Depth-integrated $[\text{bSiO}_2]$ throughout the five DBO regions also agreed well with measurements in the southeastern Bering Sea, and in the Southern Ocean (Table 2.5 and references therein).

Table 2.5. Regional comparison of depth-integrated $[\text{bSiO}_2]$ and ρSi among mid- (35°N – 50°N and S) and high-latitude ($>50^\circ\text{N}$ or S) studies. Data are integrated to the bottom of the euphotic zone (1% - 0.1% I_0) unless otherwise noted. (-) = no data.

otherwise noted. (–) = no data.					
Region	[bSiO ₂] (mmol m ⁻²)		ρSi (mmol m ⁻² d ⁻¹)		Reference
	Range	Mean	Range	Mean	
<i>Arctic and Subarctic (50°N – 90°N)</i>					
Northeastern Chukchi Shelf	97 - 168	132	8.2 - 27.8	14.3	This study
Southeastern Chukchi Shelf	41 - 1172	336	9.0 - 61.6	35.9	This study
Northeastern Bering Shelf	1.5 - 296	133	0.3 - 22.2	7.2	This study
Southeastern Bering Sea	35 - 680	261	1.8 - 50.9	17.7	Banahan and Goering (1986)
<i>Temperate Regions (50°N – 35°N and 35°S – 50°S)</i>					
Monterey Bay	44 - 175	106	4.8 - 108	42.8	Brzezinski et al. (2003)
Gulf Stream warm core rings	5.2 - 47	27	4.4 - 11.7	7.1	Brzezinski and Nelson (1989)
<i>Antarctic and Subantarctic (50°S – 90°S)</i>					
Southern Ocean, Pacific Sector	12 - 793	233	0.2 - 45.5	13.2	Nelson and Gordon (1982), Brzezinski et al. (2001)
Southern Ocean, Atlantic Sector	30 - 1231	328	2.4 - 60.7	19.4	Treguer et al. (1991), Queguenier et al. (2002)
Southern Ocean, Indian Sector	0.5 - 488	104	0.1 - 11.4	3.7	Beucher et al. (2004), Fripiat et al. (2011)
Weddell Sea	7.5 - 98.8	43	1.8 - 16.1	5.9	Treguer et al. (1991), Leynaert et al. (1993), Queguenier et al. (2002)
Ross Sea (ice-edge bloom)	-	-	25.5 - 49.6	34	Nelson et al. (1991)

In addition to driving the low $[\text{NO}_3^-]$ and high Chl *a* in DBO3W (Chapter 1), the seasonal bloom also likely drove the low $[\text{Si}(\text{OH})_4]$ and high $[\text{bSiO}_2]$ observed in this region (Table 2.2; Figures 2.2a-b, 2.4a-b). In general, spatial patterns in $[\text{Si}(\text{OH})_4]$ and

[bSiO₂] were similar to those observed for concurrent measurements of [NO₃⁻] and Chl *a* (Chapter 1), although differences between DBO regions for [Si(OH)₄] and [bSiO₂] were not as pronounced. In addition, [Si(OH)₄] was always greater than ~0.5 μmol L⁻¹ in the upper euphotic zone. This is in contrast to [NO₃⁻], which was often observed to reach undetectable levels in the upper euphotic zone (Figure 1.2 in Chapter 1).

The high [bSiO₂] often observed near the bottom of the euphotic zone at 1 and 0.1% I₀ generally corresponded to higher ρSi, although there were some cases when high [bSiO₂] did not correspond to high ρSi. With the exception of DBO2, ρSi at 1% I₀ in all DBO regions was typically as high, or higher than those rates measured at shallower light depths, which suggests that the high [bSiO₂] are the result of an actively growing diatom assemblage. This is further supported by the relatively high Chl *a* measured at these same stations and depths (Chapter 1). This was also true for 0.1% I₀ in DBO4-5. Discrepancies between the vertical trends of [bSiO₂] and ρSi near the bottom of the euphotic zone (i.e. at 1% and 0.1% I₀ in DBO2 and at 0.1% I₀ in DBO1 and 3W) could be caused either by particle settling, or sediment resuspension. Infaunal bivalves, polychaetes, crustaceans and sipunculids dominate the DBO benthic hotspots (e.g. Grebmeier et al., 2015), and bivalves and polychaetes are likely to especially contribute to high levels of bioturbation and sediment resuspension in these regions (e.g. Mathis et al., 2014). Given these active benthic communities that underlie the DBO hotspots (e.g. Grebmeier et al., 2015), and that the bottom of the euphotic zone was generally close to the bottom the water column (Table 2.1), it seems probable that high [bSiO₂] without correspondingly high ρSi are the result of sediment resuspension.

Reports of euphotic-zone $[\text{ISiO}_2]$ in the global ocean are limited, but our values were similar to those measured in other shallow coastal environments in both temperate and polar oceans (e.g. Treguer et al., 1990; Shipe et al., 2001). Lithogenic SiO_2 concentrations increased with depth and were highest at stations where the water column depth was <50 m (i.e. DBO2, DBO3W and DBO4, Tables 2.1-2.2), which is likely the result of sediment resuspension and advective transport across the shelf in these regions (e.g. Baskaran and Naidu, 1995; Drake and Cacchione, 1986; Smith et al., 2003; Chen et al., 2012). The high $[\text{ISiO}_2]$ near the bottom of the euphotic zone also supports that sediment resuspension is likely driving the high $[\text{bSiO}_2]$ observed when ρSi is otherwise low, as resuspension would serve to increase both $[\text{ISiO}_2]$ and $[\text{bSiO}_2]$.

2.5.1.2 Rates of biogenic silica production

Our measurements of ρSi are the first for the PAR and, like $[\text{bSiO}_2]$, they agree well with previous measurements from the southeastern Bering Sea and the Southern Ocean (Table 2.5). The spatial trends in depth-integrated ρSi were similar to the concurrent observations of depth-integrated ρC and ρNO_3 (Chapter 1), although profiles of ρSi , ρC and ρNO_3 did not always exhibit the same vertical trends. In DBO1, profiles of ρSi and ρNO_3 were similar, with maxima occurring at 1% I_0 , although the ρC maxima typically occurred at 15% I_0 . This discrepancy could be driven by differences in the phytoplankton assemblage and nitrogen source, with low $[\text{NO}_3^-]$ from 100 – 15% I_0 limiting diatom productivity, in addition to a decreased contribution of diatoms to the overall phytoplankton assemblage in DBO1 (Chapter 1). The abundance of NO_3^- and Si(OH)_4 throughout the water column in DBO2 likely drives the similarity in the profiles of ρSi , ρC and ρNO_3 in this region, such that diatom growth is not limited by the availability of NO_3^- in surface waters. In DBO3W and DBO4, ρSi exhibited somewhat similar vertical

trends to those of ρC and ρNO_3 , although, in contrast to ρC and ρNO_3 , we observed relatively high rates of ρSi in the deep euphotic zone (1% I_0 for DBO3W, and 1% and 0.1% I_0 for DBO4) similar to those observed at shallower depths. This could result from the Si metabolism of diatoms being less light dependent than C and N (e.g. Goering et al., 1973; Martin-Jezequel et al., 2000), resulting in more Si uptake at depth compared to C or NO_3^- . Similarly, in DBO5, we observed higher rates of ρSi at 1% and 0.1% I_0 , which could be driven in part by the depletion of NO_3^- in surface waters in this region, and again, the decoupling of Si from the C and N metabolism at lower light levels (e.g. Claquin et al., 2002).

Like ρC and ρNO_3 , latitudinal patterns in ρSi and V_{AVE} reflected differences in the timing of the seasonal bloom (Figures 2.3-2.4; Table 2.3; Chapter 1). The seasonal bloom in the PAR is linked to the timing of the annual sea-ice retreat, which begins in May in DBO1 and progresses northward throughout the growing season (Brown et al., 2011, 2013; Frey et al., 2015). The seasonal bloom in DBO1 generally occurs around mid-May (Brown et al., 2013), meaning that by the time of our July sampling, the bloom in DBO1 would have already passed. This would leave $[\text{NO}_3^-]$ depleted in surface waters and result in low productivity throughout most of the water column as was observed (Chapter 1). The similarity in the profiles of ρSi and ρNO_3 suggest diatoms were primarily utilizing NO_3^- as a nitrogen source in DBO1, which is also supported by the higher V_{Si} in the lower euphotic zone where $[\text{NO}_3^-]$ is high (Figure 2.3b; Chapter 1). Biogenic silica production in DBO1 was the lowest of the five DBO regions (Table 2.3; Figure 2.3), consistent with our concurrent observation of low rates of C and NO_3 utilization in this

region (Chapter 1). All of these measurements support that DBO1 was in a post-bloom condition at the time of our sampling.

Low ρSi and V_{Si} were observed in DBO2 despite high nutrient concentrations throughout the water column. This may be driven by both bloom timing and top-down controls from zooplankton grazing. Like DBO1, by the time of our sampling in DBO2, the seasonal bloom would have likely passed. While rates of bSiO_2 production were higher in DBO2 compared to DBO1, this may in part be driven by the high $[\text{NO}_3^-]$ in the upper euphotic zone in this region (Chapter 1). The similarity in profiles of ρSi , V_{Si} , and ρNO_3 again suggests that diatoms were primarily utilizing NO_3^- as a nitrogen source in this region. The low ρSi and V_{Si} in the lower euphotic zone could be a result of increased ammonium (NH_4^+) concentrations from zooplankton excretion potentially inhibiting NO_3^- utilization by diatoms (Chapter 1; Steinberg and Saba, 2008), although it is also possible that rates are simply low because of the low light levels.

Overall, ρSi were significantly higher in the Chukchi Sea regions compared to the Bering Sea regions, with the highest ρSi usually found on the western side of DBO3 (Table 2.3; Figures 2.3-2.4). In contrast, V_{AVE} were highest in DBO4, although differences in V_{AVE} between the Chukchi Sea regions were not significant (Table 2.3; Figure 2.4). Turbulent mixing in the Chirikov Basin and Bering Strait and bloom timing likely drive the high productivity signals in the Chukchi Sea regions we observe, with mixing providing nutrients to surface waters that stratify as they transit further northwards into the Chukchi Sea, and the seasonal bloom in the Chukchi Sea regions occurring closer to the time of our sampling in July. Biogenic silica production rates decreased northwards from DBO3 to DBO5, suggesting that the seasonal bloom is well

established in DBO3W by the time of our sampling, but may be yet to start in the more northern regions. Considering the good agreement between profiles of ρSi and ρNO_3 , especially in the upper euphotic zone, the decrease in ρSi northwards could be also driven by the decrease in $[\text{NO}_3^-]$ in surface waters that results from the intense productivity in DBO3W (Chapter 1); however, the higher V_{AVE} in DBO4 compared to DBO3W suggests that the seasonal bloom may be initiating in DBO4 by the time of our sampling, especially given that the location of the seasonally retreating ice-edge was often encountered in DBO4 (Chapter 1).

2.5.1.3 Diatom contribution to primary productivity and nitrate uptake

The diatom contribution to primary productivity (PP, ρC) and nitrate uptake (ρNO_3) can be determined using rates of C, NO_3^- and Si utilization and the Si:C:N particulate elemental ratios in the following equations:

$$\text{Diatom \% PP} = 100 \times \rho\text{Si} / (\rho\text{C} \times \text{Si:C}) \quad (1)$$

$$\text{Diatom \% } \rho\text{NO}_3 = 100 \times \rho\text{Si} / (\rho\text{NO}_3 \times \text{Si:N}) \quad (2)$$

Concentrations of bSiO_2 were used with concurrently measured PC and PN (unpubl. data) to calculate mean particulate Si:C and Si:N values of 0.20 and 1.32 for the entire study region from 2013-2016, which are close to the ratios measured for cultured diatoms grown under nutrient replete conditions ($\text{Si:C} = 0.13 \pm 0.04$ and $\text{Si:N} = 1.12 \pm 0.33$; Brzezinski, 1985). These calculated ratios were then used with the ρC and ρNO_3 reported in Chapter 1 to determine the average diatom contribution to PP and ρNO_3 for each year from 2013-2016 in each of the five DBO regions (Table 2.3).

Diatoms accounted for an average of $61 \pm 8\%$ of PP and $87 \pm 6\%$ of ρNO_3 in the PAR from 2013-2016 (Tables 2.3 and 2.6), which is consistent with previous studies suggesting that phytoplankton $>5 \mu\text{m}$ (primarily diatoms) are the major contributor to the

autotrophic productivity and biomass in this region (e.g. Lee et al., 2012; 2013; Wyatt et al., 2013; Varela et al., 2013; Chapter 1).

Table 2.6. The diatom contribution to phytoplankton biomass and productivity from several studies conducted in the Pacific Arctic Region from 2004 – 2016. Data for concurrent measurements of PP and ρNO_3 used in the calculation of % diatom PP and % diatom ρNO_3 are from Chapter 1. Data presented are averages for the region $\pm$ standard error of the mean (SE). n = number of observations. * = significant difference from % diatom PP. ** = significant difference from % diatom ρNO_3 .

Parameter	Average ($\pm$ SE)	n
Chapters 1-2: Jul 2013 – 2016		
% diatom PP	62% $\pm$ 8%	17
% diatom ρNO_3	87% $\pm$ 6%	17
Chapter 1: Jul 2006 – 2016		
% diatom abundance	65% $\pm$ 5%	20
% >5 μm Chl <i>a</i>	65% $\pm$ 4%	27
Lee et al. (2012): Aug – Sep 2008		
% >5 μm POC	45% $\pm$ 7%	9
% >5 μm ρC	80% $\pm$ 7%	9
Lee et al. (2013): Aug – Sep 2004		
% >5 μm POC	41% $\pm$ 13%	16
% >5 μm ρC	68% $\pm$ 6%	16
% >5 μm ρNO_3	62% $\pm$ 7%**	16
Varela et al., (2013): Jul 2008		
% >5 μm Chl <i>a</i>	56% $\pm$ 7%	7
% >5 μm ρC	71% $\pm$ 7%	7
% >5 μm ρNO_3	77% $\pm$ 7%	7
Crawford et al., (2018): Jul 2008		
% diatom abundance	30% $\pm$ 10%	5
% diatom phyto C	38% $\pm$ 13%	5

The average % diatom ρNO_3 was lowest in DBO1, which appears to be tied to a decrease in ρSi with time (see section 2.4.3.3; Table 2.3); however, diatoms still contributed to an average of 54% of the ρNO_3 in this region. We found no significant differences between our estimates of % diatom PP and previous estimates of the percent contribution of >5 μm cells to Chl *a*, POC, or ρC (Table 2.6). Similarly, we did not find any differences between % diatom PP and the % diatom abundance or the percent contribution of diatoms to total phytoplankton C (% diatom phyto C) in the PAR (Table 2.6). Our estimate of % diatom ρNO_3 was not significantly different from the % >5 μm ρNO_3 given in Varela et al. (2013) (Table 2.6); however, we did observe a significant

difference between our results and the % >5 μm ρNO_3 from Lee et al. (2013). This difference may result from different sampling times - July for our study vs. Aug-Sep for Lee et al. (2013) and/or concomitant changes in phytoplankton assemblage composition. Our results indicate that diatoms control much of the primary productivity and essentially all of the ρNO_3 in the PAR.

Our findings show that diatoms contribute a disproportionately large amount to the NO_3^- utilization while their contribution to primary productivity is proportionate to their contribution to autotrophic biomass (based on the >5 μm contribution to Chl *a*). This is likely driven by the high $[\text{NO}_3^-]$ observed throughout the PAR, which supports high rates of primary production (e.g. Walsh et al., 1989; Hansell and Goering, 1990; Springer and McRoy, 1993; Lee et al., 2007; 2012; 2013; Varela et al., 2013; Chapter 1). These results are consistent with our finding in Chapter 1 that it is NO_3^- utilization by diatoms that drives the high rates of primary productivity throughout the PAR in July. It is therefore clear from our and previously published results that diatoms have a major impact on the biogeochemical processes in this region.

2.5.2 Drivers of regional differences in diatom bloom dynamics

2.5.2.1 Environmental controls

2.5.2.1.1 Correlation Analysis

We expanded on the correlation analysis from Chapter 1 to include euphotic-zone integrated parameters related to biogenic silica dynamics, in addition to the euphotic-zone integrated biological parameters and several physical parameters presented in Chapter 1 (see Chapter 1 for additional discussion). Our expanded analysis indicated that there were geographical differences in the bottom-up environmental influences on biogenic silica

dynamics between the Bering Sea (DBO1, DBO2) and Chukchi Sea regions (DBO3-DBO5) (Table 2.4).

In the Bering Sea, the positive correlations between $[\text{NO}_3^-]$, $[\text{Si}(\text{OH})_4]$ and $[\text{bSiO}_2]$ and between % Chl *a* > 5 μm , total Chl *a*, $[\text{bSiO}_2]$ and ρSi indicate that diatom utilization of NO_3^- results in the high autotrophic and siliceous biomass observed in this region. The positive correlations between ρSi , ρC and ρNO_3 further support this, in addition to indicating that diatoms also drive the high rates of primary production and NO_3^- utilization.

In the Chukchi Sea, the negative correlation of $[\text{Si}(\text{OH})_4]$ with bottom T and positive correlation with surface S could be indicative of water mass composition, with the nutrient-rich BSW/AW having lower temperatures and higher salinity. The positive correlation between $[\text{Si}(\text{OH})_4]$ and Z_{eu} (higher $[\text{Si}(\text{OH})_4]$ when Z_{eu} is deeper) is likely driven by the higher $[\text{Si}(\text{OH})_4]$ at depth, while the positive correlation between $[\text{Si}(\text{OH})_4]$ and $[\text{NO}_3^-]$ may be an indication of diatom nutrient utilization. We observed similar correlations between biomass and productivity to those seen in the Bering Sea regions, e.g. correlations between $[\text{bSiO}_2]$ and % Chl *a* > 5 μm and total Chl *a*, and between ρSi , ρC and ρNO_3 , all of which suggest that, again, it is diatom utilization of NO_3^- that supports the high biomass and drives the high rates of primary production and nitrate utilization.

Overall, our results confirm our finding in Chapter 1 that diatom utilization of NO_3^- drives primary productivity throughout the PAR in July.

2.5.2.1.2 *Light effects*

The significant decrease in ρSi that corresponded to the decreasing levels of light during our time-course experiment provided some indication of light affecting bSiO_2 production (Figure 2.5). This dependence of ρSi on light is further supported by the significant correlation between the weighted average irradiance and ρSi for each experimental time point (Kendall's $\tau = 0.83$, $p < 0.03$). Evidence for the light dependence of ρSi in the literature is mixed. Several studies examining the diurnal changes in ρSi in temperate and oligotrophic ecosystems found no systematic or significant differences between average rates measured during the day or night (e.g. Brzezinski and Nelson, 1989; Nelson and Brzezinski, 1997; Shipe and Brzezinski, 2001), although variability between individual day/night comparisons were sometimes high. In contrast, experiments conducted primarily in the subtropical and equatorial Pacific found a strong diurnal variation in ρSi , with daytime rates consistently being 2-3 times higher than nighttime rates (Goering et al., 1973; Azam and Chisholm, 1976; Leynaert et al., 2001; Krause et al. 2011).

Laboratory studies indicate that the energy for Si metabolism in diatoms is more closely linked to respiration than to photosynthesis (Martin-Jezequel et al., 2000). This would explain why relatively high rates of Si utilization are observed in the dark (Martin-Jezequel et al., 2000); however, species-specific differences in the coupling of Si metabolism to the photocycle have also been observed. Studies have shown that some species of diatoms take up Si during the light and dark periods, but only deposit SiO_2 in the light, while for other species these processes have only been observed in the dark period (Martin-Jezequel et al., 2000). Coupled with a potential lack of synchronicity in cellular division in natural phytoplankton populations, this could explain the contrasting

results with respect to the light dependence of Si utilization in field studies. Our results strongly suggest a dependence of ρ_{Si} on light in the PAR, with decreased light resulting in decreased ρ_{Si} (Figure 2.5). This is further supported by the relationship we find between light, V_{Si} and $[Si(OH)_4]$ (see following discussion).

2.5.2.1.3 *Interactive effects of light and $Si(OH)_4$*

In a similar analysis to that performed by Krause et al. (2011) in the Eastern Equatorial Pacific, we found evidence of Si limitation of Si utilization, and that light modulated the response of Si utilization to changes in $Si(OH)_4$ availability in the PAR (Figure 2.6).

When V_{Si} were grouped by light depth, we found statistically significant increases in the response of V_{Si} to increasing $[Si(OH)_4]$ for 100% to 15% I_0 (Figure 2.6a-d) that we did not observe when data from all stations and all depths were pooled together. We also found no significant relationship between V_{Si} and $[Si(OH)_4]$ at 1 or 0.1% I_0 , suggesting that light rather than $Si(OH)_4$ is the limiting factor at these low light levels (Figure 2.6e-f). The positive correlations between $[Si(OH)_4]$ and V_{Si} when the data were grouped by light depth are suggestive of Si limitation, which is further supported by the significant positive correlation between euphotic-zone averaged $[Si(OH)_4]$ and V_{AVE} ($r = 0.48$, $p < 0.05$). These results are also consistent with direct observations of Si limitation at 55% I_0 (see Appendix A). That we only see significant positive correlations when $[Si(OH)_4]$ and V_{Si} are grouped by light depth or are depth-integrated is likely because of the interactive effects of light and $[Si(OH)_4]$ on Si utilization rates. When grouped by light depth, the impact of changing $[Si(OH)_4]$ on V_{Si} is isolated from changes in light, while depth-integration averages through the vertical light gradient, thus masking the impact of light on the response of V_{Si} to changing $[Si(OH)_4]$.

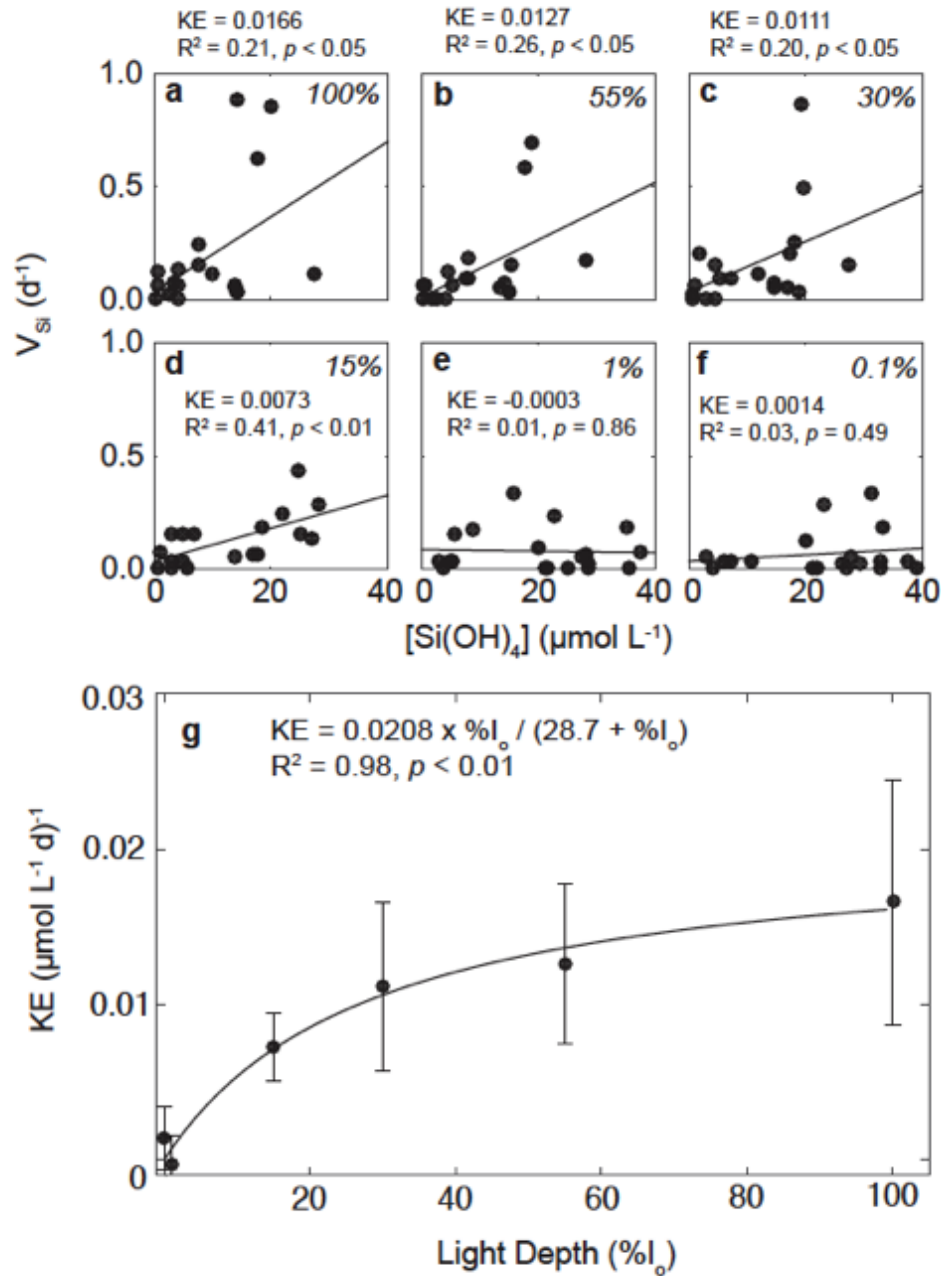


Figure 2.6. Dependence of specific Si utilization rates (V_{Si} , d^{-1}) on $[Si(OH)_4]$ at different light depth (% I_0) as follows: (a) 100% I_0 , (b) 55% I_0 , (c) 30% I_0 , (d) 15% I_0 , (e) 1% I_0 , (f) 0.1% I_0 . Straight lines in (a)-(f) are the linear least-squares regression for data presented in each panel. The slope from the least-squares regression is assumed to be the kinetic efficiency (KE) of Si utilization (see text). (g) Plot of KE ($\mu mol L^{-1} d^{-1}$) versus light depth (%), with error bars representing the standard error of the slopes from the regression analyses in (a)-(f). The black line in (g) represents a non-linear Michaelis-Menten fit to the data represented by equation (3).

Based on Michaelis-Menten kinetics, the efficiency of Si uptake at low concentration is indicated by the steepness of the initial slope of the asymptotic curve (kinetic efficiency,

$KE = V_{\max}/K_s$; Healey, 1980), with higher values corresponding to more efficient Si utilization. The slope from the linear regressions between $[Si(OH)_4]$ and V_{Si} at each light depth likely approximate this initial slope of a Michaelis-Menten fit to the data, especially given that there was no significant difference between the slope from a linear fit to the data compared to the initial slope from a Michaelis-Menten fit. Although Michaelis-Menten fits to the data were not statistically significant at $p < 0.10$, this lack of significance could be the result of differences in the kinetic parameters of different diatom communities for each of our sample sites, times, or depths. Thus, we assume that the slope of the linear regression between V_{Si} and $[Si(OH)_4]$ approximate a regional ‘average diatom assemblage’ KE of Si uptake for each light depth for the PAR. A regional ‘average diatom assemblage’ KE at each light depth for the PAR is also supported by kinetic experiments performed at 55% (Appendix A). These experiments enabled a more precise estimation of KE by exposing natural diatom assemblages to a range of $[Si(OH)_4]$ and using measurements of V_{Si} at these different $[Si(OH)_4]$ to determine $V_{\max}$ and K_s based on Michaelis-Menten kinetics. These results showed that there were no significant differences in KE between DBO regions at 55% I_0 .

The interactive effect of light and $[Si(OH)_4]$ on Si utilization is further evidenced by the relationship between KE and light (Figure 2.6g). We found that the uptake of Si at low concentrations was most efficient (i.e. had the steepest slope/highest KE) at the surface, and this efficiency declined with decreasing light level (Figure 2.6a-f). Given that V_{Si} no longer reflected changes in $Si(OH)_4$ at low light, it stands to reason that at some light level, the response of V_{Si} to changes in $Si(OH)_4$ will no longer reflect any increase in light. This essentially describes the two-layered model of oceanic euphotic

zones from Dugdale (1967), where nutrient limitation controls productivity in the well-lit upper euphotic zone, while light limitation controls productivity at greater depths. It is also consistent with the relationship between K_s and light level observed for both Si and N utilization by phytoplankton (e.g. Goering et al., 1973; MacIsaac and Dugdale, 1972). Thus, we assume that the relationship between KE and light can be fit to a Michaelis-Menten style curve using the following equation:

$$KE = \frac{KE_{max} \cdot \%I_o}{(K_L + \%I_o)} \quad (3)$$

where KE is the slope of the linear regression at a specific light level (% I_o), KE_{max} is the maximum kinetic efficiency, % I_o is the light level, and K_L is the half-saturation constant for light, or the light level at which $KE = \frac{1}{2}KE_{max}$. We found a strongly significant non-linear relationship between KE and % I_o (Figure 2.6g). Our results indicate that the ambient irradiance in surface waters of the PAR may not be sufficient to maximize the Si utilization by diatoms given that the KE_{max} we determine from this fit is greater than the KE at 100% I_o (i.e. 0.0208 vs 0.0166 ($\mu\text{mol L}^{-1} \text{d}^{-1}$)). In other words, even at the surface, Si utilization exhibits some light limitation. This is likely because the decreased angle of sunlight at higher latitudes (such as in the PAR) results in lower light levels compared to other locations in the world's oceans. We found K_L to be 28.7%, which indicates that below that threshold, light exerts a greater influence on Si utilization than changes in $[\text{Si}(\text{OH})_4]$.

Our results showing a relationship between nutrient utilization rates and light are consistent with previous studies conducted both in the PAR (Lee et al., 2013), and in the Eastern Equatorial Pacific (Krause et al., 2011). At similar sampling locations to our

own, Lee et al. (2013) found that in near-surface waters (2-5 m), light exerted a greater influence on primary productivity compared to $[\text{NO}_3^-]$. In contrast to our analysis, which looks at the response of the regional aggregate phytoplankton assemblage to changes in light and $[\text{Si}(\text{OH})_4]$, their experiments were conducted at only one depth, thus exposing a single phytoplankton assemblage to differences in light and $[\text{NO}_3^-]$; however, given that they observe an increase in primary productivity in response to differing light levels at all locations sampled, their results support our findings that the sensitivity of phytoplankton nutrient utilization and growth to changes in light is ubiquitous throughout the PAR. In the Eastern Equatorial Pacific, Krause et al. (2011) found a similar relationship between light level and the response of V_{Si} to changing $\text{Si}(\text{OH})_4$. They suggested that the relationship may be related to the interactive effects of light and iron (Fe) in this region, given that Fe-depleted diatoms have compromised photosystems (e.g. Sunda and Huntsman, 1997). While this may be true in the Eastern Equatorial Pacific, it is unlikely that diatoms in the PAR are Fe-limited. Although no trace-metal measurements were made during our cruises, previous measurements of dissolved Fe concentrations ($[\text{DFe}]$) throughout the water column in our study region from August 2007 and July 2008 were consistently $>1 \text{ nmol L}^{-1}$ and increased with depth (Nishimura et al., 2010). In addition, low $[\text{DFe}]$ were only observed when $[\text{NO}_3^-]$ and $[\text{Si}(\text{OH})_4]$ were also depleted (Nishimura et al., 2012), so it is unlikely that Fe was limiting growth any more than NO_3^- or Si may have had. In our case, the reason for the observed light dependence of the KE of Si may be simply that changes in light regulate the available cellular energy required for Si uptake and bSiO_2 production.

2.5.2.2 Water mass effects on $bSiO_2$ dynamics

We found a strong east-west gradient in dissolved and biogenic SiO_2 concentrations, $bSiO_2$ production rates, and the diatom contribution to PP in the southern Chukchi Sea in 2014 (Figure 2.7; Table 2.7). Biogenic silica concentrations and ρSi were at least 3 times higher on the western side of DBO3 compared to the eastern side, and the diatom contribution to PP on the western side was twice that of the eastern side (Table 2.7). In contrast, $[Si(OH)_4]$ in DBO3W was much lower than that in DBO3E (Table 2.7). These differences coincided with changes in T, S and $[NO_3^-]$ in 2014 (Figure 2.7; data from Cooper et al., 2016f). Although the T, S, $[NO_3^-]$ and $[Si(OH)_4]$ data we present in Figure 2.7 are only for 2014, similar differences between W and E for these parameters were also observed during other years (Chapter 1; Cooper et al., 2016a-g; 2017). These results are consistent with several previous studies that found similarly strong east-west gradients in nutrients and phytoplankton biomass, productivity, and assemblage composition likely driven by differences in water mass composition (e.g. Walsh et al., 1989; Lee et al., 2007; Cooper et al., 2012; Danielson et al., 2017; Chapter 1). The measurements presented in Chapter 1 come from concurrent samples to those presented in this chapter. Results for 2014 from Chapter 1 are summarized in addition to our own in Table 2.7. The only parameters measured as part of this study that did not show east-west differences were $[LSiO_2]$ and the diatom contribution to ρNO_3 (Table 2.7).

Our results suggest that $[NO_3^-]$ plays a greater role in controlling the longitudinal differences in diatom biomass and productivity in this region than $[Si(OH)_4]$. Euphotic-zone integrated $[Si(OH)_4]$ was 2 times higher in DBO3E compared to DBO3W in 2014, while euphotic-zone integrated $[NO_3^-]$ was 24 times higher in DBO3W compared to DBO3E.

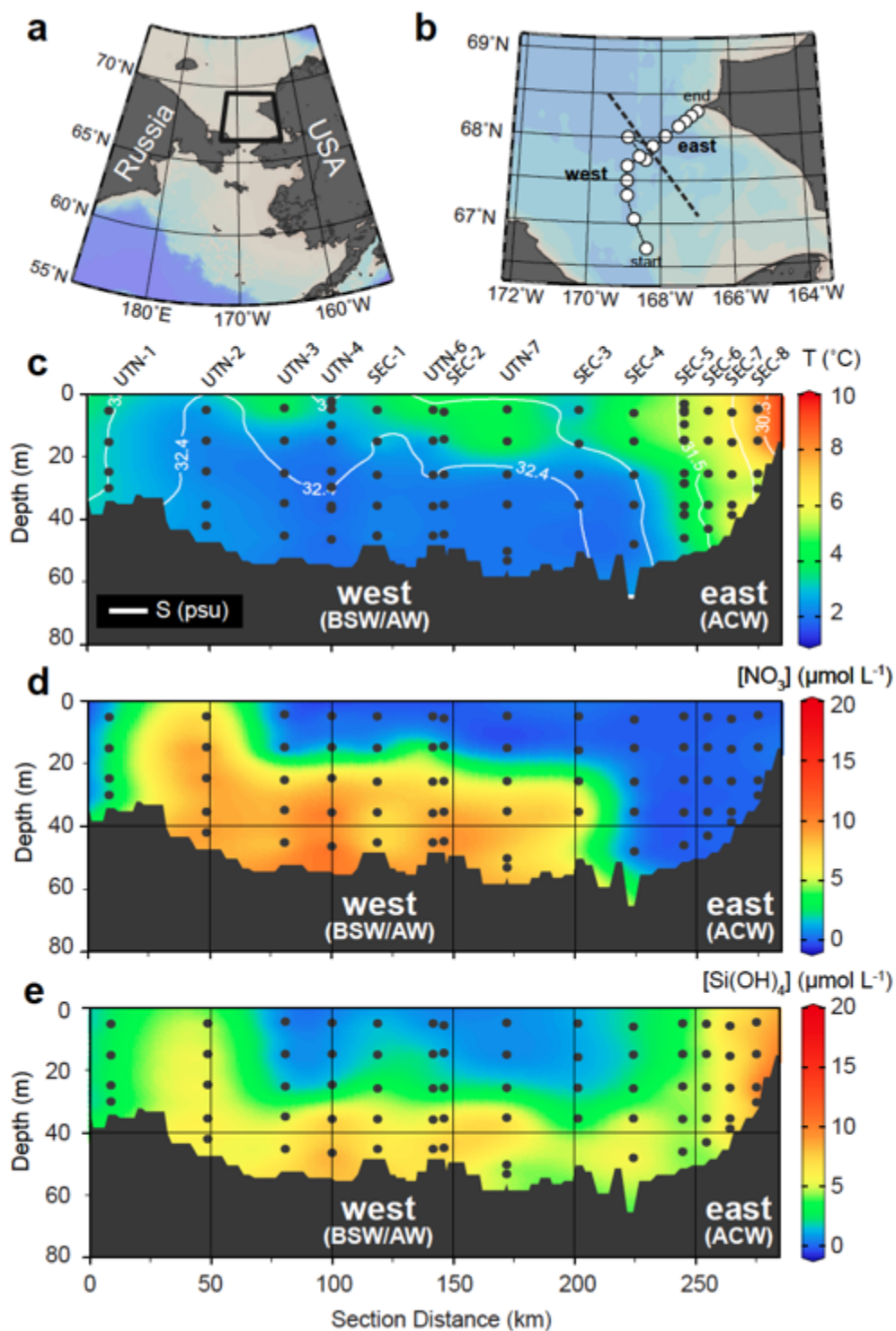


Table 2.7. Chemical and biological differences between the western (DBO3W) and eastern (DBO3E) sides of DBO3 in 2014. Depth-integrated $[\text{NO}_3^-]$, Chl *a*, % >5 μm Chl *a*, ρC and ρNO_3 are from the concurrent measurements reported in Chapter 1. Data for % diatoms in the phytoplankton assemblage are for the same stations, but from measurements in 2013 as reported in Chapter 1. When reported, errors are $\pm$ 1SD based on triplicate samples collected at one or more depths at each station.

Parameter	DBO3W	DBO3E
<i>Nutrients</i>		
$[\text{NO}_3^-]$ (mmol m^{-2})*	157 ± 12	6.4 ± 2
$[\text{Si}(\text{OH})_4]$ (mmol m^{-2})	38 ± 6	71 ± 12
<i>Particulates</i>		
Chl <i>a</i> (mg m^{-2})*	128 ± 2	14 ± 1
% >5 μm Chl <i>a</i> *	89 ± 2	33 ± 9
$[\text{bSiO}_2]$ (mmol m^{-2})	265 ± 6	91 ± 12
$[\text{lSiO}_2]$ (mmol m^{-2})	166 ± 8	134 ± 14
<i>Phytoplankton assemblage</i>		
% diatoms***	72%	5%
<i>Rates</i>		
ρC ($\text{mmol m}^{-2} \text{d}^{-1}$)*	110 ± 2	18 ± 0.2
ρNO_3 ($\text{mmol m}^{-2} \text{d}^{-1}$)*	7.8 ± 1.4	0.6 ± 0.2
ρSi ($\text{mmol m}^{-2} \text{d}^{-1}$)	9.0 ± 0.2	0.6 ± 0.2
V_{AVE} (d^{-1})	0.054 ± 0.005	0.008 ± 0.005
<i>Diatom contribution to productivity</i>		
% diatom PP	41%	17%
% diatom ρNO_3	87%	82%

*data from Chapter 1, **data for July 2013

The longitudinal difference in $[\text{Si}(\text{OH})_4]$ is likely due to the depletion of $[\text{Si}(\text{OH})_4]$ in waters <20 m depth in DBO3W, while waters >20 m in DBO3W and throughout the water column in DBO3E had similarly high $[\text{Si}(\text{OH})_4]$ (Table 2.7; Figure 2.7e). In contrast, $[\text{NO}_3^-]$ was near or below the detection limit throughout the water column on the eastern side of DBO3. While $[\text{NO}_3^-]$ were low or undetectable in the surface waters of DBO3W, $[\text{NO}_3^-]$ at >20 m were much higher ($\sim 10 \mu\text{mol L}^{-1}$; Figure 2.7d). Given that $[\text{bSiO}_2]$ and ρSi were, respectively, 3 and 14 times higher on the western side of DBO3 compared to the eastern side indicates that diatoms respond more to differences in $[\text{NO}_3^-]$

than those in $[\text{Si}(\text{OH})_4]$ (Table 2.7). This is also supported by the similarity in the diatom contribution to ρNO_3 on the eastern and western sides of DBO3 (Table 2.7).

The east-west gradient we observed in DBO3 illustrates the significant spatial variability that can exist in physical, chemical and biological parameters of the water column, even within each of the DBO regions. Our results confirm that diatoms are the major contributor to phytoplankton biomass and productivity in the nutrient-rich waters that overlay benthic hotspots (Chapter 1). Given that the spatial variations in water mass composition and properties coincide with changes in the benthic ecosystem of the PAR (e.g. Grebmeier et al., 2015), it is important to consider how changes in the distribution and properties of these water masses might affect the marine food web and the degree of pelagic-benthic coupling. Our results suggest that decreases in $[\text{NO}_3^-]$ would result in a decrease in the diatom contribution to biomass and productivity, which would likely cascade up the food web and result in dramatic shifts in the marine ecosystem such as loss of benthic hotspots. Changes in the nutrient content of waters flowing further into the Arctic, and loss of a highly productive phytoplankton assemblage on the Bering and Chukchi shelves could also have far reaching consequences for biogeochemical fluxes and climate feedbacks in the PAR and throughout the Arctic (Tozzi et al., 2004).

2.5.2.3 Interannual trends and variability

Despite consistent sampling times (always in mid-July), locations and methodologies, the large interannual variations observed in all measured parameters make it difficult to draw any significant conclusions regarding changes in biogenic silica dynamics in the PAR (Table 2.3; Figures 2.2-2.4). In Chapter 1, we reported similarly high interannual variability for our concurrent measurements of phytoplankton biomass and productivity. Our results further demonstrate the difficulty in identifying long-term trends in this

region, especially from sampling that occurs only once per year; however, despite the large interannual variability, we observed interannual trends in some Si-related parameters.

In DBO1, we found that ρSi , V_{Si} and the contribution of diatoms to primary production and ρNO_3 decreased from 2013 to 2016 (Table 2.3). This decrease corresponded to a similar decrease in the contribution of phytoplankton $>5\ \mu\text{m}$ to Chl *a* that we documented in Chapter 1. In Chapter 1, we attributed this trend to a shift in the timing of the spring bloom to earlier in the growing season, meaning that, by the time of our sampling in mid-July, we were sampling progressively later stages of the seasonal bloom each year. Changes in the timing of the seasonal sea-ice breakup may have driven this shift in the seasonal bloom given that: (1) the timing of the spring bloom in DBO1 is dependent on the timing of this event (Brown et al., 2013), and (2) the mean timing of sea-ice breakup has decreased over the 2013-2016 period (Grebmeier et al., 2018; Frey et al., in DBO special issue).

The interannual trends we observe in DBO1 support our claim in Chapter 1 that phytoplankton phenology responds to short-term environmental changes; however, as we state in Chapter 1, it is difficult to draw any conclusions with regards to whether these trends indicate a longer-term shift in the ecosystem or are just a response to interannual variability. It is only with long-term and consistent monitoring programs, like DBO, that we will better understand the present and future climate-induced changes on the productive ecosystems of the PAR.

2.6 Conclusions

We present the first study to directly quantify rates of bSiO_2 production rates in the Pacific Arctic Region. From the decade of summertime dissolved and particulate silica

measurements and four years of biogenic silica production rates, we confirm that diatoms control much of the biomass and productivity in regions influenced by the nutrient rich AW. Rates of bSiO_2 production in the Pacific Arctic Region were high, and exhibited similar spatial trends to concurrent measurements of primary productivity and nitrate utilization rates that track the northward progression of the seasonal bloom. Diatoms drive most of the primary production and nitrate utilization in the PAR during July, but contribute a disproportionately large amount to the NO_3^- utilization ($87 \pm 6\%$), while their contribution to primary productivity ($61 \pm 8\%$) is proportionate to their contribution to autotrophic biomass ($65 \pm 4\%$). Finally, although interannual variability was high for all measured parameters, we found that phytoplankton phenology responds to short-term environmental changes, with a shift in the timing of the spring bloom due to earlier sea-ice breakup resulting in a decrease in bSiO_2 production and the contribution of diatoms to primary production and nitrate utilization at the time of our sampling in July. Considering that the north Bering Sea and the Bering Strait act as the main import gateway for Si(OH)_4 to the Arctic (Torres-Valdez et al., 2013), such changes have the potential to significantly affect the nutrient and food-web dynamics not only in the Pacific Arctic Region, but also in other parts of the Arctic influenced by these waters.

Although NO_3^- is believed to be the main limiting nutrient in Arctic marine waters, our results indicate that the influence of Si(OH)_4 on diatom growth should not be overlooked. While the east to west gradient in $[\text{bSiO}_2]$ and ρSi in the southeastern Chukchi Sea shows that changes in relative distribution of NO_3^- can result in significant changes in the composition of phytoplankton assemblages, we also found evidence of Si limitation of bSiO_2 production, and that light may also be affecting bSiO_2 production in the PAR.

Climate-induced changes in any of these factors could further impact food-web dynamics and biogeochemical cycling in the PAR.

Light also appeared to modulate the response of silica production to changes in Si(OH)_4 availability and ambient irradiance in surface waters of the PAR may not be sufficient to maximize bSiO_2 production by diatoms. The influence of light on bSiO_2 production seems to primarily affect the kinetic efficiency of diatom Si utilization, with increasing light making diatoms more efficient at taking up Si(OH)_4 at low concentrations. Increases in the amount of available light to the euphotic zone due to decreased sea-ice extent could thus result in diatoms becoming more kinetically efficient in utilizing Si. This could mitigate potential decreases in nutrient supply, but could also lead to changes in the Si:C:N ratios as the metabolisms of C and N become decoupled from that of Si under low light conditions. Such changes could subsequently impact the diatom contribution to the biological carbon pump and downward fluxes of bSiO_2 and N in the Arctic.

Chapter 3
Recycling of biogenic silica in the Pacific Arctic Region from
2013–2016

3.1 Abstract

We present the first measurements of net biogenic silica production ($\Delta bSiO_2$) and biogenic silica dissolution rates (ρSi_{diss}) made over a period of four years within five biological ‘hotspots’ in the Bering and Chukchi Seas from south of St. Lawrence Island to Barrow Canyon. Rates of net $bSiO_2$ production ($\Delta bSiO_2$) revealed that the rate of production exceeded those of dissolution only in the highly productive waters of the southeastern Chukchi Sea. Negative rates of $\Delta bSiO_2$ (i.e. higher rates of $bSiO_2$ dissolution than production) in the other regions of the Pacific Arctic suggest limited export of $bSiO_2$ to the benthos, i.e. a weak silica pump. Rates of $bSiO_2$ dissolution were high throughout the region, with the highest values in the southeastern Chukchi Sea. These high rates could be linked to low water column Al:Si ratios and limited incorporation of aluminum into $bSiO_2$, as low Al:Si ratios in $bSiO_2$ have been shown to enhance ρSi_{diss} . We also observed an east to west gradient in ρSi_{diss} that may be driven by water mass differences in temperature, nutrients, and phytoplankton biomass and productivity, and thus on the activity of heterotrophic bacteria, whose abundance is affected by these parameters. Heterotrophic bacteria break down the protective coating on the siliceous shells of diatoms, resulting in increased $bSiO_2$ dissolution. Despite the dynamic nature of the Pacific Arctic Region driving strong interannual variability within each DBO region, we observed a decrease in the ratio of $bSiO_2$ dissolution to production from 2013 to 2016, which may be related to changes in phytoplankton and zooplankton phenology. Such changes may have far reaching consequences on other regions of the Arctic influenced by the Pacific-origin waters flowing through this important gateway to the Arctic.

3.2 Introduction

The balance between euphotic-zone integrated bSiO₂ production ($\int P$) and dissolution ($\int D$) controls the marine Si cycle in surface waters (Tréguer and De La Rocha, 2013). The ratio of these two parameters ($\int D:\int P$) is a major determinant of how diatom production translates into the export of both particulate carbon and bSiO₂ from the euphotic zone, yet it remains one of the most poorly defined parameters of the marine silica cycle (Nelson et al., 1995; Brzezinski et al., 2003; Tréguer and De La Rocha, 2013). Current estimates set the annual global $\int D:\int P$ ratio at ~ 0.56 , meaning that $\sim 56\%$ of bSiO₂ produced in surface waters is dissolved and regenerated into Si(OH)₄ in the euphotic zone rather than exported; however, measurements from specific studies range from <0.02 to ~ 6 (Tréguer and De La Rocha, 2013). Although instances when the rate of bSiO₂ dissolution exceeds that of production ($\int D:\int P > 1$) are presumably only possible on short timescales or within small areas, high $\int D:\int P$ ranging from 2 to 6 have been measured in a variety of different locations, demonstrating that there is great uncertainty regarding the factors that control the temporal and spatial variability of this ratio (e.g. Nelson and Goering, 1977; Brzezinski et al., 2001; Beucher et al., 2004; Demarest et al., 2011). Despite the importance of bSiO₂ dissolution in recycling Si(OH)₄ in the euphotic zone, the influence that this process has on phytoplankton dynamics, the silica cycle, and the links between the silica cycle and organic matter production and export remains unclear.

The mechanisms controlling bSiO₂ dissolution in the water column are also somewhat poorly constrained. Dissolution rates are primarily dependent on the surface area of the dissolving silica, aluminum (Al) content of the frustule, temperature, and the degree of undersaturation of seawater Si(OH)₄ (e.g. Van Cappellen et al., 2002 and references

therein). Warmer temperatures and a decreased incorporation of Al into bSiO₂ both serve to increase bSiO₂ dissolution rates (Kamatani, 1982; Bidle et al., 2002; Van Cappellen et al., 2002; Natori et al., 2006; Loucaides et al., 2012). Any exposed bSiO₂ surface in seawater will undergo chemical dissolution given that surface seawater everywhere is undersaturated with Si(OH)₄, although living diatoms have an organic coating that hinders this dissolution (e.g. Hurd, 1972; Kamatani, 1982). Laboratory and field studies have shown that heterotrophic bacteria are able to degrade this protective coating, greatly enhancing bSiO₂ dissolution, and thus far being the only biological process found to affect bSiO₂ dissolution rates in the ocean (Bidle and Azam, 1999; 2001; Bidle et al., 2003; Brzezinski et al., 2003).

In the western Arctic, only one study estimated bSiO₂ dissolution for the entire water column in regions of the southeastern Bering Sea (Banahan and Goering, 1986). Their estimates, based on fluxes of [Si(OH)₄] from sediments relative to annual estimates of bSiO₂ production, indicate that 34 to 65% of the surface bSiO₂ production is permanently buried within the sediments. There have been no direct measurements of water column bSiO₂ dissolution on the northern Bering Shelf or in the Chukchi Sea, or in other regions of the Arctic.

We present summertime measurements of net bSiO₂ production rates and bSiO₂ dissolution rates collected using consistent methodologies within the five DBO regions that span the period from 2013 to 2016. Our primary objectives were to quantify a baseline for bSiO₂ dissolution and evaluate the spatial and interannual variability between each DBO region. We also wanted to identify any interannual trends that might indicate shifts in the marine cycling of Si in this rapidly changing region. Finally, we sought to

elucidate potential environmental controls on this variability to better predict how marine bSiO₂ dynamics might vary under current or predicted climate changes.

3.3 Methods

3.3.1 Study Locations and Seawater Sampling

Water samples were collected at six depths throughout the water column corresponding to light levels of 100%, 50%, 30%, 15%, 1% and 0.1% of the surface incident irradiance (I_0) for the stations and cruises from 2013-2016 as described in Chapters 1 and 2. At each light level, we measured the net bSiO₂ production rates (Δ bSiO₂). The precision of all analytical techniques was determined from triplicate subsamples collected at one or more depths at each station every year. Seawater samples were collected for the concentrations of silicic acid (Si(OH)₄) and particulate silica (as bSiO₂ and lSiO₂), and for bSiO₂ production rates using the radioisotope ³²Si (ρ Si) from the same stations and depths presented in Chapter 2. Phytoplankton biomass (as Chl a) and primary productivity and nitrate uptake experiments were also collected simultaneously from the same water samples and data are presented in Chapter 1.

3.3.2 Dissolved and particulate silica concentrations

Water samples for dissolved and particulate silica concentrations (bSiO₂ and lSiO₂) were collected and processed as described in Chapter 2.

3.3.3 Rates of biogenic silica production, net production, and dissolution

Water samples for biogenic silica production rate experiments with ³²Si were collected and processed as described in Chapter 2. The net production rate of bSiO₂ (Δ bSiO₂) was determined as the difference between [bSiO₂] from initial seawater samples (described in Chapter 2) and [bSiO₂] after a 24 h incubation (Brzezinski and Nelson, 1989; Krause and Nelson, 2010). Both the initial and incubated samples received no nutrient amendments

or dilution. Samples were collected in acid-cleaned 2L polycarbonate bottles and placed in acrylic tubes covered with neutral density and blue-coloured photographic film to simulate the *in-situ* irradiance level and wavelengths at the sampling depths. Samples in the tubes were incubated for 24 h in on-desk acrylic tanks, which were temperature-controlled using flowing surface seawater. Incubations were terminated by gentle vacuum filtration (<27 kPa) onto 0.6 µm PC filters. Filters were processed as described in Chapter 2 for [bSiO₂] measurements. The initial and final [bSiO₂] were used to calculate the net production rate of bSiO₂ ($\Delta b\text{SiO}_2$) that occurred during the 24 h incubation period. The median CV for $\Delta b\text{SiO}_2$ was 13% (n = 15).

Silica dissolution rates ($\rho\text{Si}_{\text{diss}}$) were calculated as the difference between ρSi and $\Delta b\text{SiO}_2$. In a closed system, the two processes affecting the concentration of bSiO₂ are bSiO₂ production (ρSi) and dissolution ($\rho\text{Si}_{\text{diss}}$). Thus, the difference between these two processes ($\rho\text{Si} - \rho\text{Si}_{\text{diss}}$) should be equal to $\Delta b\text{SiO}_2$, such that

$$\Delta b\text{SiO}_2 = \rho\text{Si} - \rho\text{Si}_{\text{diss}} \quad (1)$$

If ρSi and $\Delta b\text{SiO}_2$ are measured in the same closed system, then it follows that

$$\rho\text{Si}_{\text{diss}} = \rho\text{Si} - \Delta b\text{SiO}_2 \quad (2)$$

While ideally $\Delta b\text{SiO}_2$ should be measured from the same ³²Si enriched sample used for ρSi , logistical and safety reasons do not make this possible. Instead, it was assumed that mass balance was conserved within each of the incubated ρSi and $\Delta b\text{SiO}_2$ samples; however, this does introduce some additional error in estimates of $\rho\text{Si}_{\text{diss}}$ due to bottle-to-bottle variability. Triplicate measurements of ρSi and $\Delta b\text{SiO}_2$ was conducted at 100% I_0 to constrain these errors, with an estimated mean CV of 17% for $\rho\text{Si}_{\text{diss}}$.

The bSiO₂ dissolution to production ratio ($\overline{D}:\overline{P}$) was estimated from the ratio of depth-integrated $\rho\text{Si}_{\text{diss}}$ to ρSi (Brzezinski et al., 2003).

3.3.4 Temperature effects on biogenic silica production and dissolution rates

Biogenic silica production and dissolution are temperature sensitive. Incubation can introduce a bias (i.e. overestimation of rates) because the flowing seawater used during incubation originates from the sea surface, which is typically warmer than waters deeper in the euphotic zone. The relationship between temperature and a given biological or chemical rate can be expressed by the following equation:

$$R_{T \text{ corrected}} = Q_{10}^{(\Delta T/10)} \times R_{\text{uncorrected}} \quad (4)$$

where $R_{T \text{ corrected}}$ is the temperature corrected biological rate, Q_{10} is the temperature coefficient (i.e. the factor by which a biological or chemical rate is increased by a 10°C rise in temperature), ΔT is the change in temperature in °C, and $R_{\text{uncorrected}}$ is the uncorrected biological rate. This method allows for the correction of biological rate measurements for differences in temperature assuming there is an Arrhenius-type relationship between rates and temperature and that chemical kinetics control the observed rate (Ahlgren, 1987).

Temperature coefficients (Q_{10}) for $\rho\text{Si}_{\text{diss}}$ range from 2.3 (Kamatani et al., 1982; Bidle et al., 2002) to 2.6 (Natori et al., 2006), with an average $Q_{10} = 2.4$. Only one study reported a Q_{10} value for ρSi ($Q_{10} = 2$; Azam et al., 1974). Using these literature values, biogenic silica production and dissolution rates can be corrected for differences in temperature according to the following two equations:

$$\rho\text{Si}_{T \text{ corrected}} = 2^{(\Delta T/10)} \times \rho\text{Si} \quad (5)$$

$$\rho\text{Si}_{\text{diss}, T \text{ corrected}} = 2.4^{(\Delta T/10)} \times \rho\text{Si}_{\text{diss}} \quad (6)$$

where ΔT is the difference between the incubator (surface seawater) and the *in-situ* temperature for each sample depth.

Correcting ρSi and ρSi_{diss} for temperature changes also allows for correction of $\Delta bSiO_2$ using the following equation:

$$\Delta bSiO_{2,T \text{ corrected}} = \rho Si_{T \text{ corrected}} - \rho Si_{diss, T \text{ corrected}} \quad (7)$$

All rates presented are temperature-corrected (i.e. $\rho Si_{T \text{ corrected}}$, $\Delta bSiO_{2,T \text{ corrected}}$, and $\rho Si_{diss, T \text{ corrected}}$) and referred to throughout the rest of this chapter as ρSi , $\Delta bSiO_2$ and ρSi_{diss} . Uncorrected rates for ρSi are presented in Chapter 2. These temperature corrections resulted in an average decrease of 17% for ρSi , 32% for $\Delta bSiO_2$, and 23% for ρSi_{diss} . In some cases, even after temperature correction, ρSi_{diss} at specific light depths was < 0 , i.e. $\Delta bSiO_2 > \rho Si$. We assume this is driven by bottle-to-bottle variability as the average difference between $\Delta bSiO_2$ and ρSi in these cases was $0.41 \mu mol L^{-1} d^{-1}$, which is similar to our mean SD for $\Delta bSiO_2$ ($0.36 \mu mol L^{-1} d^{-1}$). Given the higher precision of ρSi (mean SD = $0.06 \mu mol L^{-1} d^{-1}$) compared to $\Delta bSiO_2$, when $\Delta bSiO_2 > \rho Si$ it was assumed that $\rho Si_{diss} = 0$ and that $\Delta bSiO_2 = \rho Si$.

3.3.5 Data organization and analysis

Data were depth-integrated using trapezoidal integration from the surface to the bottom of the euphotic zone (0.1% of surface irradiance). The term ‘time-averaged’ represents an average of data from 2013 to 2016. For DBO3, only data from DBO3W is included in the time-averaged results and discussion, because sampling in DBO3E occurred in only 1 out of the 4 cruises. A discussion of the differences between DBO3W and E is still included in section 3.5.2.2. Unless otherwise stated, linear relationships were determined using Pearson linear correlation tests, significant differences between measured parameters

were determined using student's t-tests, and $\alpha < 0.05$ was used to determine significance.

Matlab R2014b was used to conduct all statistical tests..

3.4 Results

3.4.1 Time-averaged net biogenic silica production and dissolution rates

The time-averaged $\Delta bSiO_2$ was close to zero throughout the euphotic zone for all of the DBO regions (Figure 3.1a).

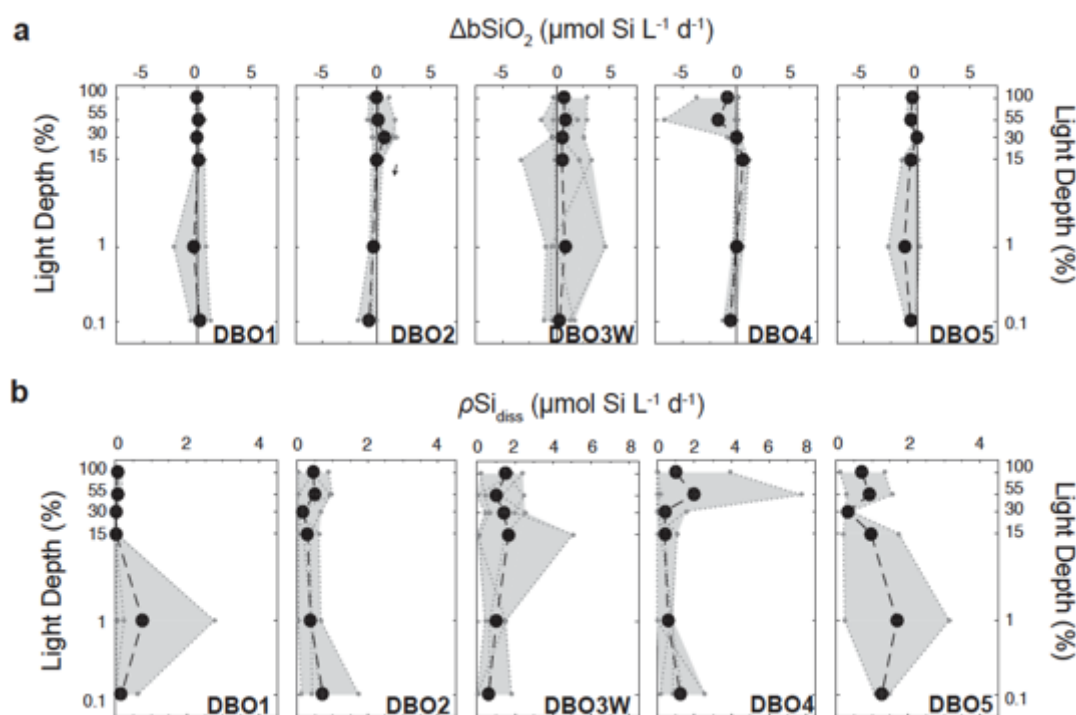


Figure 3.1. Time-averaged vertical profiles of (a) net accumulation rate of $bSiO_2$ ($\Delta bSiO_2$) and (b) $bSiO_2$ dissolution rates (ρSi_{diss}) over the 2006-2016 period for each DBO region. Data are plotted using light depths (i.e. percentage of incident surface irradiance, I_0) to account for differences in depths sampled among years. The depth scale is logarithmic to reflect the exponential attenuation of irradiance in the water column. Filled black dots and black dashed lines signify the time-averaged vertical profiles, calculated as the average of 2013 to 2016 for each light depth. Smaller grey dots and grey dashed lines represent vertical profiles from each year sampled. Shaded grey areas indicate the range of values (maximum and minimum) for each parameter in each region. Note the different x-axes scales for DBO3W and DBO4 in panel b.

Internationally, $\Delta bSiO_2$ rates were the most variable in DBO3W. Silica dissolution rates exhibited different vertical trends between regions (Figure 3.1b). Rates were higher in the lower euphotic zone in DBO1 and DBO5 and in the upper euphotic zone for DBO4. ρSi_{diss} were similar throughout the euphotic zone of DBO2 and DBO3W. The

highest $\rho\text{Si}_{\text{diss}}$ and most variable interannually were observed throughout the euphotic zone in DBO3W, and at 100 and 50% I_0 in DBO4 (note different scales for DBO3W and DBO4 in Figure 3.1b).

The depth-integrated distributions of ΔbSiO_2 exhibited spatial and temporal variations that showed some differences from those of $\rho\text{Si}_{\text{diss}}$ (Table 3.1; Figure 3.2).

Table 3.1. Temperature-corrected depth-integrated measurements of bSiO₂ production (ρSi), net bSiO₂ production (ΔbSiO_2), Si dissolution rates ($\rho\text{Si}_{\text{diss}}$) and the [D]:[P] ratio for the five DBO regions in the Bering and Chukchi Seas in July from 2006-2016. For DBO3, due to limited sampling in the eastern side of the region, only data from the western side (DBO3W) is presented here (similar to Chapter 2, but in contrast to Chapter 1). Depth integrations were done from the ocean surface to the 0.1% I_0 depth. (-) indicates that data is not available.

Region	Year	ρSi (mmol m ⁻² d ⁻¹)	ΔbSiO_2 (mmol m ⁻² d ⁻¹)	$\rho\text{Si}_{\text{diss}}$ (mmol m ⁻² d ⁻¹)	[D]:[P]
<i>Northern Bering Shelf</i>					
DBO1	2013	16.9	12.0	4.89	0.29
	2014	6.69	-24.3	31.0	4.63
	2015	0.49	-1.74	2.23	4.53
	2016	0.34	-0.59	0.94	2.72
	Mean ($\pm\text{SE}$)	6.10 $\pm$ 3.88	-3.67 $\pm$ 7.55	9.76 $\pm$ 7.13	3.04 $\pm$ 1.02
DBO2	2013	4.63	-22.6	27.2	5.88
	2014	22.2	20.2	1.98	0.09
	2015	4.26	-9.60	13.9	3.26
	2016	1.87	-3.92	5.79	3.09
	Mean ($\pm\text{SE}$)	8.24 $\pm$ 4.69	-3.98 $\pm$ 8.96	12.2 $\pm$ 5.56	3.08 $\pm$ 1.18
<i>Southeastern Chukchi Sea</i>					
DBO3W	2013	26.1	-33.1	59.1	2.27
	2014	9.01	-1.59	10.6	1.18
	2015	61.6	25.4	36.1	0.59
	2016	47.0	34.5	12.5	0.26
	Mean ($\pm\text{SE}$)	35.9 $\pm$ 11.5	6.30 $\pm$ 15.2	29.6 $\pm$ 11.4	1.07 $\pm$ 0.44
<i>Northeastern Chukchi Sea</i>					
DBO4	2013	17.1	-27.7	44.9	2.62
	2014	10.7	-0.96	11.7	1.09
	2015	27.8	3.31	24.5	0.88
	2016	11.3	-4.54	15.8	1.40
	Mean ($\pm\text{SE}$)	16.7 $\pm$ 3.97	-7.50 $\pm$ 6.93	24.2 $\pm$ 7.37	1.50 $\pm$ 0.39
DBO5	2013	8.24	-24.4	32.6	3.96
	2014	-	-	-	-
	2015	10.6	0.23	10.4	0.98
	2016	-	-	-	-
	Mean ($\pm\text{SE}$)	9.42 $\pm$ 1.18	-12.1 $\pm$ 12.3	21.5 $\pm$ 11.1	2.47 $\pm$ 1.49

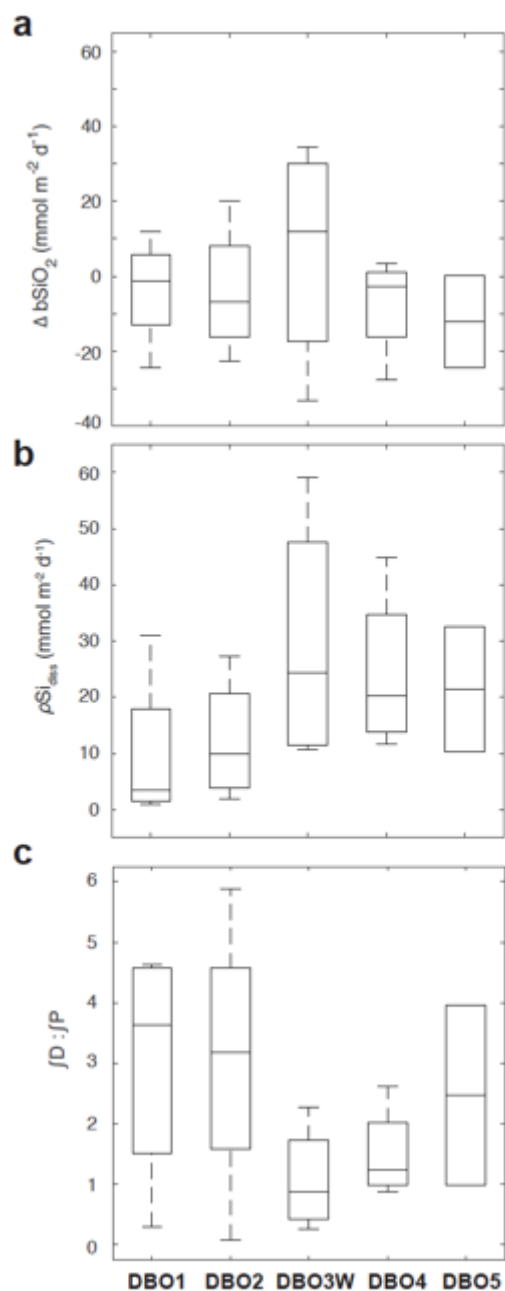


Figure 3.2. Box plots of depth-integrated (a) net accumulation rate of bSiO₂ ($\Delta bSiO_2$) (b) bSiO₂ dissolution rates (ρSi_{diss}) and (c) [D]:[P] ratios for each DBO region from 2013 to 2016 as in Figure 3 of Chapter 1. Data from the DBO3 region are separated into east (DBO3E) and west (DBO3W) to reflect water mass differences (west = nutrient rich AW/BSW; east = nutrient poor ACW). For DBO3, due to limited sampling in the eastern side of the region, only data from the western side (DBO3W) is presented here (similar to Chapter 2, but in contrast to Chapter 1).

Depth-integrated $\Delta b\text{SiO}_2$ was highest in DBO3W, close to zero for DBO1 and DBO4, and negative in DBO2 and DBO5 (Table 3.1; Figure 3.2a). Depth-integrated $\rho\text{Si}_{\text{diss}}$ were higher in DBO3-5 compared to DBO1-2 (Table 3.1; Figure 3.2b). Interannual variability in $\Delta b\text{SiO}_2$ and $\rho\text{Si}_{\text{diss}}$ was highest in DBO3W (Figure 3.2a-b). An increasing trend in $\Delta b\text{SiO}_2$ was observed in DBO3W, although this did not result in a corresponding trend in $\rho\text{Si}_{\text{diss}}$ (Table 3.1). Other clear year-to-year trends were not observed in either $\Delta b\text{SiO}_2$ or $\rho\text{Si}_{\text{diss}}$.

The time-averaged ratio of $b\text{SiO}_2$ dissolution to production, i.e. $\int D:\int P$, was highest in DBO1-2 and DBO5 and lowest in DBO3W (Table 3.1; Figure 3.2c). Interannual variability was also high for DBO1-2, and low for DBO3W and DBO4. A decreasing trend in $\int D:\int P$ from 2013 to 2016 was observed in DBO3W, which likely corresponds to the increasing trend in $\Delta b\text{SiO}_2$ observed over the same time period in this region. No other regions exhibited any clear interannual trends.

3.4.2 Statistical comparisons between DBO regions and years sampled

No statistical differences in depth-integrated $\Delta b\text{SiO}_2$, $\rho\text{Si}_{\text{diss}}$ and $\int D:\int P$ between DBO regions or between years sampled were observed, as determined by a nonparametric Kruskal-Wallis test with post hoc comparison (at $p < 0.05$). If data were grouped geographically into either the Bering Sea (DBO1 and DBO2) or the Chukchi Sea (DBO3 to 5), $\rho\text{Si}_{\text{diss}}$ was significantly higher in the Chukchi Sea, but this difference was only significant if the one year of data (2014) from DBO3E were included as part of the Chukchi Sea region.

3.4.3 Correlation analysis between physical and biological parameters in the Bering and Chukchi Seas

We expanded on the correlation analysis from Chapters 1 and 2 to include euphotic zone integrated measurements of net bSiO_2 production and dissolution rates to further identify potential environmental influences on bSiO_2 dynamics in the PAR (Table 3.2). All data were grouped geographically into either Bering Sea (DBO1-2) or Chukchi Sea (DBO3-5) regions, and a separate analysis was conducted for each. Significant correlations were found in both the Bering and Chukchi Seas.

In the Bering Sea, rates of ΔbSiO_2 and $\rho\text{Si}_{\text{diss}}$ were negatively correlated with each other. We also found that $[\text{D}]:[\text{P}]$ was negatively correlated with ρSi and ρNO_3 at $p < 0.05$ and with $[\text{Si}(\text{OH})_4]$, $\text{Chl } a$ and ΔbSiO_2 at $p < 0.10$. In the Chukchi Sea, we found that $[\text{D}]:[\text{P}]$ was negatively correlated with bottom S, and % $\text{Chl } a > 5 \mu\text{m}$. Furthermore, ΔbSiO_2 was positively correlated with ρSi and negatively correlated with $\rho\text{Si}_{\text{diss}}$.

3.5 Discussion

3.5.1 Regional patterns of biogenic silica dissolution in the Pacific Arctic Region from 2013-2016

Our measurements of ΔbSiO_2 and $\rho\text{Si}_{\text{diss}}$ are the first for the Pacific Arctic Region. The latitudinal patterns in ΔbSiO_2 , $\rho\text{Si}_{\text{diss}}$ and $[\text{D}]:[\text{P}]$ reflect the timing of the seasonal bloom in each DBO region, consistent with the findings in Chapters 1 and 2. The low ΔbSiO_2 and high $\rho\text{Si}_{\text{diss}}$ in DBO1-2 suggest that these regions were in a late or post-bloom condition by the time of our sampling (Table 3.1). The generally high $[\text{D}]:[\text{P}] > 1$ indicate that no bSiO_2 was being exported out of the euphotic zone at this time. The western side of DBO3 was the only region in which time-averaged ΔbSiO_2 was positive, meaning that there was net production of bSiO_2 .

Table 3.2. Correlation matrix between physical, chemical and biological parameters for the Bering and Chukchi Seas from 2006 to 2016. Physical data (temperature and salinity) is presented for surface and bottom depths, and biological and chemical data are presented as depth-integrated values from the ocean surface to the 0.1% I_0 depth. Data for concurrent measurements of T and S (surf and bot), $[\text{NO}_3^-]$, Chl a , % Chl $a > 5 \mu\text{m}$, ρC and ρNO_3 are from Chapter 1. Data for $[\text{bSiO}_2]$ are from Chapter 2. Significant relationships at $p < 0.05$ and $p < 0.01$ are in bold. Significant relationships at $p < 0.10$ are in italics. Surf = surface (1-2m), Bot = bottom (2-5m from the seafloor), T = temperature, S = salinity, Z_{eu} = euphotic zone depth.

	Surf T	Bot T	Surf S	Bot S	Z_{eu}	$[\text{NO}_3^-]$	$[\text{Si}(\text{OH})_4]$	Chl a	% Chl $a > 5 \mu\text{m}$	$[\text{bSiO}_2]$	ρC	ρNO_3	ρSi	ΔbSiO_2	$\rho\text{Si}_{\text{diss}}$
Bering Sea (DBO1, DBO2)															
Bottom T	-0.56**														
Surface S	-0.73*	0.22													
Bottom S	0.00	-0.07	0.37												
Z_{eu} (m)	0.41	-0.66*	-0.06	-0.18											
$[\text{NO}_3^-]$	-0.41	0.18	0.56**	0.64*	-0.05										
$[\text{Si}(\text{OH})_4]$	-0.12	-0.12	0.38	0.40	0.38	0.68*									
Chl a	0.18	-0.25	-0.27	-0.08	-0.09	-0.28	-0.25								
% Chl $a > 5 \mu\text{m}$	-0.28	-0.01	-0.09	0.20	-0.41	0.12	-0.28	0.59**							
$[\text{bSiO}_2]$	-0.18	0.15	0.07	0.39	-0.26	0.67*	0.27	0.18	0.63**						
ρC	-0.28	<i>0.45†</i>	0.19	0.09	-0.32	0.19	0.05	0.22	0.21	0.22					
ρNO_3	-0.15	0.07	0.02	-0.02	-0.25	-0.10	0.00	<i>0.44†</i>	0.39	0.11	0.78*				
ρSi	-0.01	0.19	-0.18	0.49	-0.38	0.15	-0.08	<i>0.66†</i>	0.87*	0.76**	0.74**	0.89*			
ΔbSiO_2	0.15	0.01	-0.31	0.13	0.10	0.17	0.38	0.50	0.60	0.26	0.59	0.46	<i>0.64†</i>		
$\rho\text{Si}_{\text{diss}}$	-0.20	0.11	0.27	0.16	-0.38	-0.11	-0.54	-0.20	-0.18	0.18	-0.26	0.00	-0.15	-0.85*	
$[\text{D}]:[\text{P}]$	-0.26	-0.01	0.29	-0.35	-0.10	-0.11	<i>-0.66†</i>	<i>-0.65†</i>	-0.38	-0.60	-0.62	-0.76**	-0.91*	<i>0.66†</i>	-0.26
Chukchi Sea (DBO3, DBO4, DBO5)															
Bottom T	0.65*														
Surface S	0.65*	0.78*													
Bottom S	<i>-0.41†</i>	-0.52**	-0.24												
Z_{eu} (m)	0.03	-0.20	-0.24	-0.21											
$[\text{NO}_3^-]$	-0.02	0.01	0.01	0.21	0.50**										
$[\text{Si}(\text{OH})_4]$	-0.12	<i>-0.42†</i>	<i>-0.40†</i>	0.27	0.60*	0.77*									
Chl a	0.01	0.23	0.34	0.05	<i>-0.42†</i>	-0.20	-0.39								
% Chl $a > 5 \mu\text{m}$	-0.23	-0.18	0.01	<i>0.50†</i>	-0.14	0.36	0.20	0.55**							
$[\text{bSiO}_2]$	-0.11	0.22	0.29	0.04	-0.22	-0.06	-0.34	0.88*	0.59**						
ρC	0.14	0.39	0.39	0.23	-0.55**	-0.05	-0.28	0.84*	0.46	0.72*					
ρNO_3	0.20	0.35	0.38	0.03	0.12	0.67*	0.43	0.00	0.19	0.13	0.18				
ρSi	0.42	0.42	0.48	0.32	-0.43	0.31	0.00	0.52	0.39	0.34	0.83*	0.89*			
ΔbSiO_2	0.41	0.12	0.24	0.05	0.06	0.31	0.21	0.46	0.25	0.30	0.52	0.46	0.70**		
$\rho\text{Si}_{\text{diss}}$	-0.08	0.31	0.23	0.29	<i>-0.58†</i>	-0.06	-0.29	-0.02	0.11	-0.02	0.25	0.39	0.19	<i>-0.57†</i>	
$[\text{D}]:[\text{P}]$	0.29	0.42	0.16	-0.67**	0.36	-0.44	-0.34	-0.27	-0.74*	-0.31	-0.30	-0.31	-0.40	-0.42	0.12

* $p < 0.01$, ** $p < 0.05$, † $p < 0.10$

Overall, $\rho\text{Si}_{\text{diss}}$ was significantly higher in the Chukchi Sea compared to the Bering Sea. The highest $\rho\text{Si}_{\text{diss}}$ was observed in DBO3W. While the average $[\text{D}]:[\text{P}]$ value for this region was 1/3 of that observed in the Bering Sea, values still indicated that all of the bSiO_2 produced in the euphotic zone was being re-dissolved into $\text{Si}(\text{OH})_4$ rather than exported (Table 3.1; Figure 3.2). Biogenic silica dissolution decreased northwards from DBO3 to DBO5, while $[\text{D}]:[\text{P}]$ increased; however, $[\text{D}]:[\text{P}]$ values were still lower than those observed in the Bering Sea regions.

Regardless of the spatial differences in $[\text{D}]:[\text{P}]$, the fact that most $[\text{D}]:[\text{P}]$ values for most years are >1 is likely the result of our ‘snapshot’ measurements of bSiO_2 production and dissolution, as any value >1 is higher than what would be expected on an annual basis for this region. It is possible that the high $[\text{D}]:[\text{P}]$ we observe could be driven by sediment resuspension of detrital bSiO_2 given the very shallow water depths in this region (~ 50 m), but the fact that ΔbSiO_2 are close to zero throughout the water column, and that depth profiles of $\rho\text{Si}_{\text{diss}}$ do not generally show any increasing trend with depth suggests this is not the case. It is also possible that these high values are driven by phytoplankton bloom phenology, with our sampling occurring in the late or post-bloom phase for some regions, or at the height of the bloom in others. With our sampling only occurring once per year, it is clear that it is only with better temporal resolution on a seasonal basis that we might be able to resolve these discrepancies.

Values for $\rho\text{Si}_{\text{diss}}$ were most comparable to rates observed within an ice-edge diatom bloom in the Ross Sea (Nelson et al., 1991), but otherwise high compared to other observations in the world’s oceans (Table 3.3).

Table 3.3. Regional comparison of depth-integrated $\rho\text{Si}_{\text{diss}}$ and $[\text{D}]:[\text{P}]$ for mid- (35°N and S) and high-latitude ($>50^{\circ}\text{N}$ or S) studies. Data are integrated to the bottom of the euphotic zone ($1\% - 0.1\%I_0$) unless otherwise noted. (-) = no data.

Region	$\rho\text{Si}_{\text{diss}}$ (mmol m ⁻² d ⁻¹)		[D]:[P]		Reference
	Range	Mean	Range	Mean	
<i>Arctic and Subarctic (50°N – 90°N)</i>					
Northeastern Chukchi Shelf	10.4 - 44.9	23.2	0.90 - 4.00	1.82	This study
Southeastern Chukchi Shelf	10.6 - 59.1	29.6	0.26 - 2.27	1.07	This study
Northeastern Bering Shelf	0.9 - 31.0	11.0	0.10 - 5.90	3.06	This study
Southeastern Bering Sea	-	-	-	-	Banahan and Goering (1986)
<i>Temperate Regions (50°N – 35°N and 35°S – 50°S)</i>					
Monterey Bay	0.63 - 6.5	2.9	0.02 - 0.61	0.15	Brzezinski et al. (2003)
Gulf Stream warm core rings	<0.19 - 5.4	3.0	<0.19 - 0.79	0.46	Brzezinski and Nelson (1989)
<i>Antarctic and Subantarctic (50°S – 90°S)</i>					
Southern Ocean, Pacific Sector	0.2 - 10.9	3.5	0.01 - 0.95	0.37	Nelson and Gordon (1982), Brzezinski et al. (2001)
Southern Ocean, Indian Sector	0.0 - 18.8	4.8	0.00 - 3.10	1.14	Beucher et al. (2004), Fripiat et al. (2011)
Ross Sea (ice-edge bloom)	16.2 - 27.5	21.6	0.43 - 1.07	0.64	Nelson et al. (1991)

A possible explanation for the high $\rho\text{Si}_{\text{diss}}$ that we observed is that diatom bSiO_2 in the PAR may have low Al:Si ratios. Laboratory studies have shown that aluminum incorporation has significant effects on the solubility and dissolution kinetics of bSiO_2 , with a greater incorporation of Al (i.e. higher Al:Si ratios) resulting in less reactive and less soluble bSiO_2 (Van Cappellen et al., 2002; Loucaides et al., 2012 and references therein). Van Bennekom et al. (1991) found that the solubility and dissolution rate constants of bSiO_2 in Antarctic diatoms collected from the Weddell Sea were much higher than those of diatoms from temperate regions. They attributed this difference to the very low Al:Si ratios in the diatom bSiO_2 from the Weddell Sea, which they believed was driven by the very low dissolved Al:Si ratio in seawater in this region. While $\rho\text{Si}_{\text{diss}}$ in the Weddell Sea has not been directly measured, very low amounts of bSiO_2 in surface sediments despite relatively high ρSi also suggests that bSiO_2 dissolution rates in the

water column might be very high (DeMaster, 1981; Treguer et al., 1991; Queguiner et al., 1991; Leynaert et al., 1993).

Although surface sediments of the PAR are relatively rich in bSiO_2 , the high amount of preservation could be due to the shallow water-column depths, high productivity (Chapters 1-2) and high sedimentation rates (de Vernal et al., 2005; Astakhov et al., 2015). No direct measurements of the Al:Si ratio in diatom bSiO_2 or water column dissolved Al:Si ratios have been made in the PAR; however, studies in the Canadian Basin (i.e. Canada and Markarov Basins) found very low dissolved Al:Si ratios in the upper halocline waters, with values similar to those observed in the Weddell Sea (Middag et al., 2009; Giesbrecht et al., 2013). The nutrient-rich upper halocline waters in the Canadian Basin are of Pacific-origin, meaning that they flow through the Bering and Chukchi Seas prior to entering the rest of Arctic. Thus, it is likely that the nutrient-rich waters of the PAR have a similarly low dissolved Al:Si signature, which, based on the findings of van Bennekom et al. (1991) suggests that diatom bSiO_2 in the PAR may also have low Al:Si ratios that drive the observed high rates of $\rho\text{Si}_{\text{diss}}$.

3.5.2 Drivers of regional differences in diatom bloom dynamics

3.5.2.1 Environmental controls

Our expanded correlation analysis indicated there were geographical differences in bottom-up controls on biogenic silica dynamics between the Bering Sea (DBO1, DBO2) and Chukchi Sea (DBO3-DBO5) (Table 3.2). In the Bering Sea, the negative correlations between [D]:[P] , and ρSi and ρNO_3 are consistent with increased regeneration of $[\text{Si}(\text{OH})_4]$ when diatom productivity is low, typically near the end of a diatom bloom. The negative correlation between ΔbSiO_2 and $\rho\text{Si}_{\text{diss}}$ is likely because $\rho\text{Si}_{\text{diss}}$ is calculated from ρSi and ΔbSiO_2 (equation 2). In the Chukchi Sea, the negative correlation between [D]:[P] and

bottom S may be related to water mass composition, with high salinity waters usually having higher $[\text{Si}(\text{OH})_4]$ and primary productivity in this region (Chapters 1-2). The negative correlation between $[\text{D}]:[\text{P}]$ and % Chl $a > 5 \mu\text{m}$ could be related to the stage of the phytoplankton bloom, with regions of high biomass being more likely to be in an active bloom state, with diatoms being less susceptible to bSiO_2 dissolution. We also observed a negative correlation between ΔbSiO_2 and $\rho\text{Si}_{\text{diss}}$, which, again, is because of the way in which $\rho\text{Si}_{\text{diss}}$ is calculated (equation 2).

3.5.2.2 Water mass effects on bSiO_2 dynamics

We found a strong east-west gradient in ρSi , ΔbSiO_2 , $\rho\text{Si}_{\text{diss}}$, and $[\text{D}]:[\text{P}]$ in the southern Chukchi Sea in 2014 (Table 3.4).

Table 3.4. Chemical and biological differences between the western (DBO3W) and eastern (DBO3E) sectors of DBO3 in 2014. Data for $[\text{NO}_3^-]$, $[\text{Si}(\text{OH})_4]$, $[\text{bSiO}_2]$, and $[\text{lSiO}_2]$ are from the concurrent measurements as reported in Chapters 1 and 2. Data for % diatoms for the phytoplankton assemblage are for the same stations, but from measurements in 2013 as reported in Chapter 1.

Parameter	DBO3W	DBO3E
<i>Nutrients</i>		
$[\text{NO}_3^-]$ (mmol m^{-2})*	157	6.38
$[\text{Si}(\text{OH})_4]$ (mmol m^{-2})**	38.1	70.8
<i>Particulate silica</i>		
$[\text{bSiO}_2]$ (mmol m^{-2})**	265	90.7
$[\text{lSiO}_2]$ (mmol m^{-2})**	166	134
<i>Phytoplankton assemblage</i>		
Diatoms (% of total assemblage)*,†	72	5
<i>Rates</i>		
ρSi (mmol $\text{m}^{-2} \text{d}^{-1}$)	9.01	0.62
ΔbSiO_2 (mmol $\text{m}^{-2} \text{d}^{-1}$)	-1.59	-29.6
$\rho\text{Si}_{\text{diss}}$ (mmol $\text{m}^{-2} \text{d}^{-1}$)	10.6	30.2
<i>Silica pump</i>		
$[\text{D}]:[\text{P}]$	1.18	49.0

*data from Chapter 1, **data from Chapter 2, †data for July 2013

Biogenic silica production rates (ρSi) were ~ 15 times higher on the western side of DBO3 compared to the eastern side. In contrast, $\rho\text{Si}_{\text{diss}}$, and $[\text{D}]:[\text{P}]$ were at least 2-3 times lower on the western side of DBO3 compared to the eastern side. These differences coincided with changes in T, S and $[\text{NO}_3^-]$ in the same year (Figure 2.7 and Table 2.7 in Chapter 2) and are consistent with Chapters 1 and 2, where we found similarly strong east-west gradients in nutrients and phytoplankton biomass, productivity and assemblage composition for 2006 - 2016.

It is possible that the large differences we observed in $\rho\text{Si}_{\text{diss}}$ and $[\text{D}]:[\text{P}]$ between DBO3E and DBO3W are influenced by differences in primary productivity, temperature, and subsequently heterotrophic bacterial activity. Previous studies have shown that heterotrophic bacteria mediate much of the biogenic silica dissolution in surface waters, while the effect of zooplankton grazing is unclear (Ragueneau et al., 2006). Heterotrophic bacteria enhance bSiO_2 dissolution through degradation of the protective organic coating on diatom frustules (e.g. Bidle and Azam, 1999; 2001; Bidle et al., 2003). Bidle et al. (2003) reported that inhibiting bacterial activity in natural phytoplankton assemblages significantly decreased bSiO_2 dissolution rates. The abundance of these bacteria is generally observed to increase when phytoplankton biomass and productivity are low, temperatures are warmer, and/or in the later stages of a phytoplankton bloom (Gasol et al., 1997; Tian et al., 2003; Müren et al., 2005; Kirchman et al., 2009). In addition, Kirchman et al. (2007) also found that the relative abundance of bacteria increased with decreasing $[\text{NO}_3^-]$ in the Chukchi Sea. Thus, there may have been a greater abundance of heterotrophic bacteria on the eastern side of DBO3 compared to the western side given the much lower $[\text{NO}_3^-]$, warmer temperatures, and lower phytoplankton biomass and

productivity observed in DBO3E (Table 3.4; Table 2.7 in Chapter 2). This increased abundance could have resulted in the much higher $\rho\text{Si}_{\text{diss}}$ and $[\text{D}]:[\text{P}]$ we observed in DBO3E, especially given the low rates of biogenic silica production (Table 3.4).

3.5.2.3 Temporal trends and interannual variability

Despite consistent sampling times (mid-July), locations and methodologies, the large interannual variations we observed in all measured parameters make it difficult to draw any significant conclusions regarding changes in bSiO_2 dynamics in the Pacific Arctic Region (Table 3.1; Figures 3.1-3.2). We reported similarly high interannual variability for our concurrent measurements of phytoplankton biomass and productivity in Chapter 1, and for diatom production and biomass in Chapter 2. The results presented in this chapter further demonstrate the difficulty in identifying long-term trends in this region, especially from sampling that occurs only once per year. However, despite the large interannual variability, we identified interannual trends in some Si-related parameters.

In DBO3W, we observed an increasing trend in ΔbSiO_2 and decreasing trend in $[\text{D}]:[\text{P}]$ from 2013 to 2016 that may be linked to changes in zooplankton grazing rates and heterotrophic bacterial activity. A change in zooplankton grazing rates could be tied to the significant shift in the timing of the annual sea-ice breakup in DBO3 to earlier in the season (Grebmeier et al., 2015). This change in sea-ice breakup would result in an earlier seasonal bloom that could have significantly reduced the copepod biomass. Successful recruitment of copepods is dependent on both copepod reproduction matching the timing of the ice-algal bloom, and copepodite growth matching the timing of the subsequent pelagic algal bloom (Søreide et al., 2010; Leu et al., 2011). However, the effect of copepod grazing on bSiO_2 dissolution is still unclear (e.g. Ragueneau et al., 2006). Dissolution in copepod fecal pellets is low (Tande and Slagstad, 1985), but grazing

activity also increases the number of broken diatom frustules in the water column (e.g. Roman and Rublee, 1980), which could facilitate subsequent colonization by bacteria. Given that heterotrophic bacteria mediate bSiO_2 dissolution (e.g. Bidle and Azam, 1999; 2001; Bidle et al., 2003), a decrease in broken frustules in the water column as a result of less grazing activity could result in a decrease in $\rho\text{Si}_{\text{diss}}$. Thus, a reduction in copepod biomass and grazing rates as a result of a shift in the timing of the seasonal bloom in DBO3W may have had an indirect effect on $\rho\text{Si}_{\text{diss}}$.

It is also possible that these changes in ΔbSiO_2 and $[\text{D}]:[\text{P}]$ are primarily influenced by a decrease in the activity of heterotrophic bacteria, rather than a combination of zooplankton and bacteria; however, it is difficult to draw any conclusions as to what may have caused changes in bacterial activity during our study period given that (1) the distribution and activity of heterotrophic bacteria are highly variable in the Pacific Arctic Region (e.g. Kirchman et al., 2009; Nelson et al., 2014; Cooper et al., 2015), and (2) the environmental controls on bacterial production (BP) and respiration are not well constrained (e.g. Kirchman et al., 2009). While Kirchman et al. (2009) found that primary productivity, phytoplankton biomass and temperature all explained similar amounts of the variability in BP (although there was no significant relationship between BP and temperature above 0°C), they found the relationship between bacterial respiration and primary productivity to be even more variable and difficult to interpret. We observed no year-to-year trends in temperature, primary productivity or phytoplankton biomass in DBO3W over the 2013-2016 period that might explain the trends in ΔbSiO_2 and $[\text{D}]:[\text{P}]$. Given the limited research that has been done on heterotrophic bacterial activity in this region, it is possible that other factors may have contributed to changes in the bacterial

community, although it seems equally likely that the trend we observed is indirectly tied to changes in phytoplankton and zooplankton phenology.

We cannot be sure that the interannual trends observed in DBO3W are driven by changes in grazing and/or heterotrophic bacterial activity, especially given that we do not see concurrent changes in parameters that may affect bacterial abundance such as nutrients or phytoplankton biomass or productivity (Chapters 1 and 2). However, if decreases in $[D]:[P]$ are sustained in the long-term, this may have a significant effect on the input of $Si(OH)_4$ to the rest of the Arctic, regardless of the cause. Lower $[D]:[P]$ would mean more efficient export of $bSiO_2$ to the benthos. If the preservation efficiency of $bSiO_2$ in sediments is as high as that observed in other highly productive polar environments (i.e. up to 86% in the Ross Sea, Antarctica; DeMaster et al., 1996; Smith et al., 2000), this could result in a significant and sustained decrease in the water column $[Si(OH)_4]$. This is possible considering the relatively high preservation efficiency of particulate organic C on the Bering and Chukchi shelves and that organic C tends to be remineralized faster than $bSiO_2$ (Naidu et al., 2004; DeMaster et al., 1996). Such a decrease could have far-reaching consequences on the Arctic marine Si cycle.

3.6 Conclusions

We present the first study that directly quantifies rates of net $bSiO_2$ production and dissolution in the Pacific Arctic Region. Dissolution rates of $bSiO_2$ were high compared to other parts of the world's oceans, but the factors influencing these high rates remain unclear. It is possible that the high rates of ρSi_{diss} are related to low water column Al:Si ratios, and/or increased heterotrophic bacterial activity. No studies have directly measured dissolved Al concentrations in Pacific-origin waters that flow through the Bering and Chukchi Seas, although measurements further along the flow path of these

nutrient-rich waters indicate that these ratios are very low. While a handful of studies have investigated heterotrophic bacterial dynamics in the PAR, the environmental controls on bacterial biomass and production are not firmly established, and how they may affect bSiO₂ dissolution in the relatively cold waters of the PAR is yet unstudied. Our work highlights the need for a better understanding of the links between the cycling of Al and Si and the influence of heterotrophic bacteria on bSiO₂ dissolution in the PAR.

Although interannual variability was high for all measured parameters, we observed a decrease in the ratio of bSiO₂ dissolution to production and an increase in the net bSiO₂ production rate from 2013 to 2016, which have the potential to result in significant decreases in [Si(OH)₄]. A sustained decrease in water column [Si(OH)₄] throughout the Chukchi Sea could significantly affect marine Si cycling within the Arctic Ocean, especially considering that the Bering Strait supplies the majority of Si(OH)₄ to the Arctic (Torres-Valdes et al, 2013). Changes in [Si(OH)₄] could have drastic consequences for diatom productivity along the flow path of these currently nutrient-rich waters, such as in the Canadian Arctic Archipelago (CAA) and Baffin Bay. In these regions, diatoms dominate the phytoplankton assemblage, and nutrients from waters of Pacific-origin help sustain the high rates of productivity observed (e.g. Tremblay et al., 2002; Michel et al, 2002; Michel et al., 2006; Varela et al., 2013; Crawford et al., 2018; Chapter 4). Therefore, decreased [Si(OH)₄] could result in a shift in phytoplankton assemblage composition that could have consequences on both the marine food web and biogeochemical fluxes in the PAR and further into the Arctic. It is only with long-term and consistent monitoring programs that we will better understand the present and future climate-induced changes on the productive ecosystems of the Pacific Arctic Region, and

how these changes might affect other regions of the Arctic that are influenced by the waters flowing through this region.

Chapter 4

Diatoms in the Canadian Arctic Ocean: Silica production and diatom contributions to primary production and nitrogen uptake during the 2015 Canadian Arctic GEOTRACES

4.1 Abstract

We present dissolved and particulate silica concentrations and the first direct measurements of biogenic silica production rates in the Eastern Canadian Subarctic and Arctic Ocean, showing that diatoms are both abundant and productive throughout the region in summer. Euphotic zone concentrations of silicic acid (Si(OH)_4), biogenic silica (bSiO_2) and lithogenic silica (lSiO_2), and rates of bSiO_2 production (ρSi) were measured between July and August 2015 along a transect that spanned from the Labrador Sea, through Baffin Bay and into the Canadian Arctic Archipelago (CAA). We also evaluated the contribution of diatoms to rates of primary production and nitrate uptake, and assessed the extent of kinetic limitation of bSiO_2 production by $[\text{Si(OH)}_4]$. Our results revealed that $[\text{bSiO}_2]$, ρSi and the diatom contributions to primary production and nitrate utilization rates increased towards the northwest to the ice-edge in the CAA, tracking the pelagic phytoplankton bloom that occurs with the seasonal retreat of sea-ice characteristic of the Arctic. Rates of bSiO_2 production in the CAA were comparable to those measured during the austral summer in the diatom-dominated Southern Ocean, indicating that the CAA is an important region in the Arctic marine Si cycle. While ρSi in Baffin Bay were lower, there was some indication of the onset of a second diatom bloom, which is consistent with climate-induced changes in the phytoplankton phenology in this region. We observed widespread Si limitation of bSiO_2 production in the low-nutrient surface waters along our transect, with $[\text{Si(OH)}_4]$ decreasing to levels that were not only limiting Si uptake, but also diatom growth. Similar to observations from other polar regions, diatom assemblages in the Eastern Canadian Arctic were inefficient at taking up Si(OH)_4 when concentrations were low, which may be driven by lower temperatures and light levels at high latitudes. These results indicate that the climate-induced warming and

changing light regimes already observed in the Arctic could drive a significant change not only in the marine cycling of Si, but also in the marine cycling of carbon and nitrogen.

4.2 Introduction

Marine diatoms are the dominant primary producers in coastal and shelf regions, contributing to about 20% of the annual photosynthesis on Earth (Nelson et al., 1995; Field et al., 1998). Diatoms exert a major control on the marine silicon (Si) cycle through the formation of biogenic silica (bSiO₂) and, through the photosynthetic process, couple the marine cycles of silicon, carbon, and nitrogen (Si, C, and N). Ballasted by their heavy silica frustules, diatoms are also a major contributor to the export of C, N and bSiO₂ from the euphotic zone (Buesseler, 1998). The Arctic continental shelves account for approximately half of the total marine area in the Arctic, and a quarter of the world's continental shelves (Wassmann, 2015), yet our knowledge of the cycling of Si and its relationship to other marine biogeochemical cycles in this diatom-dominated (e.g. Gosselin et al., 1997; Crawford et al., 2018) and critically climate-impacted region is limited.

The Arctic is one of the least studied and fastest changing regions in the global ocean (Wassmann et al., 2011; Wassmann, 2015), with only a handful of studies that have investigated bSiO₂ production and the diatom contribution to phytoplankton production and export (Tremblay et al., 2002; Sampei et al., 2010; Krause et al., 2018). Using changes in water column Si(OH)₄ inventories over a three-month period, Tremblay et al. (2002) estimated summertime (May – July) bSiO₂ production in the highly productive North Water Polynya, a region in Northern Baffin Bay between Greenland and Ellesmere Island. Their results showed that diatoms contributed up to 80% of the new primary

production during this period. In a study in the Barents Sea near Svalbard, Krause et al. (2018) observed significantly elevated rates of bSiO_2 export and, using direct measurements of Si and C uptake rates, found that the diatom contribution to primary production was variable, ranging from $<10\%$ to $\sim 100\%$ depending on bloom stage and phytoplankton assemblage composition. Sampei et al. (2010) reported large fluxes of bSiO_2 and a positive correlation between annual POC and bSiO_2 fluxes using sediment traps on the Mackenzie Shelf. They also found that the vertical attenuation of the POC flux increased with increased bSiO_2 flux, suggesting that diatoms increase the retention of POC in the surface layer, which is then diverted to the pelagic food web. All of these studies indicate that diatoms are an important mediator of C transfer to both the herbivorous food web and deep waters in the Arctic.

Most of the Arctic is believed to be limited by the availability of NO_3^- (e.g. Tremblay and Gagnon, 2009), though limited availability of Si(OH)_4 may also affect diatom Si uptake, and, if Si(OH)_4 concentrations are low enough, growth rates can also be reduced (Popova et al., 2012). Both Si and N are required in approximately equimolar amounts in diatoms (Brzezinski et al., 1985), and Si(OH)_4 and NO_3^- are also often found at similar concentrations in seawater. Changes in the availability of Si(OH)_4 relative to NO_3^- ($\text{Si:N} < 1$) may result in diatoms experiencing Si limitation before N limitation. While Si metabolism is closely tied to the regulation of cell growth and division, the silicification process itself is not energetically expensive (Martin-Jézéquel et al., 2000). In contrast, N metabolism is closely coupled to C metabolism, which provides the significant amount of energy required during NO_3^- assimilation (Mulholland and Lomas, 2008). Si limitation decreases silicification (e.g. Harrison et al., 1977), but likely increases the amount of C in

the cell (Flynn and Martin-Jézéquel, 2000). N limitation affects both C and N metabolisms and decreases the cellular N quota, but has little effect on the cellular C or Si quotas (Flynn and Martin-Jézéquel, 2000). Thus, nutrient limitation can have significant, but very different effects on the coupling between the Si, C and N cycles in the oceans. In the only of Si limitation in the Arctic, Krause et al. (2018) showed that Si limitation was widespread near Svalbard in the Barents Sea, with diatoms being less adapted to take up Si at low concentrations compared to those at lower latitudes. Their results also indicated that Si limitation may have been intense enough to limit growth, rather than just Si uptake.

To improve our understanding of the contribution of diatoms to Arctic productivity and how these organisms link the marine cycles of Si, C and N, we evaluated euphotic zone biogenic silica production and the contribution of diatoms to primary production (PP) and nitrate (NO_3^-) uptake from the Labrador Sea to the Canadian Arctic Archipelago (CAA). The main objective of this study was to quantify a baseline for bSiO_2 production and to evaluate spatial variability in bSiO_2 dynamics in a large sector of the marine Arctic ecosystem. We also aimed to determine if the contribution of diatoms to primary and new production was comparable to other proxies of diatom biomass and productivity such as size fractionated Chl *a* and primary production. Finally, we sought to elucidate potential silicon limitation to better predict how marine bSiO_2 production might vary under current or predicted climate changes.

4.3 Methods

4.3.1 Sampling Locations and Seawater Sampling

Samples were collected at nine stations onboard the *CCGS Amundsen* between 15th July and 16th August 2015 as part of the Canadian Arctic GEOTRACES program (Figure 4.1; Table 4.1).

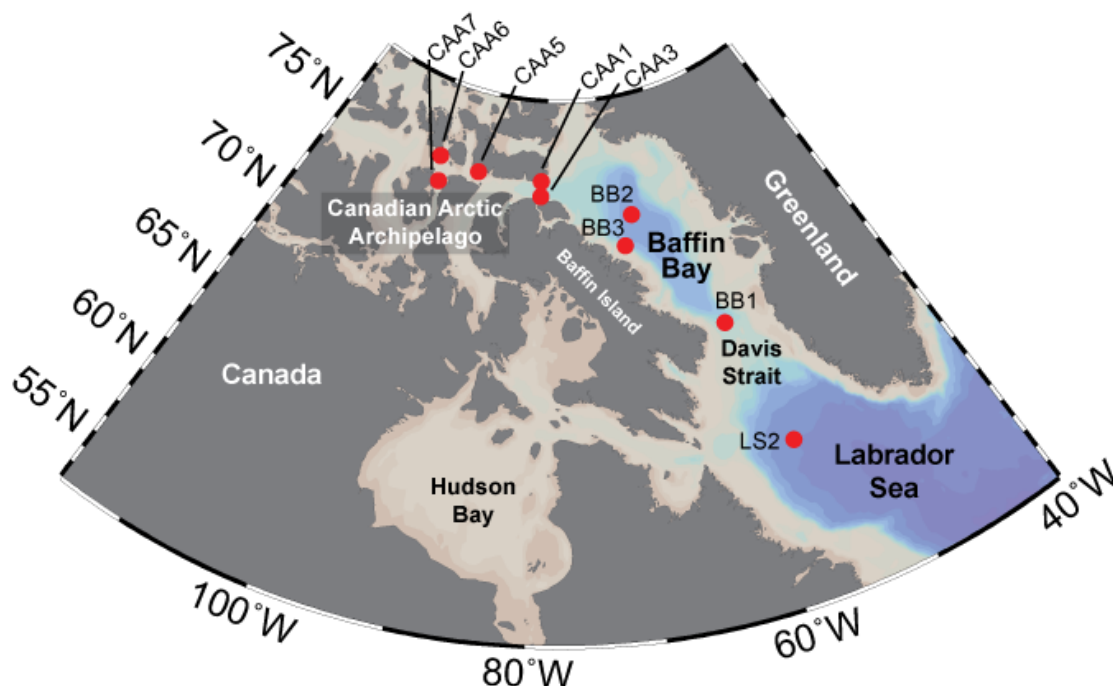


Figure 4.1. (a) Stations (in red) sampled for phytoplankton and diatom productivity and biomass in the euphotic zone during July-August of 2015 as part of the Canadian Arctic GEOTRACES program. Major geographic and oceanographic areas are indicated on the map as outlined in Table 4.1.

A depth profile of photosynthetically active radiation was obtained using a PNF-300 radiometer (Biospherical Instruments) to determine the depths corresponding to light levels of 100%, 55%, 30%, 15%, 1% and 0.2% of the surface incident irradiance (I_0). Seawater samples at these six depths were collected from 12-L Niskin bottles on a rosette equipped with a conductivity-temperature-depth sensor (Seabird 911), with waters for 100% I_0 collected at a ‘surface’ depth of 1-2 m. At each light level, we measured the concentrations of silicic acid ($\text{Si}(\text{OH})_4$) and particulate silica (as bSiO_2 and lSiO_2) and conducted experiments to measure bSiO_2 production rates using the radioisotope ^{32}Si .

(ρSi). The precision of all analytical techniques was determined from triplicate subsamples collected at one or more depths at each station. Seawater samples for nitrate (NO_3^-) and phosphate (PO_4^{3-}) concentrations, phytoplankton biomass (as Chl a), particulate C (PC) and N (PN) concentrations, and primary productivity and NO_3^- and NH_4^+ uptake experiments were also collected simultaneously from the same water samples and are presented in Appendix B.

Table 4.1. Physical and hydrographic characteristics of sampling stations. Regions are indicated as in Figure 1. Z_{eu} = euphotic zone depth. Domains are LS = Labrador Sea, BB = Baffin Bay, CAA = Canadian Arctic Archipelago. Note the ~3 week gap between sampling in the Labrador Sea and Baffin Bay.

Station	Date	Latitude (°N)	Longitude (°E)	Bottom Depth (m)	Z_{eu} (m)	Region	Domain
LS2	17-Jul-15	60.46	-56.56	3023	63	Labrador Sea	LS
BB1	3-Aug-15	66.86	-59.06	1040	65	Davis Strait	BB
BB3	6-Aug-15	71.42	-68.61	1252	50	Baffin Bay (shelf)	BB
BB2	8-Aug-15	72.75	-67.00	2369	56	Baffin Bay (basin)	BB
CAA1	10-Aug-15	74.52	-80.57	636	43	Lancaster Sound (N)	CAA
CAA3	11-Aug-15	73.83	-80.49	674	57	Lancaster Sound (S)	CAA
CAA5	13-Aug-15	74.54	-90.80	241	61	Barrow Strait	CAA
CAA6	15-Aug-15	74.76	-97.46	260	46	Barrow Strait (ice-edge)	CAA
CAA7	16-Aug-15	73.67	-96.54	218	56	Peel Sound	CAA

4.3.2 Dissolved and particulate silica concentrations

Filtered (0.2 μm) samples for $[\text{Si}(\text{OH})_4]$ were stored at 4°C in the dark until analysis onboard using a nutrient autoanalyzer (Bran and Luebbe Autoanalyzer III) within a few hours of collection. Water samples for particulate silica concentrations (bSiO_2 and lSiO_2) were collected and processed as described in Chapter 2. The median coefficient of variation (CV) was 8% for $[\text{bSiO}_2]$ and 13% for $[\text{lSiO}_2]$ ($n = 9$).

4.3.3 Rates of biogenic silica production

Water samples for biogenic silica production rate experiments were collected and processed as described in Chapter 2. Biogenic silica production rates (ρSi , $\mu\text{mol L}^{-1} \text{d}^{-1}$) and the specific rate of biogenic silica production (V_{Si} , d^{-1}) were calculated as in Brzezinski and Phillips (1997). Median CV values were 10% for ρSi and 9% for V_{Si} , with

average SDs of $0.004 \mu\text{mol L}^{-1} \text{d}^{-1}$ and 0.003d^{-1} respectively ($n = 9$). Note that deck-board incubations can introduce a bias (i.e. overestimation) in ρSi and V_{Si} . This is because bSiO_2 production is temperature sensitive, and the flowing seawater used during incubation originates from the sea surface, which is typically warmer than waters deeper in the euphotic zone. Regardless, rates presented in this Chapter were not corrected so as to maintain consistency with other published ρSi and V_{Si} in the world's oceans, as these measurements are typically not corrected for differences between *in situ* and incubation temperatures in the literature.

4.3.4 Diatom contribution to primary production and nitrate utilization

The diatom contribution to primary productivity (PP, ρC) and nitrate uptake (ρNO_3) were calculated as described in Chapter 2. Concentrations of bSiO_2 were used with concurrently measured POC and PON (Appendix B) to calculate mean particulate Si:C and Si:N values of 0.12 and 1.01 for the entire study region. These ratios were then used with the ρC and ρNO_3 reported in Appendix B to determine the average diatom contribution to PP and ρNO_3 .

4.3.5 Kinetics of silicon utilization

Limitation of silica production rates was evaluated at all stations at the 55% light depth (5 – 7 m depth). Duplicate 300 mL seawater samples were collected in acid-cleaned polycarbonate bottles. One sample was augmented with a 3mmol L^{-1} isotopically natural Si(OH)_4 solution to increase the ambient $[\text{Si(OH)}_4]$ by $20 \mu\text{mol Si L}^{-1}$. Following this addition, high specific activity $^{32}\text{Si(OH)}_4$ ($\sim 25,000 \text{MBq } \mu\text{mol Si}^{-1}$) was added to both samples, with the non-augmented sample receiving $100 \mu\text{L}$ of a 3700Bq mL^{-1} solution of $^{32}\text{Si(OH)}_4$ and the augmented sample receiving $300 \mu\text{L}$, for total activities of 370 and 1110 Bq respectively. A higher activity of $^{32}\text{Si(OH)}_4$ was added to the augmented sample

to enhance the final specific activity of the tracer and ensure measurement sensitivity.

Samples were incubated for 24 h at 55% I_0 and processed as for ρSi in Chapter 2.

Specific uptake rates (V_{Si} , d^{-1}) were calculated as in Brzezinski and Phillips (1997) using the measured ^{32}Si activity in the samples, the final $[\text{Si}(\text{OH})_4]$ (ambient + added Si), and the ambient $[\text{bSiO}_2]$. The specific uptake rates from these experiments were used to determine the rate-enhancement statistic (Enh), defined as:

$$\text{Enh} = \frac{V_{\text{Si,enhanced}}}{V_{\text{Si,ambient}}} \quad (1)$$

where $V_{\text{Si,enhanced}}$ is the specific uptake rate at $20 \mu\text{mol Si L}^{-1}$ above ambient, and $V_{\text{Si,ambient}}$ is the specific uptake rate at ambient $[\text{Si}(\text{OH})_4]$ (Brzezinski et al., 1997). This statistic assumes that the addition of $20 \mu\text{mol L}^{-1}$ saturates the Si uptake, such that when $\text{Enh} \approx 1.0$, it indicates that the ambient $[\text{Si}(\text{OH})_4]$ was not limiting to the natural diatom assemblage. In contrast, $\text{Enh} > 1.0$ indicates that ambient $[\text{Si}(\text{OH})_4]$ was limiting the rate of Si uptake, with greater values of Enh indicating the severity of the limitation. Given the uncertainties associated with each estimate of V_{Si} , Enh values must be > 1.2 to be indicative of Si limitation. Specific uptake rates from the two-point kinetic experiments can also be used to estimate the kinetic parameters V_{max} and K_s assuming that $V_{\text{Si,enhanced}}$ and $V_{\text{Si,ambient}}$ represent two points falling exactly on a Michaelis-Menten hyperbola:

$$V = \frac{V_{\text{max}}[\text{Si}(\text{OH})_4]}{(K_s + [\text{Si}(\text{OH})_4])} \quad (1)$$

and using the equations described by Nelson et al. (2001). Validation of this assumption based on measurements using the same methodology is described in Appendix A.

4.3.6 Data organization and analysis

Data were depth-integrated using trapezoidal integration from the surface to the bottom of the euphotic zone (0.2% of surface irradiance). The mean V_{Si} for the euphotic zone (V_{AVE}) was calculated by trapezoidally integrating V_{Si} measurements as above, and dividing the integrated value by the depth of the euphotic zone (Z_{eu}). Figures 4.1-4.3 were created using Ocean Data View version 5.0.0 (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2012). For statistical comparisons between broad domains, data were classified into regional groupings of the Canadian Arctic Archipelago (CAA), Baffin Bay (BB) and the Labrador Sea (LS). These regions are defined by distinct water masses as identified by T-S correlations following that of Carmack and McLaughlin (2011). Unlike Carmack and McLaughlin (2011), we separated BB and LS into separate regions due to logistical issues that resulted in the 3+ week span between our sampling at LS2 and the remaining stations along our transect. We consider the CAA to encompass the stations spanning from Peel Sound up to Lancaster Sound and BB to include both Baffin Bay and Davis Strait. Unless otherwise stated, linear relationships were determined using Pearson linear correlation tests, significant differences between measured parameters were determined using student's t-tests, and $\alpha < 0.05$ was used to determine significance. Matlab R2014b was used to conduct all statistical tests..

4.4 Results

4.4.1 Physical characteristics

The euphotic zone distributions of temperature and salinity decreased from east-to-west along our sampling transect (Figure 4.2a-c). At the beginning of the transect in the Labrador Sea, waters were warm and saline throughout the euphotic zone. Warm waters persisted at the surface (0 – 20 m) from Davis Strait, through Baffin Bay and into the

CAA up to Barrow Strait, and below these depths, waters were $<0^{\circ}\text{C}$. In Peel Sound, waters $<0^{\circ}\text{C}$ were found below ~ 10 m. Salinity similarly decreased from east to west, with the appearance of a freshwater ‘wedge’ extending from the western side of our transect. In the top 5 m, salinity decreased from ~ 34 in the Labrador Sea to <24 at the far western edge of our sampling transect in Peel Sound, where we observed a freshwater lens in these surface waters.

4.4.2 Dissolved and particulate silica concentrations

Concentrations of Si(OH)_4 increased with depth at all stations along our sampling transect (Figure 4.2d). In addition, $[\text{Si(OH)}_4]$ were strongly negatively correlated with temperature ($r = -0.72$, $p < 0.001$; Figure 4.2b,d). The highest $[\text{Si(OH)}_4]$ of $>20 \mu\text{mol L}^{-1}$ was found at the bottom of the euphotic zone in Peel Sound, while in the Labrador Sea, $[\text{Si(OH)}_4]$ was undetectable in the top 20 m of the water column. Concentrations were above $4 \mu\text{mol L}^{-1}$ throughout the euphotic zone in Davis Strait and Baffin Bay; however, in the CAA, $[\text{Si(OH)}_4]$ were depleted to $\sim 1 \mu\text{mol L}^{-1}$ from 0 - 20 m, with the exception of Peel Sound, where $[\text{Si(OH)}_4]$ were $\sim 5 \mu\text{mol L}^{-1}$ above 20 m. Euphotic-zone inventories of Si(OH)_4 were variable along our sampling transect, but generally increased from southeast-northwest (Table 4.2; Figure 4.3a). Concentrations of Si(OH)_4 ranged from 95 mmol m^{-2} in the Labrador Sea up to 644 mmol m^{-2} in Peel Sound in the CAA, with an overall average for the entire study region of 315 mmol m^{-2} .

Biogenic SiO_2 concentrations did not exhibit the same spatial trends as those we observed for T, S and $[\text{Si(OH)}_4]$ (Figure 4.2e). In the Labrador Sea, $[\text{bSiO}_2]$ were highest in the top 10 m, while $[\text{bSiO}_2]$ in Davis Strait were low and showed little vertical structure. Subsurface $[\text{bSiO}_2]$ maxima were observed below ~ 15 m at 15% or 1% I_0 throughout the CAA and in Baffin Bay. Of the whole transect, the lowest $[\text{bSiO}_2]$ of ~ 0.2

$\mu\text{mol L}^{-1}$ were found in the top 10 m of the basin station in Baffin Bay (BB2), and increased westwards towards the highest $[\text{bSiO}_2]$ of $\sim 9 \mu\text{mol L}^{-1}$ that were found near the bottom of the euphotic zone in Barrow Strait. Concentrations of bSiO_2 in the Labrador Sea were of a similar magnitude to those measured in Lancaster Sound.

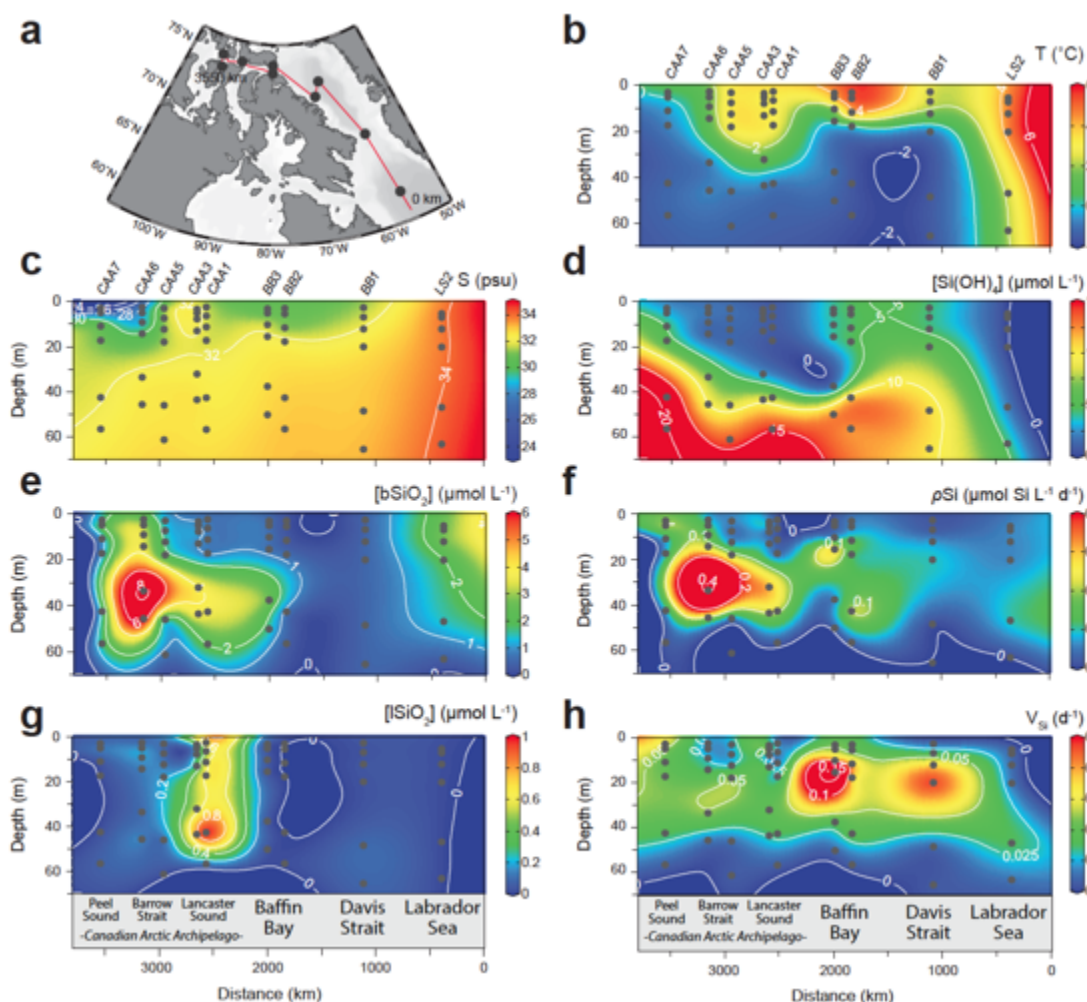


Figure 4.2. Vertical profiles of measured euphotic-zone parameters along the 2015 Canadian Arctic GEOTRACES transect. (a) GEOTRACES transect line shown in red, colour and white contour lines for (b) temperature, (c) salinity, (d) $\text{Si}(\text{OH})_4$ concentration, (e) bSiO_2 concentration, (f) bSiO_2 production rate, ρSi , (g) $[\text{SiO}_2]$ concentration, and (h) specific bSiO_2 production rate, V_{Si} . Black dots represent the sampling depths. Regions sampled as shown in Figure 1 and described in Table 1 are delineated along the bottom of panels (g) and (h). Station names are shown along the top of panels (b) and (c).

Inventories of bSiO_2 in the euphotic zone were also variable, showing only a moderate east-west increase (Table 4.2; Figure 4.3b). The highest $[\text{bSiO}_2]$ occurred at CAA6 in

Barrow Strait and the lowest $[\text{bSiO}_2]$ in the basin of Baffin Bay (BB2) and in Davis Strait (BB1) (Table 4.2).

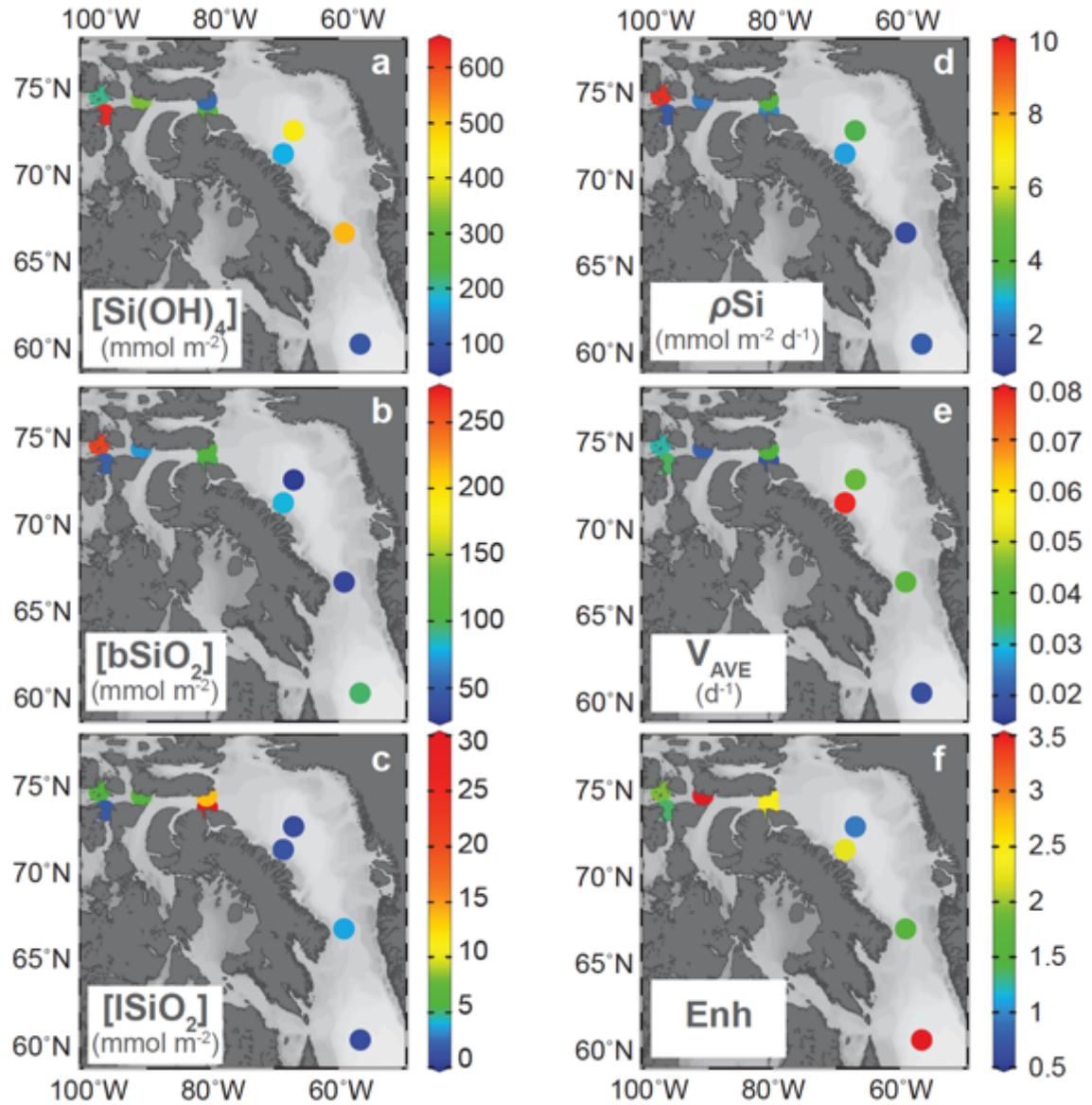


Figure 4.3. Horizontal distributions of depth-integrated parameters along the 2015 Canadian Arctic GEOTRACES transect. (a) Si(OH)_4 concentration, (b) bSiO_2 concentration, (c) lSiO_2 concentration, (d) bSiO_2 production rate, ρSi , (e) specific bSiO_2 production rate, V_{AVE} , and (f) the Si enhancement factor, Enh. For (a-d), data were depth-integrated from the ocean surface to the bottom on the euphotic zone ($0.2\% I_0$). For (e), data were depth-integrated as for (a-d), and then normalized by the depth of the euphotic zone. For (f), data are not depth-integrated, and are only from $55\% I_0$. Each coloured circle represents a sampling station.

Table 4.2. Depth-integrated measurements of silicic acid ($\text{Si}(\text{OH})_4$), biogenic silica (bSiO_2) and lithogenic silica (lSiO_2) concentrations, and Si utilization (ρSi), depth normalized specific Si utilization (V_{AVE}) and the relative contribution of diatoms to primary production (% diatom PP) and nitrate uptake (% diatom ρNO_3). Depth integrations were done from the ocean surface to the 0.2% I_0 depth.

Station	[$\text{Si}(\text{OH})_4$] (mmol m^{-2})	[bSiO_2] (mmol m^{-2})	[lSiO_2] (mmol m^{-2})	ρSi (mmol $\text{m}^{-2} \text{d}^{-1}$)	V_{AVE} (d^{-1})	% diatom PP	% diatom ρNO_3
LS2	95.21	96.07	0.85	1.85	0.018	32%	47%
BB1	511.10	30.74	3.87	1.34	0.041	26%	68%
BB3	179.95	81.07	1.35	2.73	0.079	83%	100%
BB2	446.94	26.48	0.85	3.71	0.044	83%	70%
CAA1	122.03	108.05	13.78	4.12	0.036	71%	100%
CAA3	287.39	101.54	41.18	2.54	0.019	100%	100%
CAA5	338.22	72.30	6.12	2.35	0.022	63%	61%
CAA6	212.20	263.34	5.71	9.82	0.031	100%	100%
CAA7	643.83	51.44	1.72	1.81	0.034	100%	100%

Lithogenic SiO_2 concentrations showed little vertical structure and were relatively low at $<0.2 \mu\text{mol L}^{-1}$ along most of our sampling transect, with the exception of stations within Lancaster Sound (Figure 4.2g). At these stations, [lSiO_2] was highest near the bottom of the euphotic zone, with concentrations of up to $1.1 \mu\text{mol L}^{-1}$, although the waters on the southern side of Lancaster Sound (station CAA3, Figure 4.1) had the highest [lSiO_2]. The contribution of lSiO_2 to total particulate SiO_2 (% lSiO_2) was also small, ranging from 0.6 – 16% for all stations except CAA3, where % lSiO_2 ranged from 3 – 50% in the euphotic zone. Spatial trends in euphotic-zone integrated [lSiO_2] reflected the vertical distributions, with low values of $<6 \text{ mmol m}^{-2}$ at all stations except those found in Lancaster Sound, where [lSiO_2] were at least twice as high as any other station (Table 4.2; Figure 4.3c).

4.4.3 Biogenic silica production rates

Biogenic SiO_2 production rates exhibited subsurface maxima along most of our transect, and the lowest rates occurred at the bottom of the euphotic zone (Figure 4.2f). Depth-integrated ρSi were spatially variable, but also exhibited a general east-west increase (Figure 4.3f). Values ranged from $1.34 \text{ mmol m}^{-2} \text{d}^{-1}$ in Davis Strait to $9.8 \text{ mmol m}^{-2} \text{d}^{-1}$ at station CAA6 in Barrow Strait (Figure 4.3d). The highest rates of ρSi at discrete

light depths were observed in Barrow Strait, with values reaching as high as $0.46 \mu\text{mol L}^{-1} \text{d}^{-1}$ at 34 m (1% I_0) while ρSi was $<0.05 \mu\text{mol L}^{-1} \text{d}^{-1}$ throughout the water column in the Labrador Sea and Davis Strait (Figure 4.2f). The highest values of ρSi were observed below 15 m at either 15 or 1% I_0 for all stations except in Peel Sound, where the highest ρSi were measured in surface waters (6 m) at 55% I_0 . The subsurface maxima in ρSi generally occurred at the same depths as for $[\text{bSiO}_2]$, which also coincided with an increase in $[\text{Si}(\text{OH})_4]$ (Figure 4.2d-f).

Specific rates of bSiO_2 production exhibited similar vertical trends to ρSi (Figure 4.2h). The subsurface maxima in V_{Si} and ρSi typically occurred at the same depth, although in some cases, the V_{Si} maxima was shallower (i.e. at stations BB2, CAA1 and CAA7). The highest V_{Si} were observed at the coastal station in Baffin Bay, reaching a maximum value of 0.2d^{-1} at 15 m (15% I_0) at BB3. The lowest V_{Si} of $<0.01 \text{d}^{-1}$ were observed at the bottom of the euphotic zone (0.2% I_0) for all stations. Spatial trends in V_{AVE} differed from those of ρSi , with the highest values of $>0.04 \text{d}^{-1}$ occurring in Baffin Bay and Davis Strait, while values in the CAA and Labrador Sea ranged from $0.018 - 0.036 \text{d}^{-1}$ (Table 4.2; Figure 4.3e).

4.4.4 Substrate dependence of biogenic silica production

With the exception of the coastal station in Baffin Bay (BB3), surface waters along our entire study transect exhibited Si limitation (Table 4.3; Figure 4.3f). No consistent spatial trends were observed for any of the kinetic parameters. The largest degree of Si limitation occurred in the Labrador Sea and at station CAA5 in Barrow Strait, with Enh values of 6.0 and 4.8 respectively. Enhancement factors ranged from $0.95 - 2.4$ at the other stations. Values for V_{max} ranged from $0.036 - 0.127 \text{d}^{-1}$ and were generally highest in the

CAA (Table 4.3). Half-saturation constants varied from $0.77 - 9.2 \mu\text{mol L}^{-1}$, with a median value of $2.1 \mu\text{mol L}^{-1}$.

Table 4.3. Kinetic parameters from 2-point kinetic experiments conducted at the 55% light level. The enhancement factor (Enh) was calculated as the ratio of the ambient specific production rate ($V_{\text{Si,ambient}}$) to the enhanced specific uptake rate at $20 \mu\text{mol L}^{-1}$ above ambient $[\text{Si}(\text{OH})_4]$. $V_{\text{amb}}:V_{\text{max}}$ is the relative reduction of the maximum Si uptake rate, calculated as the ratio of $V_{\text{Si,ambient}}$ to V_{max} . $V_{\text{max}}:K_s$ represents the initial slope of a Michaelis-Menten curve, which is an index of the efficiency of Si uptake at low $[\text{Si}(\text{OH})_4]$. Also shown are the ambient concentrations of dissolved and biogenic silica, $[\text{Si}(\text{OH})_4]$ and $[\text{bSiO}_2]$ respectively.

Station	$[\text{Si}(\text{OH})_4]$ ($\mu\text{mol L}^{-1}$)	$[\text{bSiO}_2]$ ($\mu\text{mol L}^{-1}$)	$V_{\text{Si,ambient}}$ (d^{-1})	Enh	V_{max} (d^{-1})	K_s ($\mu\text{mol L}^{-1}$)	$V_{\text{amb}}:V_{\text{max}}$ (%)	$V_{\text{max}}:K_s$ ($\text{mmol L}^{-1} \text{hr}^{-1}$)
LS2	0.15	2.72	0.010	6.0	0.059	0.77	16%	3.20
BB1	4.36	0.43	0.033	1.6	0.058	3.28	57%	0.74
BB3	4.53	0.18	0.052	0.95	0.049	-	106%	-
BB2	4.06	0.73	0.039	2.3	0.119	8.28	33%	0.60
CAA1	1.23	1.05	0.048	2.4	0.127	2.03	38%	2.60
CAA3	0.67	0.65	0.014	2.4	0.036	1.00	40%	1.51
CAA5	1.58	1.41	0.017	4.8	0.117	9.15	15%	0.53
CAA6	1.96	3.55	0.019	1.9	0.040	2.15	48%	0.77
CAA7	3.52	2.09	0.049	1.4	0.071	1.57	69%	1.90

4.4.5 Broad scale regional distributions and statistical comparisons between regions

The CAA exhibited more variability in depth-integrated $[\text{Si}(\text{OH})_4]$, $[\text{bSiO}_2]$, $[\text{lSiO}_2]$, ρSi and Enh when data were grouped into the CAA, BB and LS domains (Figure 4.4). The one exception was for V_{AVE} , which exhibited more variability in the BB domain (Figure 4.4e). Note that we include our single station from the Labrador Sea in the LS domain for visual comparison in Figure 4.4, but do not include it in any statistical analyses. Statistical differences in these parameters grouped by domain were determined by a nonparametric Kruskal-Wallis test with post hoc comparison at $p < 0.05$. Although median values of $[\text{bSiO}_2]$, $[\text{lSiO}_2]$ and Enh were markedly higher in the CAA compared to BB, and lower for $[\text{Si}(\text{OH})_4]$ and V_{AVE} , the only statistically significant difference observed was for V_{AVE} . Median values for ρSi were similar between the CAA and BB (Figure 4.4d).

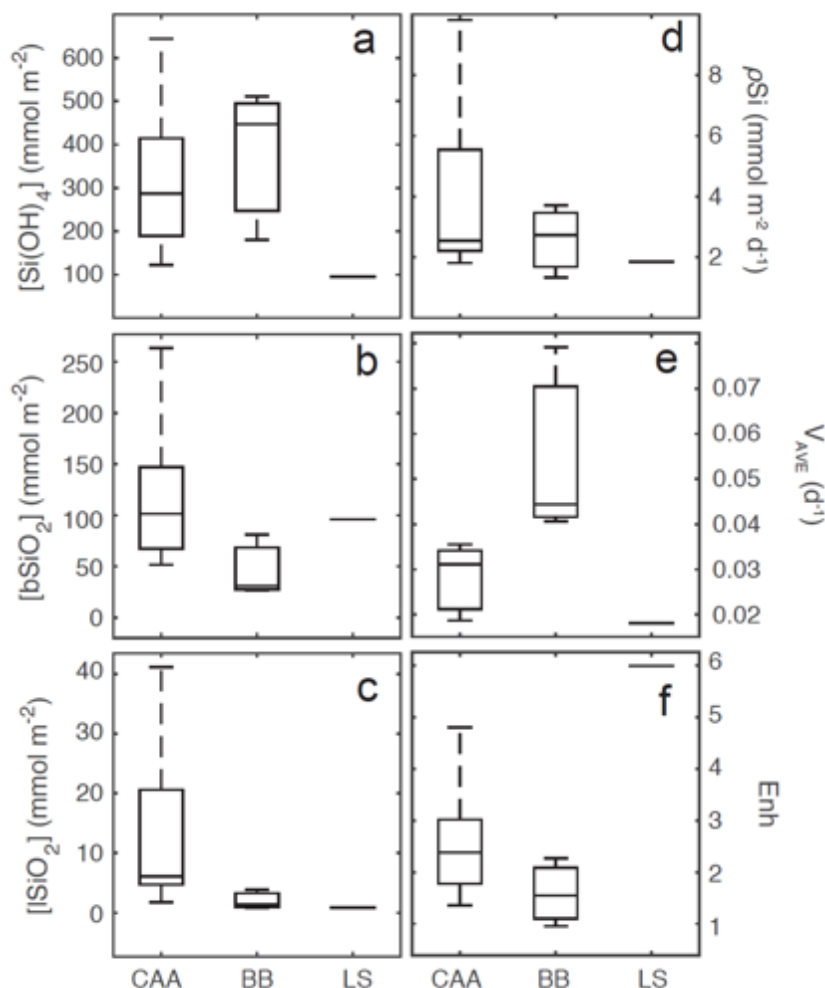


Figure 4.4. Box plots summarizing depth-integrated parameters separated into the three main oceanographic sampling regions along the GEOTRACES transect: Labrador Sea (LS), Baffin Bay (BB) and the Canadian Arctic Archipelago (CAA). (a) Si(OH)_4 concentration, (b) bSiO_2 concentration, (c) lSiO_2 concentration, (d) bSiO_2 production rate, ρSi , (e) specific bSiO_2 production rate, V_{Si} , and (f) the Si enhancement factor, Enh. For (a-d), data were depth-integrated from the ocean surface to the bottom on the euphotic zone (0.2% I_0). For (e), data were depth-integrated as for (a-d), and then normalized by the depth of the euphotic zone. For (f), data are not depth-integrated, and are only from 55% I_0 . The horizontal line in the middle of each box represents the median, and the top and bottom of the boxes represents the 25th and 75th percentiles, respectively. The whiskers extending above and below each box extend to the maximum and minimum measured values, respectively.

4.5 Discussion

4.5.1 Spatial patterns of biogenic silica dynamics in the Arctic

4.5.1.1 Dissolved and particulate silica concentrations

Spanning from the Labrador Sea, through Baffin Bay and into the CAA, the euphotic zone distributions of T, S and $[\text{Si(OH)}_4]$ exhibited vertical and horizontal gradients

reflecting the influence of Pacific and Atlantic-origin waters. Waters of Pacific origin are primarily identified by their relatively low S (<33.5) and a ~ 0.5 - $1 \mu\text{mol L}^{-1}$ excess of PO_4^{3-} relative to NO_3^- (Jones et al., 2003). The difference between these water masses can be identified by the intercept of a linear regression between $[\text{NO}_3^-]$ and $[\text{PO}_4^{3-}]$ (Figure 4.5; nutrient data from Appendix B). The slope of the regression between these parameters within the different water masses should be approximately the same and close to the expected ‘Redfield’ stoichiometric ratio of $\text{N:P} = 16$; however, waters of Pacific-origin will have an excess $[\text{PO}_4^{3-}]$ of 0.5 to $1 \mu\text{mol L}^{-1}$ when $[\text{NO}_3^-] = 0 \mu\text{mol L}^{-1}$. The only station where we observed $S > 33.5$ and did not observe an excess of PO_4^{3-} relative to NO_3^- (i.e. both $[\text{NO}_3^-]$ and $[\text{PO}_4^{3-}]$ were $\sim 0 \mu\text{mol L}^{-1}$) throughout the euphotic zone was LS2 in the Labrador Sea (Figure 4.2c and blue dots in Figure 4.5), which suggests that, for Baffin Bay and the CAA, the euphotic zone was comprised entirely of Pacific-origin waters. Pacific-origin waters are also high in Si(OH)_4 , and $[\text{Si(OH)}_4]$ in the Arctic have previously been used to trace the flow of Pacific waters within and out of the Arctic (e.g. Jones and Anderson, 1986; Wheeler et al., 1997). The depletion of Si(OH)_4 in surface waters, and west-to-east decrease we observed in the lower euphotic zone $[\text{Si(OH)}_4]$ reflects diatom utilization of Si as these waters transit through the CAA and Baffin Bay. This is supported by the abundance of diatoms (Table 4.3; Figures 4.2b and 4.3e; Wyatt et al., 2013; Schuback et al., 2017) and high rates of ρSi (Table 4.3; Figures 4.2f and 4.3d) found in these regions, especially in the CAA.

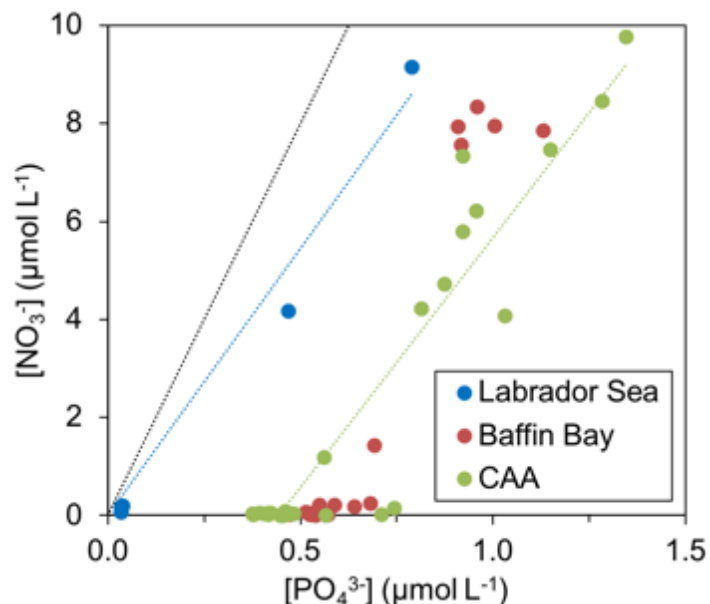


Figure 4.5. Nitrate-phosphate relationships in the euphotic zone along the GEOTRACES transect. Data are described in Appendix B and colour-coded by major oceanographic region: blue, Labrador Sea; red, Baffin Bay; green, Canadian Arctic Archipelago. Dashed lines represent the 16:1 N:P Redfield ratio (black), or linear regressions either through data from the Labrador Sea (blue), or through data from Baffin Bay and the Canadian Arctic Archipelago (green).

The variability in $[bSiO_2]$ distributions along our study transect may reflect differences in phytoplankton bloom phenology. The seasonal bloom in the Arctic progresses northwards with the retreating ice-edge (e.g. Leu et al., 2011; Wassmann and Reigstad, 2011), meaning that at the time of our sampling, we might expect phytoplankton biomass and productivity to increase northwards along our sampling transect towards the retreating ice-edge. Indeed, this is consistent with our observations of increasing $[bSiO_2]$ from Davis Strait to the ice-edge (station CAA6) in the CAA. In contrast, however, we found elevated $[bSiO_2]$ in the Labrador Sea that is not consistent with this northward progression, likely because the Labrador Sea is a Subarctic ecosystem that typically does not have any sea-ice in winter (Harrison et al., 2013). The seasonal bloom in the central Labrador Sea generally peaks in July and decreases throughout the rest of the season (Harrison et al., 2008; 2013). Given that our sampling at LS2 occurred in mid-July, at least 3 weeks earlier than any of the other stations along our transect, it is likely that the

higher [bSiO₂] we observed reflects the seasonal bloom in this region that is not as comparable in terms of spatial variability to the rest of our transect.

Spatial distributions and vertical trends in [Si(OH)₄] and [bSiO₂] (Figures 4.2-4.3) were similar to those of [NO₃⁻] and Chl *a* (Figures B.1-B.2 in Appendix B). The depletion of [Si(OH)₄] in the upper euphotic zone and subsequent increase with depth was similar to that observed for [NO₃⁻]; however, unlike [NO₃⁻], [Si(OH)₄] in the upper euphotic zone was almost never fully depleted. The only exception was in the Labrador Sea, where upper euphotic zone [Si(OH)₄] was <0.2 μmol L⁻¹, but otherwise ranged from 1 – 5 μmol L⁻¹ in all other stations. In contrast, upper euphotic zone [NO₃⁻] was <0.2 μmol L⁻¹ at all stations sampled. Subsurface maxima in [bSiO₂] generally corresponded to those of Chl *a* (Appendix B), and [bSiO₂] were strongly positively correlated with the >20-μm Chl *a* size fraction ($r = 0.86, p < 0.001$). Both the depth-integrated nutrient and biogenic particle concentrations exhibited similar spatial trends, with significant positive correlations between depth-integrated [Si(OH)₄] and [NO₃⁻] ($r = 0.81, p < 0.01$), and between depth-integrated [bSiO₂] and Chl *a* ($r = 0.78, p < 0.01$). In contrast to [NO₃⁻], there was no correlation between depth-integrated [Si(OH)₄] and [NH₄⁺]. All of these correlations suggest that diatom utilization of NO₃ is an important determinant of the levels of primary productivity in our study region.

Concentrations of lSiO₂ were generally higher when the water column was shallower, which likely reflects the influence of sediment resuspension on water column [lSiO₂] (Tables 4.1-4.2). Although suspended [lSiO₂] are less commonly reported than [bSiO₂], our measurements in the Labrador Sea, Baffin Bay and Peel Sound were comparable to those previously measured in the Beaufort Sea and Canada Basin (Varela

et al., 2016), while $[\text{LSiO}_2]$ in Barrow Strait and Lancaster Sound were most comparable to our measurements from the Bering and Chukchi Seas (Chapter 2). These comparisons also support that shallower water column depths will likely result in higher euphotic zone $[\text{LSiO}_2]$; however, the water column depths at our Lancaster Sound stations (CAA1 and CAA3) were deeper than other stations in the CAA (~600 m vs. ~250 m), yet these stations exhibited $[\text{LSiO}_2]$ at least 2x higher than any other station we sampled. Given that Lancaster Sound is a strong outflow region for the CAA (~0.7 Sv; Beszczynska-Möller et al., 2011), it is possible that these high concentrations are driven by strong current velocities resuspending sediment (Prisenberg and Hamilton, 2005).

4.5.1.2 Rates of biogenic silica production

Similar to $[\text{bSiO}_2]$, we found that ρSi and V_{Si} exhibited subsurface maxima that tended to correspond to an increase in $[\text{Si}(\text{OH})_4]$ and $[\text{NO}_3^-]$ (Figure 4.2d and Figure B.1f in Appendix B), reflecting the necessary balance of nutrients and light that phytoplankton require for growth. Our measurements of ρSi also appear to track the northwards progression of the seasonal bloom, with the highest ρSi observed at the ice-edge station at CAA6. In contrast, we observed the highest rates of V_{AVE} in Davis Strait and Baffin Bay, rather than at the ice-edge in the CAA. We would expect the seasonal bloom to be in decline or have already passed by the time of our sampling in Baffin Bay in early August, (e.g. Klein et al., 2002; Leu et al., 2011); yet, the high V_{AVE} and low ρSi suggest a diatom bloom is beginning to form. This is consistent with previous studies, which have observed a second, late-summer bloom in northern Baffin Bay (Klein et al., 2002; Caron et al., 2004). In addition, Ardyna et al. (2014) showed that there has been a 33% increase in the occurrence of a ‘double bloom’ in Baffin Bay when comparing the time periods from 1998-2001 and 2007-2012, which they attribute to climate-induced changes in sea-

ice extent. Thus, it is possible that the high V_{AVE} combined with low ρSi we observed in Baffin Bay is indicative of the beginning of this second, later bloom.

Vertical profiles of ρSi (Figure 4.2f) generally showed the same trends with depth as those of the concurrently measured rates of C and NO_3^- utilization (ρC and ρNO_3) (Figure B.1 in Appendix B). While the subsurface ρSi maxima mostly corresponded with those of ρC and ρNO_3 , there were some cases where we observed a ρSi maxima at 1% I_0 that was not reflected in the C or NO_3 utilization rates. Given the low light level, one possibility for this discrepancy is a light-driven decoupling of the C, N and Si metabolisms (e.g. Martin-Jezequel et al., 2000; Claquin et al., 2002; 2004). Unlike the C and N metabolisms, Si metabolism in diatoms is not as strongly tied to photosynthesis, and instead is more strongly coupled to the cell cycle (Martin-Jezequel et al., 2000). Low growth rates driven by lower light levels mean that diatoms spend more time in the phase of the cell cycle associated taking up and incorporating Si (Claquin et al., 2002; 2004), which can result in higher ρSi relative to ρC and ρNO_3 and higher Si:C and Si:N ratios.

The horizontal distributions of Si, C and NO_3 utilization also agreed fairly well (Figure 4.3e compared with Figure B.2 in Appendix B), with the exception of two stations: LS2 and CAA6. For LS2, as discussed above, our sampling took place 3+ weeks prior to any of the other stations we sampled and therefore the rates measured here are not comparable to the rest of our transect in terms of spatial variability or bloom progression. The high ρSi we observed at station CAA6 was not reflected in ρC and ρNO_3 . Given that that most of the Si utilization at this station occurred at 1% I_0 this discrepancy is likely due to light-driven decoupling of the Si, C and N metabolisms. Excluding these stations, ρC and ρNO_3 were both positively correlated with ρSi ($r = 0.46$ and 0.67 , respectively).

Although the correlations were only significant at $p > 0.3$ and $p > 0.1$, respectively, these results still give some indication that diatoms contribute to much of the spatial variability in ρC and ρNO_3 in late summer. The lack of significance in the correlations could be driven by a shifting phytoplankton assemblage as the seasonal bloom progresses towards a system more reliant on regenerated forms of nitrogen. This shift is evident in the HPLC measurements presented by Shuback et al. (2017). These measurements, made on the same cruise and at the same stations as our own, show a northward increase in the relative abundance of diatoms, and a greater relative abundance of dinoflagellates and prasinophytes at the more southern stations in Baffin Bay where the contribution from diatoms is small. This is also consistent with the higher ρNH_4 observed in Baffin Bay compared to the CAA (Figure B.2f in Appendix B). All of these results indicate that while diatoms may drive much of the productivity at the start of the seasonal bloom, other groups of phytoplankton become more important to the overall rates of primary production in the region as the bloom progresses.

4.5.2 Diatom contribution to primary production and nitrogen utilization

The diatom contribution to PP and ρNO_3 increased northwards (Table 4.2), with diatoms accounting for 32-100% of the PP and 47-100% of the ρNO_3 . When averaged by region (CAA vs BB-LS), we found no significant differences between our estimates of % diatom PP and concurrent measurements of the % contribution of $>5\ \mu\text{m}$ cells to Chl *a* in either region (Table 4.4). Note that we combine the BB and LS domains together so that we can compare with previous measurements from the literature.

We did find significant differences between the % diatom PP and the % contribution of $>20\ \mu\text{m}$ cells to Chl *a*, which suggests that diatoms between $5 - 20\ \mu\text{m}$ in size are likely important to productivity in these regions. We also found there was a significant

difference between % diatom PP and the relative abundance of diatoms based on HPLC data in the CAA; however, HPLC data were only collected at two depths: the mixed layer (ML, 5-8 m) and ‘sub-ML’ (20-40 m), while % diatom PP represents a weighted average over the entire euphotic zone. Biogenic silica concentrations and production rates tended to be much higher below the mixed layer (i.e. at 30% I_0 and below), where nutrient concentrations also increased. Thus, samples below the mixed layer likely better represent the euphotic-zone diatom assemblage.

Table 4.4. Summary of the of the diatom contribution to phytoplankton biomass and productivity from studies conducted in the Eastern Canadian Arctic. Data presented are averages for the region $\pm$ standard error of the mean (SE). n = number of observations. Note that the BB and LS domains are combined to enable comparison with previous studies that often grouped these regions together.

Parameter	CAA		BB-LS	
	Average ($\pm$ SE)	n	Average ($\pm$ SE)	n
This study: Aug 2015				
% diatom PP	86% $\pm$ 8%	5	54% $\pm$ 14%	3
% diatom ρNO_3	92% $\pm$ 8%	5	79% $\pm$ 10%	3
Appendix B: Aug 2015				
% >5 μm Chl <i>a</i>	72% $\pm$ 6%	5	42% $\pm$ 4%	3
% >20 μm Chl <i>a</i>	45% $\pm$ 10%*	5	3% $\pm$ 1%*	3
Schuback et al., (2017): Aug 2015				
% diatoms	61% $\pm$ 5%*	10	43% $\pm$ 5%	9
Varela et al., (2013): Jul 2008				
% >5 μm Chl <i>a</i>	48% $\pm$ 9%*	7	42% $\pm$ 8%	8
% >5 μm ρC	65% $\pm$ 10%	7	53% $\pm$ 10%	8
% >5 μm ρNO_3	51% $\pm$ 10%**	7	51% $\pm$ 10%	8
Crawford et al., (2018): Jul 2008				
% diatom abundance	28% $\pm$ 8%*	6	20% $\pm$ 7%*	8
% diatom phyto C	70% $\pm$ 14%	6	35% $\pm$ 12%	8
Ardyna et al., (2011): Aug-Sep 2005				
% >5 μm Chl <i>a</i>	56% $\pm$ 39%	5	54% $\pm$ 32%	5
% >5 μm ρC	42% $\pm$ 40%	5	30% $\pm$ 12%	5
% diatom abundance	30% $\pm$ 18%*	5	25% $\pm$ 14%	5
Ardyna et al., (2011): Sep-Oct 2006				
% >5 μm Chl <i>a</i>	68% $\pm$ 38%	5	75% $\pm$ 16%	10
% >5 μm ρC	43% $\pm$ 28%	5	49% $\pm$ 21%	10
% diatom abundance	53% $\pm$ 7%*	5	66% $\pm$ 6%	10

*significant difference ($p < 0.05$) from % diatom PP

**significant difference ($p < 0.05$) from % diatom ρNO_3

Indeed, when the HPLC-based relative diatom abundance from the only sub-ML are compared to % diatom PP, the difference between the two is not significant. All of these

results suggest that the diatom contributions to productivity and ρNO_3 are proportional to biomass throughout our study region.

We found that the regional patterns we observed in the diatom contributions to PP and ρNO_3 agree well with previous studies, with higher values in the CAA compared to Baffin Bay or the Labrador Sea; however, there were some significant differences when we directly compared measurements, mostly in the CAA. The contribution of diatoms to ρNO_3 in BB-LS ($79 \pm 10\%$) agrees remarkably well with the % diatom contribution to new production estimated by Tremblay et al., (2002) for the North Water Polynya (80%), despite our measurements occurring later in the season and in the less productive central/southern region of Baffin Bay. This suggests that, despite differences in the magnitude of productivity in Baffin Bay, the contribution of diatoms to new production is consistent across the region. For both BB-LS and the CAA, we found significant differences between the % diatom PP and the relative contribution of diatoms to total cell numbers from Crawford et al. (2018); however, differences were not significant if we instead compared our results to the relative abundance of diatoms in terms of phytoplankton C (% diatom phyto C) from the Crawford et al. study. In the CAA, we found some significant differences between our estimates of % diatom PP and ρNO_3 to those of the size-fractionated biomass and productivity measurements from Varela et al. (2013) and Ardyna et al. (2011). For both studies, these differences could result from interannual or seasonal variability and thus differences in phytoplankton assemblage composition, as their measurements were made at different times of the growing season (earlier for Varela et al. (2013) and later for Ardyna et al. (2011)). Differences between our results and the Varela et al. (2013) study could also result from spatial variability

within the CAA, as most of their sampling locations were farther south in the CAA than ours. Regardless, these differences we observed highlight the highly dynamic nature of the CAA.

4.5.3 Silicon limitation of biogenic silica production

Although NO_3^- concentrations were $< 0.2 \mu\text{mol L}^{-1}$ in the surface waters ($< 7 \text{ m}$) of our study region, we found that addition of Si(OH)_4 enhanced bSiO_2 production rates by up to a factor of 6, indicating that the ambient Si(OH)_4 concentrations were limiting Si uptake in our study region (Table 4.3; Figure 4.3f). Although not significantly different, we did observe a higher and broader range of values for Enh in the CAA compared to Baffin Bay, while the one value we measured for the Labrador Sea was highest of all (Figure 4.4f). These differences may be related to surface water $[\text{Si(OH)}_4]$ as the average concentrations were significantly higher ($p < 0.001$) in Baffin Bay ($4.3 \pm 0.3 \mu\text{mol L}^{-1}$) compared to the CAA ($1.7 \pm 0.9 \mu\text{mol L}^{-1}$) (Table 4.3; Figure 4.2d), while $[\text{Si(OH)}_4]$ in surface waters of the Labrador Sea were the lowest of all at $< 0.2 \mu\text{mol L}^{-1}$.

The relationship between $[\text{NO}_3^-]$ and $[\text{Si(OH)}_4]$ from the entire euphotic zone for all of our sampling stations indicates that Si(OH)_4 and NO_3^- are drawn down at a Si:N ratio of 1.3, and exhaustion of all of the available NO_3^- leaves an excess of $\sim 2.3 \mu\text{mol L}^{-1}$ of Si(OH)_4 (Figure 4.6a). This is consistent with the finding that surface waters of the Arctic are primarily limited by the availability of NO_3^- , as it is the first nutrient to become exhausted during bloom events (Tremblay and Gagnon, 2009); however, culture studies have indicated that the half-saturation constant, K_s , for NO_3^- in diatoms ranges from $0.02 - 10.2 \mu\text{mol L}^{-1}$ (mean: $1.6 \mu\text{mol L}^{-1}$), which is lower than the range of K_s for Si(OH)_4 of $0.2 - 22 \mu\text{mol L}^{-1}$ (mean: $3.9 \mu\text{mol L}^{-1}$) (review by Sarthou et al., 2005), meaning that diatoms may become limited by Si before NO_3^- if these nutrients are initially present in a

1:1 ratio. The average K_s for Si(OH)_4 from these culture studies is also consistent with both the range of K_s values we calculate from our kinetic experiments ($0.8 - 9.2 \mu\text{mol L}^{-1}$; Table 4.3) and the range of values we expect for the ‘regional assemblage’ ($2.1 - 3.5 \mu\text{mol L}^{-1}$) based on the median and average values respectively for K_s from all stations.

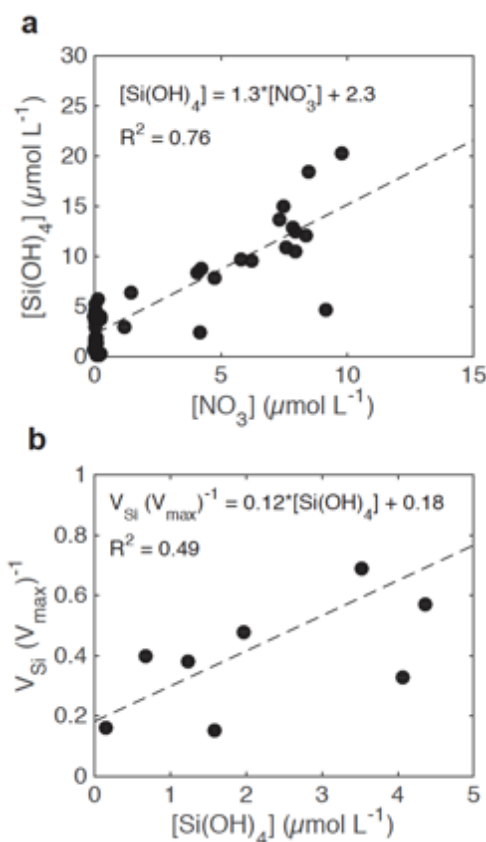


Figure 4.6. Evaluation of potential silicon limitation of diatom production during the 2015 Canadian Arctic GEOTRACES. (a) relationship between nitrate (NO_3^-) and silicic acid (Si(OH)_4) concentrations in the euphotic zone, and (b) the ratio of V_{Si} at ambient $[\text{Si(OH)}_4]$ to V_{max} versus the concentration of silicic acid at 55% I_0 . In both panels, the dashed black line represents a linear least-squares regression, with the equation and R^2 value for the best fit line listed.

Another method to estimate the regional assemblage K_s , “ $K_{s,\text{region}}$ ”, is based on that of Krause et al. (2012; 2018). The authors of these studies observed that there was a linear relationship between the ambient $[\text{Si(OH)}_4]$, and the ratio of the ambient V_{Si} (V_{amb}) to V_{max} (i.e. $V_{\text{amb}} \cdot V_{\text{max}}$) in a variety of different ocean environments, from the Eastern Equatorial Pacific and the subtropical gyres to the Barents Sea.

From a regression between $[\text{Si}(\text{OH})_4]$ and $V_{\text{amb}}:V_{\text{max}}$, we determined $K_{\text{s,region}}$ as the $[\text{Si}(\text{OH})_4]$ where $V_{\text{amb}}:V_{\text{max}} = 0.5$ (i.e. $V_{\text{amb}} = \frac{1}{2}V_{\text{max}}$; Figure 4.6b). This gives a value of $2.7 \mu\text{mol L}^{-1}$, which falls exactly between our assumed range of $K_{\text{s,region}}$ from the simpler average and median calculations (Figure 4.6b). Considering that the average $[\text{Si}(\text{OH})_4]$ in the surface waters of our study region ($2.3 \mu\text{mol L}^{-1}$) was similar to our $K_{\text{s,region}}$ estimates further indicates that $[\text{Si}(\text{OH})_4]$ in this region of the Arctic were at values potentially limiting to diatoms. Furthermore, diatoms are also able to utilize other forms of nitrogen, such as NH_4^+ and urea (e.g. Dortch et al., 1990; Peers et al., 2000; Allen et al., 2012; Bender et al., 2012; Glibert et al., 2015), and phytoplankton $>5 \mu\text{m}$ (mostly diatoms, Wyatt et al., 2013) have been previously shown to utilize these forms of N in our study region (Varela et al., 2013). Thus, despite the relatively low $[\text{NO}_3^-]$ we observe, it is possible that diatoms in this region of the Arctic are experiencing Si limitation prior to total N ($\text{NO}_3^- + \text{NH}_4^+ + \text{urea}$) limitation.

Although Si limitation appeared to be essentially ubiquitous throughout our study region, this does not necessarily indicate that $\text{Si}(\text{OH})_4$ levels have become low enough to actually limit growth. When Si uptake is limited, diatoms can adjust their internal nutrient quotas to produce less silicified frustules and avoid growth limitation, but only to a certain extent (Morel, 1987; Harrison et al., 1977; Martin-Jezequel et al., 2000). Culture studies have shown that diatoms can alter their Si per cell by up to a factor of four prior to experiencing growth limitation, meaning that it is only diatom assemblages with $V_{\text{amb}}:V_{\text{max}} < 25\%$ (in terms of V_{Si}) that must slow growth in order to take up enough Si to produce a new cell (Martin-Jezequel et al., 2000). Thus, while $V_{\text{amb}}:V_{\text{max}}$ ranged from 15 – 69% at the stations where we observed Si limitation, it is only at stations LS2 and

CAA5 where $V_{\text{amb}}:V_{\text{max}}$ ratios were $<25\%$ and where we can conclude $[\text{Si}(\text{OH})_4]$ were low enough to restrict diatom growth in addition to Si uptake. Using our regression from Figure 6b and assuming a $V_{\text{amb}}:V_{\text{max}} = 0.25$, we estimate a ‘regional assemblage’ $[\text{Si}(\text{OH})_4]$ growth limitation threshold ($K_{\mu, \text{region}}$) of $0.9 \mu\text{mol L}^{-1}$, below which diatom growth, in addition to Si uptake, will be limited. We observe some discrepancies between this value compared to our observations of $V_{\text{amb}}:V_{\text{max}}$ relative to ambient $[\text{Si}(\text{OH})_4]$ (Table 4.3). At station CAA3, $[\text{Si}(\text{OH})_4]$ was below the $K_{\mu, \text{region}}$ threshold at $0.67 \mu\text{mol L}^{-1}$, yet $V_{\text{amb}}:V_{\text{max}}$ was 40%, indicating that growth was likely not yet restricted. In contrast, we did observe $V_{\text{amb}}:V_{\text{max}} <25\%$ at station CAA5, yet $[\text{Si}(\text{OH})_4]$ was $1.58 \mu\text{mol L}^{-1}$. These results indicate that $K_{\mu, \text{region}}$ likely varies from at least $0.7 - 1.6 \mu\text{mol L}^{-1}$, with assemblages having varying adaptations to decreased $\text{Si}(\text{OH})_4$ availability. Our results also show that irrespective of the low $[\text{NO}_3^-]$ in surface waters, diatoms in this region of the Arctic are affected by the availability of $\text{Si}(\text{OH})_4$, and in some cases to a point where their growth is limited.

4.5.4 Diatom Si dynamics compared to other regions

4.5.4.1 Dissolved and particulate silica concentrations

Our measurements of euphotic-zone $[\text{Si}(\text{OH})_4]$ and $[\text{bSiO}_2]$ in all regions were comparable to previous summertime measurements and followed similar spatial trends (e.g. Ardyna et al., 2011; Wyatt et al., 2013; Varela et al., 2013; Blais et al., 2017). Concentrations of bSiO_2 in the CAA were within the range of values found in the Southern Ocean (Table 4.5), a region that accounts for approximately one-third of the total marine production of bSiO_2 (Treguer and De La Rocha, 2013). Biogenic silica concentrations in the CAA were also comparable to those measured in the highly-productive diatom-dominated waters of the Bering and Chukchi Seas (Table 4.5; Chapter

2). The Labrador Sea had $[bSiO_2]$ most comparable to the NE Subarctic Atlantic, while measurements in Baffin Bay compared well to those from the NE Subarctic Pacific (Table 4.5). For all of our regions studied, $[bSiO_2]$ were at least 2x higher than values measured in Svalbard fjords during the spring phytoplankton bloom, indicating that, even later in the season, diatoms are an important component of the phytoplankton assemblage from the Labrador Sea to the CAA.

4.5.4.2 Rates of biogenic silica production

To our knowledge, ours are the first direct measurements of ambient biogenic silica production reported for our study region. Of the three main regions we sampled – Labrador Sea, Baffin Bay and the CAA - only two previous studies have reported $bSiO_2$ production rates, and only for Baffin Bay. For these studies, $bSiO_2$ production rates were either measured following an ocean acidification manipulation experiment (Hoppe et al., 2017), and so do not represent the ambient rate of $bSiO_2$ production, or rates were estimated from the seasonal nutrient drawdown (Tremblay et al., 2002) and thus do not represent directly measured rates. Our measurements of ρSi in Baffin Bay are ~ 2.5 times lower than those reported for July by Tremblay et al. (2002). Apart from differences in methodology, this discrepancy could be the result of either spatial or seasonal differences. The Tremblay et al. (2002) study focused on the highly-productive North Water Polynya (NOW) in northern Baffin Bay during the seasonal bloom period from May-July, while our own sampling occurred at stations farther south and later in the season (August).

Table 4.5. Regional comparison of depth-integrated [bSiO₂], and ρ Si for mid- (35-50°N and S) and high-latitude (>50°N or S) studies. Data are integrated to the bottom of the euphotic zone (1% - 0.1% I₀). Values for ρ Si represent direct measurements of the bSiO₂ production rate using isotopic traces unless otherwise noted. (-) = no data.

Region	Month	[bSiO ₂] (μmol L ⁻¹)		ρSi (mmol m ⁻² d ⁻¹)		Reference
		Range	Mean	Range	Mean	
Arctic and Subarctic (50°N – 90°N)						
Atlantic Ocean						
NE Subarctic	May	10 - 148	79	5.9 - 166	35.5	Brown et al. (2003)
Barents Sea						
Svalbard Fjords*	May	2 - 42	21	0.3 - 1.5	0.8	Krause et al. (2018)
Baffin Bay and Labrador Sea						
Entire region	Jul	9 - 163	48	-	-	Wyatt et al. (2013)
North Water Polynya	Jul	-	-	-	7.2**	Tremblay et al. (2002)
Labrador Sea	Jul	-	96	-	1.9	This study
Baffin Bay	Aug	36 - 81	46	1.3 – 2.7	2.6	This study
Canadian Arctic Archipelago						
Entire region	Jul	25 - 183	114	-	-	Wyatt et al. (2013)
Entire region	Aug	51 - 263	119	1.8 – 9.8	4.1	This study
Bering and Chukchi Seas						
Entire region	Jul	117 - 213	156	-	-	Wyatt et al. (2013)
NE Chukchi Sea	Jul	97 - 168	132	8.2 - 27.8	14.3	Chapter 2
SE Chukchi Sea	Jul	41 - 1172	336	9.0 - 61.6	35.9	Chapter 2
NE Bering Sea	Jul	1.5 - 296	133	0.3 - 22.2	7.2	Chapter 2
SE Bering Sea	May-Jul	35 - 680	261	1.8 - 50.9	17.7	Banahan and Goering (1986)
Pacific Ocean						
NE Subarctic	Jul	15 - 46	33	10.3 – 28.8	16.3	Giesbrecht et al. unpubl.
Temperate Regions (50°N – 35°N and 35°S – 50°S)						
Pacific Ocean						
Saanich Inlet	Mar-May	28 - 179	89	8.3 – 44.8	24.3	Giesbrecht et al. unpubl.
Monterey Bay	Apr	44 - 175	106	4.8 - 108	42.8	Brzezinski et al. (2003)
Atlantic Ocean						
Gulf Stream warm core rings	Apr-Jun	5.2 - 47	27	4.4 - 11.7	7.1	Brzezinski and Nelson (1989)
Antarctic and Subantarctic (50°S – 90°S)						
Southern Ocean						
Pacific Sector	Oct-Mar	12 - 793	233	0.2 - 45.5	13.2	Nelson and Gordon (1982), Brzezinski et al. (2001)
Atlantic Sector	Sep-Dec	30 - 1231	328	2.4 - 60.7	19.4	Treguer et al. (1991), Queguenier et al. (2002)

Region	Month	[bSiO ₂] (μmol L ⁻¹)		ρSi (mmol m ⁻² d ⁻¹)		Reference
		<i>Range</i>	<i>Mean</i>	<i>Range</i>	<i>Mean</i>	
Indian Sector	Jan-Feb	0.5 - 488	104	0.1 - 11.4	3.7	Beucher et al. (2004), Fripiat et al. (2011)
Weddell Sea						
Entire region	Sep-Dec	7.5 - 98.8	43	1.8 - 16.1	5.9	Treguer et al. (1991), Leynaert et al. (1993), Queguenier et al. (2002)
Ross Sea						
Shelf, ice-edge bloom	Jan-Feb	-	-	25.5 - 49.6	34	Nelson et al. (1991)

*bSiO₂ and ρSi integrated to 20 m depth

** estimate for July from seasonal nutrient drawdown

Thus, we would expect production to be lower at our sampling time, as the seasonal bloom would have already passed, and also because production is presumed to be lower in region of Baffin Bay south of the NOW (e.g. Klein et al., 2002). We also found our measurements of ρSi in the Labrador Sea to be much lower than those reported by Brown et al. (2003) for the NE Subarctic Atlantic, despite using the same method to measure ρSi (^{32}Si tracer incubations) and both regions presumably being sampled during the seasonal bloom, i.e. May for the NE Subarctic Atlantic, and July for our sampling location in the Labrador Sea (Harrison et al., 2008). This could be due patchiness in bloom distribution and our limited sampling of only one station in the Labrador Sea, or that our sampling occurred closer to the end of the seasonal diatom bloom. At the very least, it is likely that we sampled closer to the end of the seasonal bloom, which is supported by the low V_{AVE} we measure at this station (Table 4.2).

The highest ρSi we measured was in the CAA, although the mean value for this region still fell below that estimated for the NOW and was much lower than ρSi measured in the Bering and Chukchi Seas of the Pacific Arctic Region (PAR) (Table 4.5). This is likely because both the NOW and PAR are some of the most highly-productive regions of the Arctic, with phytoplankton assemblages dominated by diatoms (Booth et al, 2002; Sakshaug, 2004; Chapters 1 and 2). Rates of bSiO_2 production in the CAA were also lower than those from the Pacific and Atlantic sectors of the Southern Ocean; although measurements from these regions were primarily collected during the diatoms blooms of austral spring. In contrast, ρSi in the CAA was comparable to ρSi measured in austral summer in the Indian Sector of the Southern Ocean, which is most comparable to our sampling period (Table 4.5).

Our ρSi for the CAA, Baffin Bay and Labrador Sea are moderate compared to measurements from other regions in the Arctic, falling between the maxima of the high-Si/Pacific-influenced Bering and Chukchi Shelves (Chapter 2), and minima of the low-Si/Atlantic-influenced Svalbard fjords in the Barents Sea (Krause et al., 2018). Globally, our measurements of ρSi are comparable to the Southern Ocean when comparisons are made within the same season, but considerably lower than rates measured in both the more productive coastal regions of the temperate Pacific Ocean and in the Subarctic NE Pacific and Atlantic Oceans. Overall, our results indicate that bSiO_2 production in the eastern Canadian Arctic is an important, but thus far neglected, region for marine bSiO_2 production in the global ocean.

4.5.4.3 Inefficient Si uptake at low $[\text{Si(OH)}_4]$ by Arctic diatom assemblages

The efficiency of Si uptake at low concentration is indicated by the steepness of the initial slope of a Michaelis-Menten curve (V_{max}/K_s ; Healey, 1980), with higher values corresponding to steeper slopes and more efficient Si uptake. This V_{max}/K_s , or kinetic efficiency (KE), acts as an index of the ability of a diatom species or assemblage to exploit low $[\text{Si(OH)}_4]$. We calculated KE values ranging from 0.53 – 3.20 ($\text{mmol L}^{-1} \text{ hr}^{-1}$), which are comparable to those values found in other polar ecosystems such as the Pacific Arctic Region and the Southern Ocean (Figure 4.7). However; the KE values for polar regions are almost an order of magnitude lower than those reported in other parts of the world's ocean, suggesting that the kinetic inefficiency of diatom assemblages could be driven by environmental conditions common to both poles, i.e. lower temperatures and/or lower light levels.

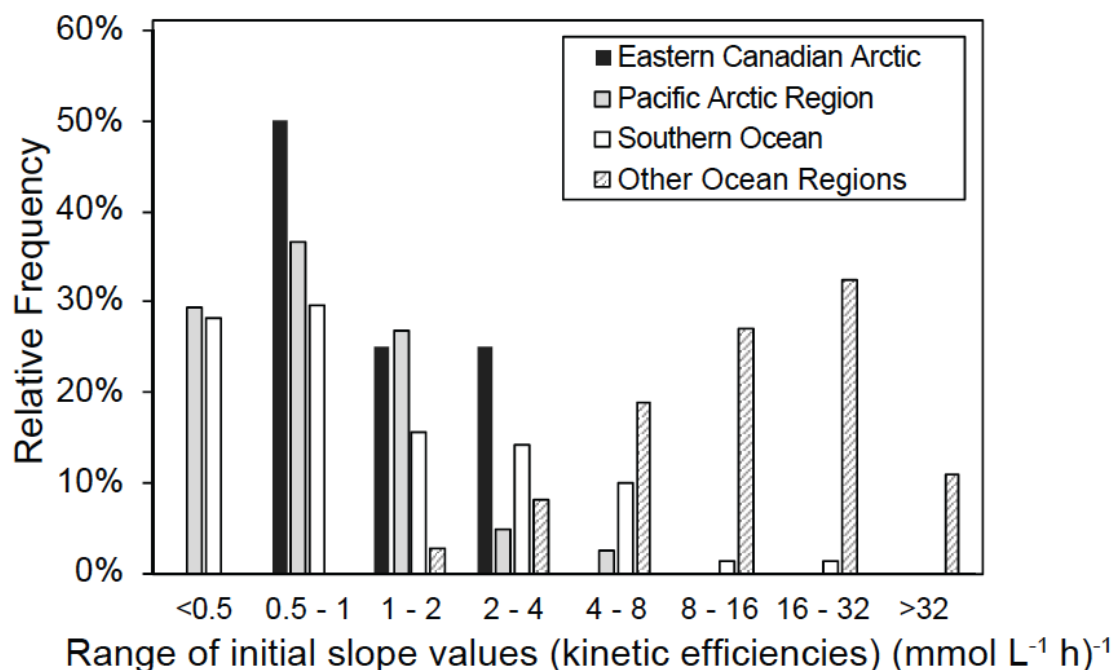


Figure 4.7. Relative frequency distribution of the initial slopes of the V_{Si} vs $[\text{Si}(\text{OH})_4]$ response (V_{max}/K_s , kinetic efficiency, KE) measured at 55% I_0 in the Eastern Canadian Arctic (in black) compared with that for the Pacific Arctic Region (from Appendix A, in grey), the Southern Ocean (from Nelson et al., 2001, in white), and other low- and mid- latitude ocean regions (from Nelson et al., 2001 and references therein and Krause et al., 2012, in hatched-grey).

The lower temperatures of the polar oceans would fundamentally result in slower enzymatic reactions and growth rates. This is confirmed by our ambient measurements of V_{AVE} (Table 4.2), which are comparable to those found in the Bering and Chukchi Seas and the Southern Ocean ($<0.01 - 0.3 \text{ d}^{-1}$ from Chapter 2; Brzezinski et al., 2001), but up to an order of magnitude lower than those found at temperature latitudes with warmer temperatures (e.g. $0.1 - 1.4 \text{ d}^{-1}$ from Brzezinski et al., 1997, Shipe and Brzezinski, 2003, Krause et al., 2011 and Krause et al., 2015). Our range of V_{max} values are also low ($0.04 - 0.13 \text{ d}^{-1}$) compared to those found in warmer waters (e.g. $0.3 - 1.5 \text{ d}^{-1}$ from Brzezinski et al., 1998, Leynaert et al., 2001, and Krause et al., 2012) while values for K_s (mean: $3.5 \mu\text{mol L}^{-1}$; Table 4.2) fall within the range of those measured in field studies throughout the world's oceans (e.g. $1.3 - 14 \mu\text{mol L}^{-1}$ from Chapter 2, Brzezinski et al., 1998, 2001;

Leynaert et al., 2001, Nelson et al., 2001, and Krause et al., 2012). Although there is some limited evidence from culture work that temperature has little effect on KE for Si uptake, this comes from only one study which included only three freshwater diatom species (van Donk and Soultau Kilham, 1990). Thus, it remains feasible that the lower temperatures of the polar oceans, and thus lower specific Si uptake rates, are driving much of the decrease in KE in the Arctic Ocean.

It is also possible that decreased light levels at high latitudes (e.g. Sakshaug, 2004) are further exacerbating the low KE observed at in the polar oceans. Our results from the Pacific Arctic Region in Chapter 2 indicate that the ‘regional diatom assemblage’ KE is light-dependent, decreasing with decreasing light level. This effect of light on the regional diatom assemblage KE has also been observed in the equatorial Pacific (Krause et al., 2010); however, values for KE from the study of Krause et al. (2010) are ~5 times larger than those values reported here in Chapter 2. Davis (1976) found there was no response to increased $[\text{Si}(\text{OH})_4]$ when the diatom *Skeletonema costatum* was grown in culture under Si and light limitation. In comparison, when cultures were grown only under Si limitation, diatoms exhibited the expected Michaelis-Menten response to increasing $[\text{Si}(\text{OH})_4]$. While the evidence for the light dependence of Si metabolism in the field is mixed (see section 2.5.2.1.2 in Chapter 2), our results indicate that light, in addition to temperature, may also influence the kinetic efficiencies of Arctic diatom assemblages.

4.6 Conclusions

We present the first dataset of concurrent measurements of bSiO_2 concentrations and direct measurement of bSiO_2 production rates and assessment of kinetic limitation by $[\text{Si}(\text{OH})_4]$ in the Eastern Canadian Arctic and Labrador Sea. Our results indicate that

these regions are important to the Arctic marine Si cycle and its link to other biogeochemical cycles. We found moderate rates of bSiO_2 production, lower than the rates observed in the Bering and Chukchi Seas, but comparable to those observed in some regions of the Southern Ocean. We also found that diatoms contributed to the majority of primary production and NO_3^- uptake. Our results are consistent with the findings of previous studies, indicating that diatoms are an important mediator of C to the food web and to vertical export. We found evidence for changes to the phytoplankton phenology in the region. The discrepancy in the spatial patterns of depth-integrated specific (V_{AVE}) and absolute (ρSi) production rates of bSiO_2 implied the onset of a second diatom bloom in Baffin Bay. Such changes have previously been reported in the literature and linked to the recent losses in Arctic sea-ice. A second phytoplankton bloom in Baffin Bay could have significant effects on the food web and biogeochemical cycling in this region.

Despite low $[\text{NO}_3^-]$ in near surface waters (0-7 m), we observed widespread Si limitation that was intense enough at some stations to not only limit Si uptake, but also diatom growth. We found the diatom assemblages of the Eastern Canadian Arctic were inefficient at taking up Si at low concentrations, compared to assemblages from more temperate ecosystems. The low kinetic efficiency of diatom assemblages appears to be ubiquitous in the polar oceans and is likely driven by both lower temperatures and potentially also lower light levels. It is possible that increasing seawater temperatures leading to decreased sea-ice extent and changing light regimes may result in diatoms becoming more kinetically efficient in utilizing Si. If these changes lead to subsequent changes in the diatom Si:C:N ratios, they could have far reaching effects on the diatom

contribution to the biological carbon pump and downward fluxes of bSiO_2 and N in the Arctic.

Chapter 5

From the Pacific Arctic Region to the Labrador Sea: Natural variations in dissolved silicon isotopes across Subarctic and Arctic Seas during 2015

5.1 Abstract

We present measurements of the silicon isotopic composition of silicic acid ($\delta^{30}\text{Si}(\text{OH})_4$) for the Bering and Chukchi Seas in the western Arctic, within the Beaufort Sea and Canada Basin, from the Canadian Arctic Archipelago to Baffin Bay in the eastern Canadian Arctic and finally in the Labrador Sea, presenting a complete transect along one of the main flow paths of Pacific-origin waters through the Arctic. These measurements were collected in the summer of 2015 as part of the Distributed Biological Observatory and Canadian Arctic GEOTRACES programs. We found that $\delta^{30}\text{Si}(\text{OH})_4$ signals reflect water mass composition, the dissolution of biogenic silica (bSiO_2) throughout the water column, and the biological utilization of Si in surface waters. In particular, we found that $\delta^{30}\text{Si}(\text{OH})_4$ signals track Pacific-origin waters and their modification by Si utilization as these waters transit from west to east. We also identified two types of NE Atlantic-origin waters that could be differentiated by their $\delta^{30}\text{Si}(\text{OH})_4$ compositions, which likely reflects the different pathways these water masses follow through the Arctic. Our $\delta^{30}\text{Si}(\text{OH})_4$ measurements suggest that the very high concentrations of $\text{Si}(\text{OH})_4$ in the deep waters of Baffin Bay are driven entirely by bSiO_2 dissolution within the water column. Similarly, bSiO_2 dissolution also appears to influence the $\delta^{30}\text{Si}(\text{OH})_4$ of the deep waters of the Canada Basin, with dissolution of sponge spicules potentially driving the relatively low $\delta^{30}\text{Si}(\text{OH})_4$ observed at depth. Using an open system model, we estimated the biogenic Si isotope fractionation factor ($^{30}\epsilon$) for the Bering and Chukchi Seas and the Canadian Arctic Archipelago to be $^{30}\epsilon = -1.07 \pm 0.14\%$, which agrees well with laboratory and field estimates. In contrast, the isotope systematics in the Canada Basin and Baffin Bay are better represented by a closed-system model. Using this approach, we were able to use our

calculated $^{30}\epsilon$ to estimate that ~42-44% of the total primary production occurring in these regions was from the contribution of sea-ice algae. These estimates are based on previous assumptions about the sea-ice/water column Si isotope systematics that still remain to be confirmed in the literature, but indicate that $\delta^{30}\text{Si}(\text{OH})_4$ measurements may be a simple and effective tool to estimate the relative proportion of annual sea-ice algae production to total primary production. Our results confirm that $\delta^{30}\text{Si}(\text{OH})_4$ is a useful tracer of Si utilization, and of water mass composition and modification in Arctic marine waters.

5.2 Introduction

Diatoms are the dominant primary producers in coastal and shelf regions, and contribute to about 20% of the annual photosynthesis on earth (Nelson et al., 1995; Field et al., 1998). These siliceous organisms are also the largest consumers of dissolved Si (silicic acid; $\text{Si}(\text{OH})_4$) in marine surface waters (Treguer and De La Rocha, 2013). Thus, in addition to their impact on the carbon cycle, diatoms exert a major control on the marine Si cycle through the formation of biogenic silica (bSiO_2). During Si uptake, diatoms preferentially take up lighter isotopes of Si (De La Rocha et al., 1997; Milligan et al., 2004; Sutton et al., 2013), subsequently enriching surface water $\text{Si}(\text{OH})_4$ in its heavier isotopes. This process results in systematic variations in the natural Si isotopic compositions ($\delta^{30}\text{Si}$) of bSiO_2 ($\delta^{30}\text{Si-bSiO}_2$) and $\text{Si}(\text{OH})_4$ ($\delta^{30}\text{Si}(\text{OH})_4$) in surface waters (e.g. Varela et al., 2004; Fripiat et al., 2011). Dissolution of sinking diatom bSiO_2 within the ocean interior may also influence the $\delta^{30}\text{Si}$ compositions of bSiO_2 and $\text{Si}(\text{OH})_4$, which may be further enhanced by Si isotope fractionation during dissolution, although the extent of the effect of dissolution and potential fractionation on $\delta^{30}\text{Si}$ is currently unclear (Demarest et al., 2009; Egan et al., 2012; Frings et al., 2014; Sun et al., 2014; Wetzel et

al., 2014). These processes, combined with meso- to macro-scale ocean circulation patterns all influence the distributions of $\delta^{30}\text{Si}(\text{OH})_4$ and $\delta^{30}\text{Si-bSiO}_2$. As a result, natural variations in $\delta^{30}\text{Si}$ can be used to trace the biogeochemical processes affecting Si and water mass characteristics on both modern (e.g. Beucher et al., 2008; de Souza et al., 2012; Brzezinski and Jones, 2015; Varela et al., 2016; Sutton et al., 2018a) and geological (e.g. De La Rocha et al., 1998; Beucher et al., 2007; Pichevin et al., 2009) timescales.

Continental shelves account for approximately half of the total marine area in the Arctic (e.g. Carmack and Wassmann, 2006; Wassmann, 2015). These vast shelf-based ecosystems are comprised of a diverse and complex range of marine environments often classified as inflow, outflow and interior shelf domains (Carmack and Wassmann, 2006; Williams and Carmack, 2015). The inflow shelves of the Bering, Chukchi and Barents Seas are especially productive (Figure 5.1a; Sakshaug, 2004; Codispoti et al., 2013; Varela et al., 2013) and diatoms are especially abundant on the shelves influenced by the nutrient-rich Pacific-origin waters (blue arrows in Figure 5.1b; Booth et al., 1997; Brugel et al., 2009; Wyatt et al., 2013; Crawford et al., 2018). Climate-induced changes such as decreasing sea-ice extent, warming temperatures and increasing freshwater runoff are driving rapid shifts in the nutrient and ecosystem dynamics of the Arctic (Post et al., 2009; Stroeve et al., 2011; Grebmeier, 2012; Ardyna et al., 2014; Yamamoto-Kawai et al., 2016), including changes in the contribution of diatoms to the phytoplankton assemblage (e.g. Li et al., 2009; Blais et al., 2017).

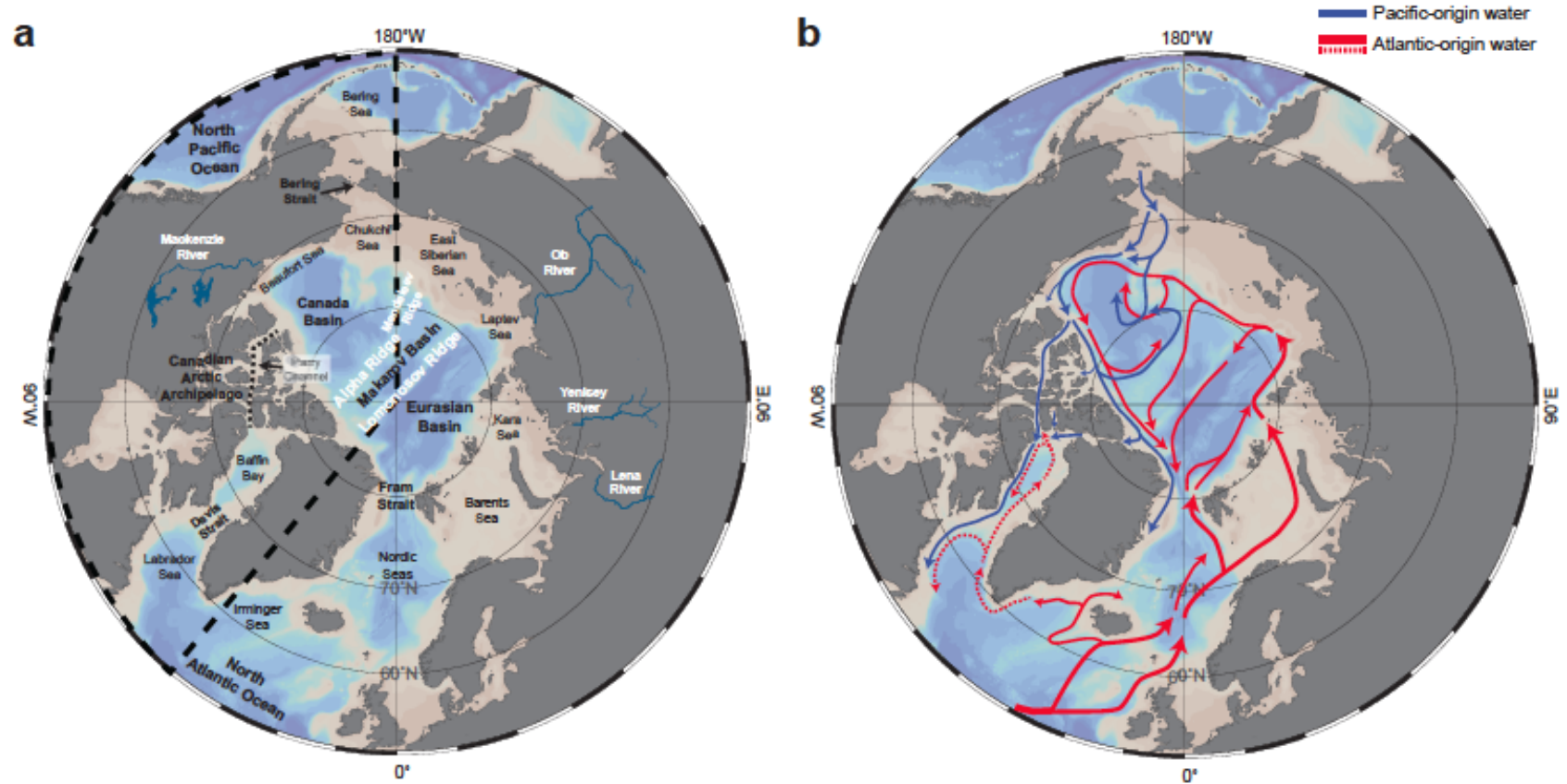


Figure 5.1. (a) Map of the Arctic Ocean indicating the major geographic features of interest in this study. The black dashed line in the CAA represents Parry Channel. The black dashed pie shape along 180°W and 30°W represents the domain of the maps shown in Figure 5.2. (b) Major flow paths of Atlantic-origin (red) and Pacific-origin (blue) waters in the Arctic Ocean. Dashed red lines indicate Atlantic-origin water modified during its transit from the Irminger Sea into the Labrador Sea and Baffin Bay. Flow paths adapted from Beszczynska-Möller et al. (2011; 2012), Cuny and Rhines (2002), Lazier et al. (2002), McLaughlin et al. (1996; 2002), Orvik and Nuler (2002), Pickart et al. (2005), Rudels et al. (1996; 2013; 2015), Shimada et al. (2005), Tang et al. (2004), and Woodgate (2018).

Although these changes are not consistent across the heterogeneous ecosystems of the Arctic, with some regions experiencing an increase in diatom abundance, while others a decrease (Blais et al., 2017), such changes will ostensibly have an effect on the marine Si cycling in the Arctic. This is especially true for Arctic regions within the flow path of Pacific-origin waters, which supply the majority of Si(OH)_4 to the Arctic (Torres-Valdés et al., 2013).

Circulation within the Arctic Ocean is influenced by both Pacific- and Atlantic-origin waters, with Atlantic-origin waters having an inflow >5 times larger than that of the Pacific (Figure 5.1b; Beszczynska-Möller et al., 2012; Woodgate, 2018). However, although comparatively small in volume, the input of relatively low salinity Pacific-origin waters through the Bering Strait serves as an important source of heat, freshwater, and nutrients to the Arctic Ocean (Grebmeier et al., 2006a; Sereze et al., 2006; Torres-Valdés et al., 2013). In addition, the subsequent outflow of these waters into the North Atlantic Ocean also serves as an important connection in the global thermohaline circulation (Wijffels et al., 1992; Goosse et al., 1997; Woodgate et al., 2010). After crossing the highly productive Chukchi shelf and oligotrophic Canada Basin (e.g. Varela et al., 2013), one of the main pathways for Pacific-origin waters is through the complex network of channels, sub-basins and sills of the Canadian Arctic Archipelago (CAA), before outflowing into Baffin Bay and the Labrador Sea (Figure 5.1a). One of the main channels through which these waters flow through the CAA is Parry Channel (Figure 5.1a), extending from McClure Strait on the northern edge of Banks Island, into Viscount Melville Sound and Barrow Strait, and outflowing into Baffin Bay via Lancaster Sound (Figure 5.2a).

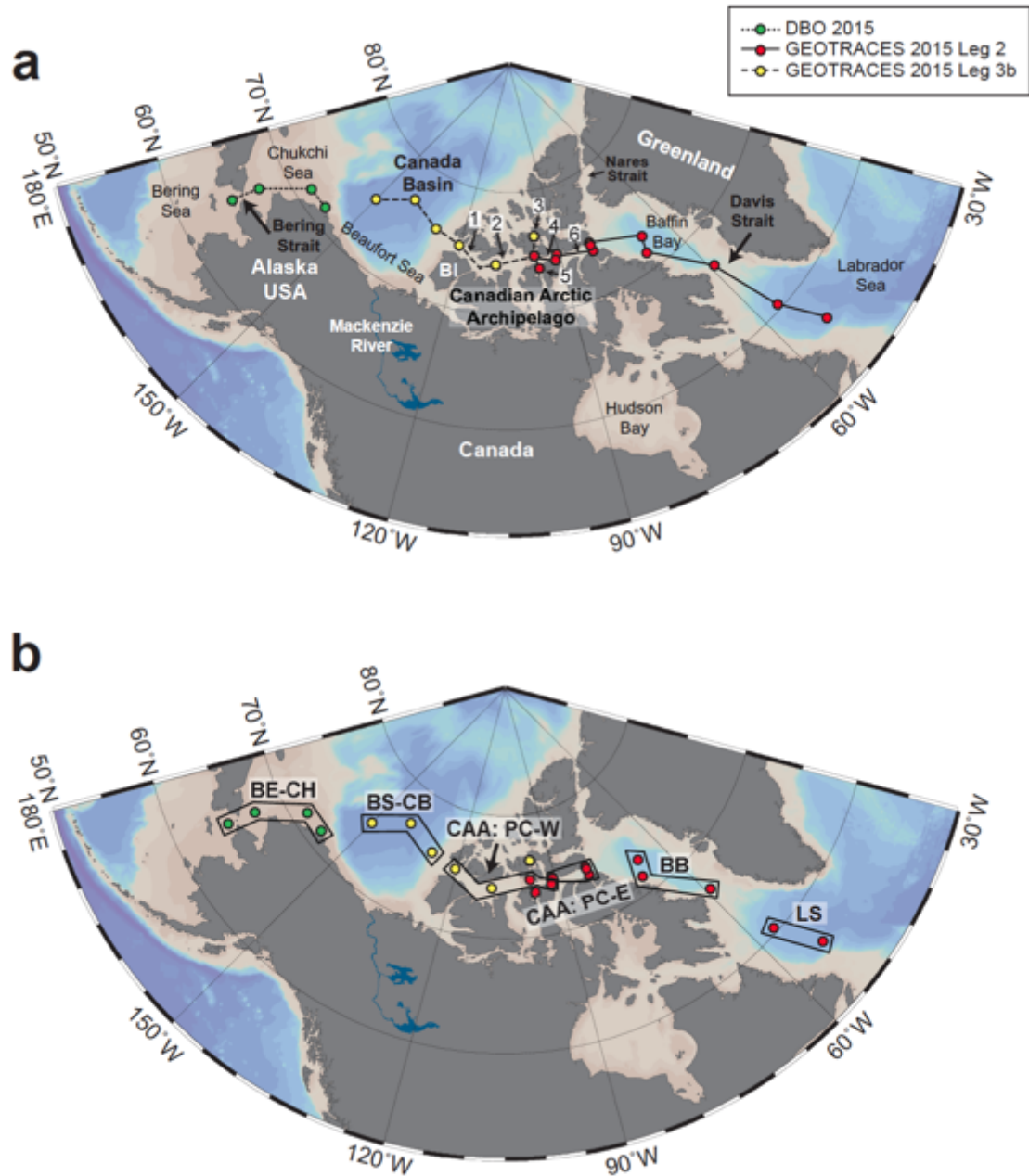


Figure 5.2. (a) Research cruise tracks and location of the eighteen stations occupied during July-August 2015 as part of the DBO (green circles) and Canadian Arctic GEOTRACES 2015 (Leg 2: red circles, Leg 3b: yellow circles) programs. For details see section 2.1 and Table 1. Major geographic locations are indicated on the map, other areas are denoted as BI = Banks Island, (1) McClure Strait, (2) Viscount Melville Sound, (3) Penny Strait, (4) Barrow Strait, (5) Peel Sound, and (6) Lancaster Sound. (b) Sampling stations grouped into 5 broad oceanographic domains (see section 5.3.5); Bering and Chukchi Seas (BE-CH), Beaufort Sea and Canada Basin (BS-CB), Canadian Arctic Archipelago (CAA), Baffin Bay (BB), and Labrador Sea (LS). The CAA domain is further grouped into the western (PC-W) and eastern (PC-E) sides of Parry Channel.

This outflow through Lancaster Sound accounts for ~50% of the volume transport into Baffin Bay from the CAA, making it an important component of the flux of $\text{Si}(\text{OH})_4$ through and out of the Arctic (Beszczynska-Möller et al., 2011).

The Arctic is a net exporter of $\text{Si}(\text{OH})_4$ to the North Atlantic, which in turn feeds the larger scale Si cycling within the global thermohaline circulation (e.g. de Souza et al., 2012; 2014; Brzezinski and Jones, 2015; Hátún et al., 2017), yet our knowledge of the cycling of Si for this critically climate-impacted region is limited compared to the rest of the global ocean (Treguer and De La Rocha, 2013). A small number of studies have investigated processes influencing Si cycling within surface waters (i.e. bSiO_2 production and dissolution; Treguer and De La Rocha, 2013), with their results highlighting the heterogeneity of the Arctic ecosystems (Chapters 1-4, Appendices A and D; Banahan and Goering, 1986; Tremblay et al., 2002; Sampei et al., 2010; Krause et al., 2018). Only one study has investigated $\delta^{30}\text{Si}$ distributions within the Arctic (Varela et al., 2016), with their results indicating that $\delta^{30}\text{Si}(\text{OH})_4$ in the Beaufort Sea and Canada Basin reflected the Si utilization in surface waters and the distribution of water masses. In addition, they found that Pacific-origin waters had much lower $\delta^{30}\text{Si}(\text{OH})_4$ compared to that of the underlying Atlantic-origin waters, indicating that $\delta^{30}\text{Si}(\text{OH})_4$ may have potential as a tracer of these different source waters within the Arctic.

To better understand how Pacific-origin waters influence the distributions of $\delta^{30}\text{Si}(\text{OH})_4$ within the Arctic, the focus of this study was to investigate variations in $\delta^{30}\text{Si}(\text{OH})_4$ along a transect that began in the Bering Sea and followed the path of these Pacific-origin waters as they transit through the Chukchi and Beaufort Seas, Canada Basin, and CAA, ultimately exiting through Baffin Bay and into the Labrador Sea. Here,

we present the first water column $\delta^{30}\text{Si}$ measurements of dissolved silica in the Bering and Chukchi Seas, the CAA and Baffin Bay, and build on previous datasets within the Beaufort Sea and Canada Basin (Varela et al., 2016) and the Labrador Sea (de Souza et al., 2012; Sutton et al., 2018). The majority of this work was conducted as part of the Canadian Arctic GEOTRACES program in 2015, with additional sampling in the Bering and Chukchi Seas conducted as part of the Distributed Biological Observatory in the same year. In addition to the overlying nutrient-rich Pacific-origin waters, this transect also intersects the relatively nutrient-poor Atlantic-origin waters, and a number of deep Arctic water masses with silicic acid concentrations ranging from 10 – 100 μM . In addition, this transect spans a large range in diatom productivity, from the highly productive Bering and Chukchi shelves to the oligotrophic Canada Basin to the moderately productive CAA. The primary focus of the Canadian Arctic GEOTRACES program was to map the distribution of chemical tracers along the flow path of Pacific-origin waters through the Arctic in order to better understand the biological, physical and chemical transformations that occur as these waters move towards the Atlantic Ocean. The collection of water masses with varying silicic acid ($\text{Si}(\text{OH})_4$) concentrations and gradients in productivity encountered along our sampling transect provides an unprecedented opportunity to significantly improve our understanding of the distribution and controls on Si isotope signatures in Arctic waters.

5.3 Methods

5.3.1 Sampling Locations and Seawater Sampling

Seawater samples were collected during three cruises spanning from the northern Bering Sea, through the Arctic and into the Labrador Sea in the east (Figure 5.2).

Vertical profiles to the ocean bottom (or as deep as 3500 m if bottom depths were greater

than this) were taken at 18 stations and to the bottom of the euphotic zone at 4 stations (Table 5.1). Sampling began at station K1 in early July 2015 onboard the CCGS Amundsen, where 12 stations were sampled in the Labrador Sea, Davis Strait, Baffin Bay, and through the Canadian Arctic Archipelago (CAA), ending in Peel Sound (Figure 5.2 and Table 5.1). On the western side of our transect, sampling began in mid-July 2015 onboard the CCGS Sir Wilfrid Laurier, where 4 stations were sampled in the Bering and Chukchi Seas. A further 6 stations were sampled in the Canada Basin and western CAA in September 2015 onboard the CCGS Amundsen. Samples were collected using a SeaBird conductivity-temperature-depth (CTD) sensor and rosette package equipped with either 24 12-L Niskin bottles (CCGS Amundsen) or 24 10-L Niskin bottles (CCGS Sir Wilfrid Laurier).

Table 5.1. Station characteristics and domain classification for the CCGS Amundsen and CCGS Sir Wilfrid Laurier cruises in July – August 2015.

Cruise ^a	Station	Location	Latitude (°N)	Longitude (°E)	Water Depth (m)	Domain ^b
CCGS Amundsen 2015 Leg 2	K1	Labrador Sea	56.12	-53.37	3309	LS
	LS2	Labrador Sea	60.44	-56.53	3377	LS
	BB1	Davis Strait	66.86	-59.07	1039	BB
	BB3	Baffin Bay (shelf)	72.75	-66.99	2371	BB
	BB2	Baffin Bay (basin)	71.41	-68.60	1251	BB
	CAA1	Lancaster Sound (N)	74.52	-80.56	632	CAA: PC-E
	CAA2	Lancaster Sound (mid)	74.33	-80.51	1464	CAA: PC-E
	CAA3	Lancaster Sound (S)	73.82	-80.49	687	CAA: PC-E
	CAA4	Barrow Strait (N)	74.13	-91.49	193	CAA: PC-W
	CAA5	Barrow Strait (S)	74.54	-90.80	254	CAA: PC-E
	CAA6	Barrow Strait (ice edge)	74.76	-97.45	260	CAA: PC-W
	CAA7	Peel Sound	73.67	-96.52	219	CAA
CCGS Amundsen 2015 Leg 3b	CAA8	Viscount Melville Sound	74.14	-108.84	563	CAA: PC-W
	CAA9	Penny Strait	76.32	-95.23	323	CAA
	CB1	McClure Strait	75.11	-120.52	430	CAA: PC-W
	CB2	Beaufort Sea (slope)	75.81	-129.24	1356	BS-CB
	CB3	Canada Basin (deep)	77.00	-140.05	3731	BS-CB
CCGS Sir Wilfrid Laurier 2015-07	CB4	Canada Basin (deep)	75.01	-150.00	3830	BS-CB
	BarC-5	Barrow Canyon	64.99	-169.15	125	BE-CH
	DBO4.4	Hanna Shoals	63.50	-168.95	44	BE-CH
	UTN-4	SE Chukchi Sea	71.37	-163.04	49	BE-CH
	UTBS-1	Chirikov Basin	71.42	-157.50	48	BE-CH

^a Cruises are identified by the ship and the cruise-ID (YEAR-ID or YEAR Leg #)

^b Stations were classified into five broad regional domains according to their T-S characteristics (see section 5.3.5 and Figure 5.2b).

Temperatures from the CTD were converted to potential temperature (i.e. the temperature at a standard reference pressure of 0 db).

Samples for $\delta^{30}\text{Si}(\text{OH})_4$ and $\text{Si}(\text{OH})_4$ concentration were filtered onboard through 0.6 μm polycarbonate filters, and the filtrate stored in acid-washed polypropylene bottles at 4°C in the dark. Suspended particulate matter for bSiO_2 and lSiO_2 concentrations was analyzed from the material collected on the 0.6 μm polycarbonate filters. Filters were dried at 60°C, and stored at room temperature until analysis onshore. Additional samples for nitrate (NO_3^-) and phosphate (PO_4^{3-}) were collected and either stored at 4°C until analysis onboard using a Bran and Luebbe Autoanalyzer III (samples filtered to 0.2 μm at collection; CCGS Amundsen cruises), or stored at -20°C until analysis onshore using an Astoria Autoanalyzer according to the method of Barwell-Clark and Whitney (1996) (samples filtered to 0.7 μm at collection; CCGS Sir Wilfrid Laurier cruise).

5.3.2 Analytical methods

Silicic acid concentrations in filtered samples stored at 4°C in the dark were measured onshore in the lab using an Astoria Autoanalyzer according to the method written by Barwell-Clark and Whitney (1996). For the CCGS Amundsen cruises, $[\text{Si}(\text{OH})_4]$ were within $\pm 3\%$ of those measured at sea from fresh samples. Biogenic and lithogenic SiO_2 concentrations were determined using a sequential sodium hydroxide-hydrofluoric acid digestion as in Chapter 2. The median standard deviation (SD) was 0.07 $\mu\text{mol L}^{-1}$ for $[\text{bSiO}_2]$ and 0.01 $\mu\text{mol L}^{-1}$ for $[\text{lSiO}_2]$ ($n = 19$).

5.3.2.1 $\delta^{30}\text{Si}$ Sample Preconcentration and Analysis

Samples for $\delta^{30}\text{Si}(\text{OH})_4$ were processed as described in de Souza et al. (2012). We typically processed 64 nmol of Si for each mass-spectrometric analysis of $\delta^{30}\text{Si}(\text{OH})_4$,

with Si first being preconcentrated from seawater by a two-step magnesium induced co-precipitation (modified MAGIC method of Karl and Tien (1992)) and then chromatographically separated from the seawater matrix using a cationic resin. Briefly, samples were first acidified in the laboratory with 0.1% (v/v) of 6 mol L⁻¹ HCl (environmental grade; Anachemia) at least 12 hr before preconcentration of Si. Samples were pH-neutralized using high-purity 1 mol L⁻¹ NaOH (99.996% purity, Alfa Aesar) and then magnesium hydroxide (Mg(OH)₂) was precipitated from seawater in two steps. In each step, ~10% of the dissolved seawater Mg was precipitated as Mg(OH)₂ by adding ~1% (v/v) of 1 mol L⁻¹ NaOH to the seawater sample. The solution was shaken for 1 hr and the resulting precipitate and scavenged Si were left to settle for 24 hr before being centrifuged. Following the second centrifugation, the supernatant was removed and analyzed for [Si(OH)₄] as described above to determine the yield of the coprecipitation. Yields were always >97.5% and typically >99%. No corrections were made for variations in the yield. The precipitate was dissolved using a very small volume of environmental grade 6 mol L⁻¹ HCl and diluted to 64 μmol L⁻¹ with ultrapure water (>18.2 MΩcm). Following the method of Georg et al. (2006), uncharged Si(OH)₄ was then separated from the cationic matrix in the dissolved precipitate solution by passing 1 mL of this preconcentrated Si solution through a cation-exchange column with a retention capacity of 1.7 meq (1 mL AG50W-X8; BioRad Laboratories). A detailed schematic of the chromatographic procedure is shown in Table 5.2. The purified Si solution was analyzed for Si isotopic composition at ETH Zürich on a high-resolution multicollector inductively coupled plasma mass spectrometer (HR-MC-ICPMS; *NuPlasma* 1700; Nu Instruments, UK) in static mode by standard-sample bracketing (SSB; 36 x 5 s integrations each)

following the methods of de Souza et al. (2012) and Georg et al. (2006) (see Table 5.3 for additional information on operating conditions for the mass spectrometer).

Table 5.2. Separation scheme for chromatographic purification of Si from preconcentrated seawater samples. Chromatography was carried out in polypropylene BioSpin columns with a polyethylene bed support and filled with 1 mL of pre-cleaned AG50W-X8 chromatographic resin.

Step	Volume	Concentration
Clean	~3 mL	3M HCl
	~3 mL	6M HCl
	0.3 mL	Conc. HNO ₃
	~3 mL	6M HCl
	~3 mL	3M HCl
	~3 mL	6M HCl
	~3 mL	3M HCl
	~3 mL	Deionized water
Rinse	<i>(...continue rinsing until eluent has a pH = 7)</i>	
Load	1 mL	Sample
Elute & collect	1 mL	Deionized water
	1 mL	Deionized water

Table 5.3. Operating conditions for the Nu Plasma 1700 HR-MC-ICPMS at ETH Zürich

Parameter	Setting
Resolution	High
RF power	1300 W
Plasma mode	Dry plasma
Desolvator	DSN-100 (Nu Instrumental)
Nebulizer	PFA nebulizer; ~75 µL min ⁻¹ uptake rate
Cones	Standard Ni cones
Torch	Semi-demountable quartz torch, alumina injector
Running concentration	600 ppb Si
Mg doping	no
Standard-sample bracketing	Yes, sample repeated 5 times: 1 block = 36 cycles of 5s each
Measurement intensity (²⁸ Si)	6 – 7 V
Blanks (²⁸ Si)	10 to 30 mV

Isotope values are expressed relative to the NBS28 quartz sand reference material using the delta notation (‰):

$$\delta^{30}\text{Si} = \left(\frac{\left(\frac{{}^{30}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{{}^{30}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{NBS 28}}} - 1 \right) \times 1000 \text{ [‰]} \quad (1)$$

Each isotope value presented in this study represents the mean (±2 standard errors of the mean, 2 SEM) of at least 5 SSB measurements of the sample. The relationship

between measured $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ ratios was used to verify mass-dependency (i.e. complete resolution of all interferences such as $^{12}\text{C}^{16}\text{O}^+$, $^{14}\text{N}^{14}\text{N}^+$, $^{14}\text{N}^{14}\text{N}^1\text{H}^+$, and $^{14}\text{N}^{16}\text{O}^+$), by ensuring that measurements fell on the mass dependant fractionation line of $\delta^{29}\text{Si} \approx 0.51 * \delta^{30}\text{Si}$ (Figure 5.3).

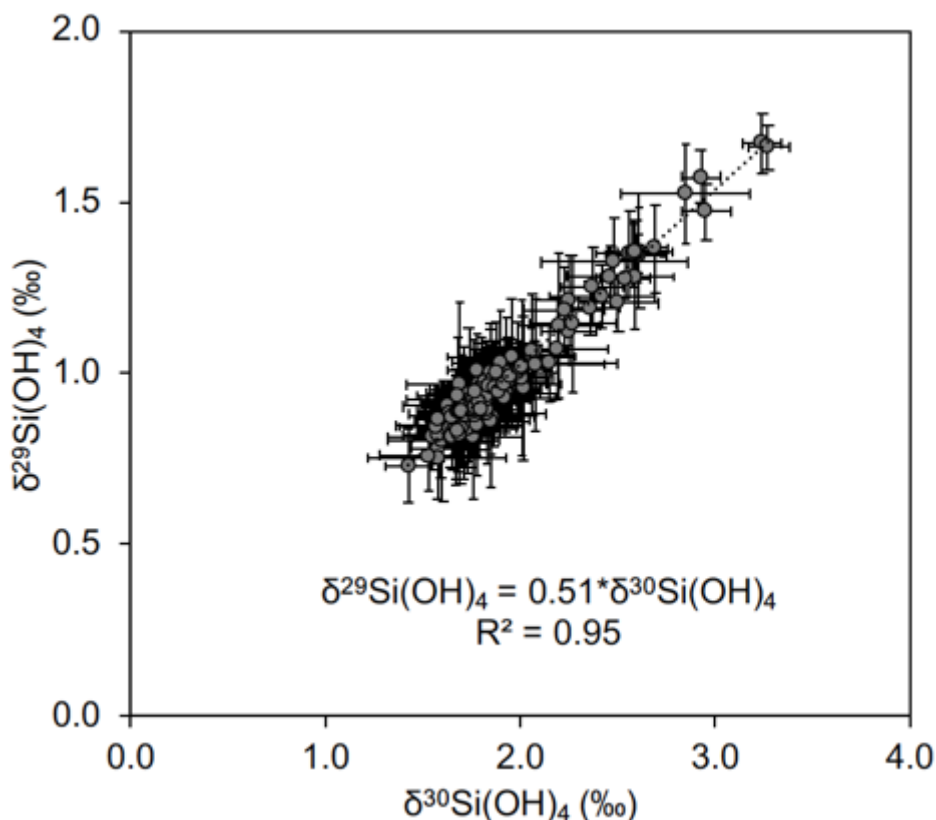


Figure 5.3. Mass-dependent fractionation (MDF) line of $\delta^{30}\text{Si}(\text{OH})_4$ vs. $\delta^{29}\text{Si}(\text{OH})_4$ (‰ vs. NBS28) for samples ($n = 88$) collected from 22 depth profiles along our sampling transect from the Bering to Labrador Seas. The dashed black line denotes a linear regression through all data points and represents the MDF line with the equation $\delta^{29}\text{Si}(\text{OH})_4 = 0.51 * \delta^{30}\text{Si}(\text{OH})_4$ ($R^2 = 0.95$).

The reproducibility of the full chemical and analytical procedure (chemical preparation plus isotopic measurements in separate analytical sessions) was estimated on a subset of samples ($n = 11$) from duplicate analyses starting from subsamples of the same water sample collected from the Niskin bottle. Mean reproducibility was $\pm 0.19\text{‰}$ (2SD). The secondary standard Diatomite was run every 4-6 field samples, yielding a mean ($\pm 2\text{SD}$) $\delta^{30}\text{Si}$ value of $+1.34 \pm 0.20\text{‰}$ ($n = 39$) during this study, well within the range of

intercalibration values reported by Reynolds et al. (2007). Measurement of the US GEOTRACES intercalibration reference seawater standard from the ALOHA station (1000 m) gave a mean (± 2 SD) $\delta^{30}\text{Si}(\text{OH})_4$ of $+1.29 \pm 0.16\text{‰}$, which also compared well with intercalibration values ($+1.24 \pm 0.20\text{‰}$; Grasse et al., 2017). Note that only the deep (1000 m) ALOHA intercalibration standard was analyzed. Further $\delta^{30}\text{Si}$ intercalibration between the Canada/GEOVIDE GEOTRACES programs was conducted on duplicate samples collected at 3 depths and 2 stations from the July 2015 CCGS Amundsen cruise in accordance with GEOTRACES intercalibration protocols. These intercalibration samples were analyzed by two different laboratories (ETH Zurich and Ifremer Plouzané) using different purification methods and MC-ICPMS instruments (see above and Sutton et al., 2018a). Intercalibration samples had similar $\delta^{30}\text{Si}(\text{OH})_4$ values, with a mean ‘between-laboratory’ $\delta^{30}\text{Si}$ difference of $<0.01\text{‰}$ (see Table 3 in Sutton et al., 2018a).

5.3.3 Water mass tracer, N^*

We used the N^* parameter as a tracer of modified Pacific Water as it transits from the Bering and Chukchi Seas to Baffin Bay. Waters of Pacific-origin in the Arctic are known to have a $0.5 - 1 \mu\text{mol L}^{-1}$ excess of PO_4^{3-} relative to NO_3^- , primarily due to denitrification in the Bering Sea decreasing the $[\text{NO}_3^-]$ of the water column (Jones et al., 2003; Lehmann et al., 2005). Following Gruber and Sarmiento (1997), we calculated $\text{N}^* = [\text{NO}_3^-] - 16 \times [\text{PO}_4^{3-}] + 2.9 \mu\text{mol kg}^{-1}$. The underlying assumption in this calculation is that organic matter remineralization produces NO_3^- and PO_4^{3-} in a 16:1 stoichiometric ratio, with deviations in N^* from zero largely caused by the processes of denitrification (N^* more negative) and N_2 fixation (N^* more positive). Sea surface values of N^* in the Bering and Chukchi Seas range from -3 to $-15 \mu\text{mol L}^{-1}$ (Lehmann et al., 2005; Codispoti

et al., 2005). Previous studies in the Canada Basin, Beaufort Sea and Amundsen Gulf have shown very negative N^* values (-5 to -14 $\mu\text{mol L}^{-1}$) in the upper halocline that are associated with waters of Pacific-origin that entered the Arctic through the Bering Strait (e.g. Wheeler et al., 1997; Tremblay et al., 2002; Simpson et al., 2008).

5.3.4 Water mass identification

Temperature versus salinity plots for 1-m averaged T-S data recorded by the CTD were used to identify the distributions of water masses within each of our study domains, and N^* values were used to confirm these identifications. The predominant water masses were identified using characteristic T-S parameters reported by previous studies within our study regions (e.g. Macdonald et al., 1989; Lazier et al., 1993; McLaughlin et al., 1996; Tang et al., 2004; Yashayaev and Clarke, 2008; Varela et al., 2016; Yashayaev et al., 2016; Danielson et al., 2017; Hamme et al., 2017; García-Ibáñez et al., 2018).

5.3.5 Domain Classification

Stations were classified into regional groupings (Table 5.1 and Figure 5.2b) to coincide with distinct water masses based on correlations between temperature (T) and salinity (S) and following similar criteria to those presented in Carmack and McLaughlin (2011). For our study, the Bering and Chukchi (BE-CH) domain begins in the Chirikov Basin north of St. Lawrence Island in the Bering Sea, crosses through the Bering Strait and across the Chukchi Sea to the shelf break near Barrow Canyon. The Beaufort Sea and Canada Basin (BS-CB) domain includes the deep stations within the Canada Basin, spanning to the Beaufort Sea slope near Banks Island. The Canadian Arctic Archipelago (CAA) is the most oceanographically complex domain, composed of a number of islands, narrow and shallow straits, and sub-basins and sills of varying bathymetry. Our transect passes through one of the most direct west-east routes through the CAA: Parry Channel. Parry

Channel spans from McClure Strait in the western CAA, through Viscount Melville Sound and Barrow Strait in the middle, culminating in Lancaster Strait in the eastern CAA (Figures 5.1-5.2). Our sampling in the CAA also included stations in Penny Strait and Peel Sound, found just north and south of Barrow Strait near Cornwallis Island, respectively. Baffin Bay (BB) comprises our fourth domain, which spans from the eastern edge of Lancaster Sound to Davis Strait. Our final domain in the basin of the western Labrador Sea (LS), spanning from just south of Davis Strait to $\sim 55^{\circ}\text{N}$.

5.4 Results

5.4.1 Broad-scale vertical distributions of T, S and N^*

Vertical distributions of temperature and salinity along the sampling transect varied by domain, although some broad scale features were observed (Figure 5.4b-c). A low salinity surface layer with variable temperature (-1.3 to $+6^{\circ}\text{C}$) was observed all along our sampling transect, with maximum depths ranging from 15 to 100 m. Surface salinities were lowest in the BS-CB and CAA domains, and highest in the LS. A subsurface tongue of cold, relatively low salinity water that corresponded to the $\sigma_t = 26.6 \text{ kg m}^{-3}$ isopycnal extended from the bottom waters of the Chukchi Shelf all the way to Davis Strait. The depth range of these waters shoaled from around 120-300 m in the Canada Basin to 25-100 m in Baffin Bay. In the BS-CB and BB domains, warm and relatively saline waters between 300 to 800 m were found below the layer of cool, fresh water. These warmer waters were also observed in some of the deeper (>200 m) sub-basins of the CAA, but were not observed in the shallow waters of Barrow Strait (CAA4-6). In the deep basins of BS-CB and BB, temperatures decreased beneath the warm, saline layer. The LS domain was the warmest and most saline of all of our sampling regions, although deep waters of the Canada Basin had a similar salinity to those of the Labrador Sea.

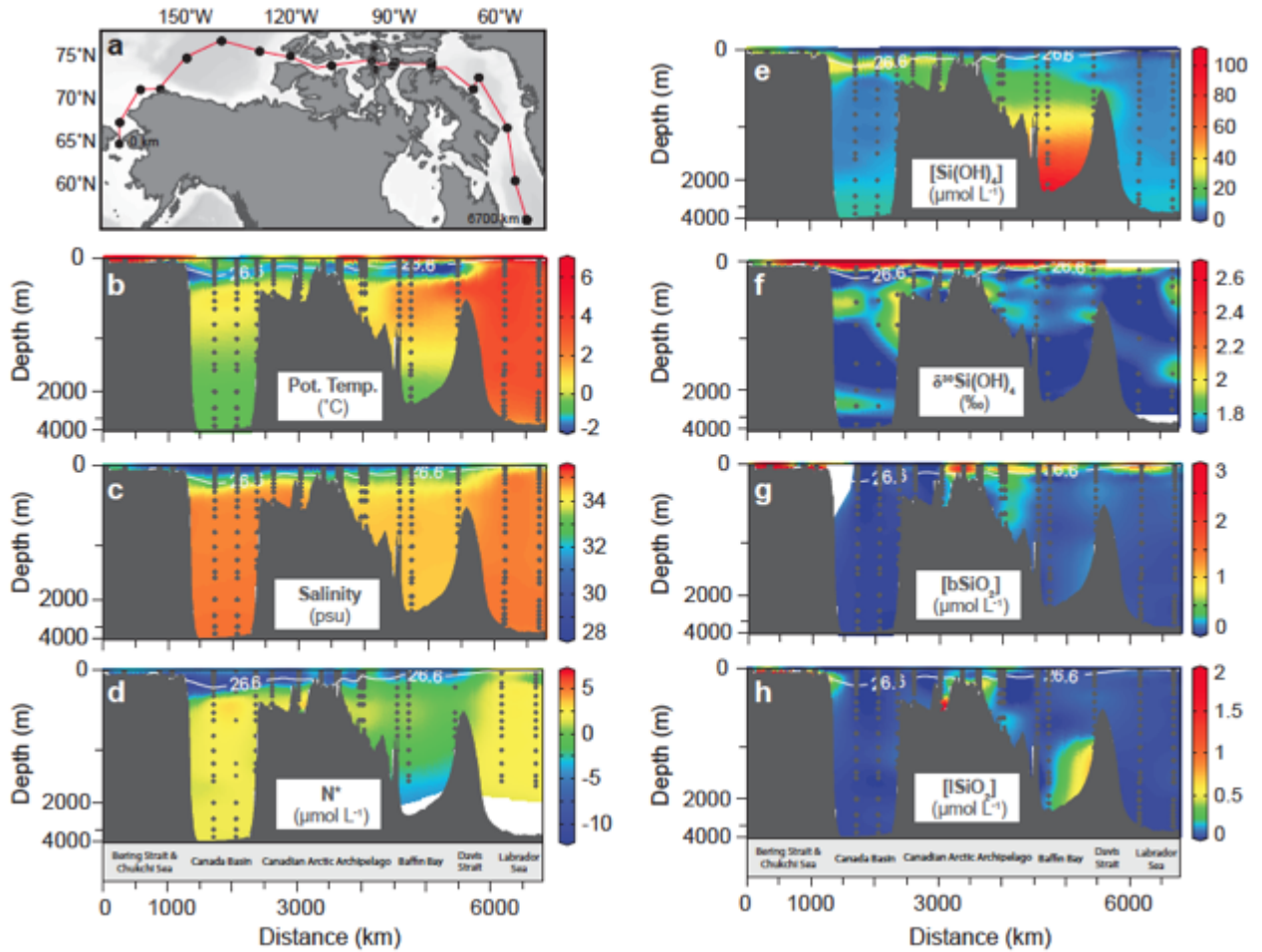


Figure 5.4. Vertical sections of measured parameters along the combined DBO and GEOTRACES transect. (a) Transect line in red, (b) potential temperature, (c) salinity, (d) N^* concentration, (e) Si(OH)_4 concentration, (f) $\delta^{30}\text{Si(OH)}_4$, (g) bSiO_2 concentration, and (h) lSiO_2 concentration. For b-h, the depth of the 26.6 kg m^{-3} isopycnal is superimposed in white, and black dots indicate sampling depths. The major oceanographic domains are denoted along the bottoms of (d) and (h).

The very low N^* signature of Pacific-origin waters is evident throughout the surface layer of our sampling transect from the Bering Strait to Davis Strait (Figure 5.4d). N^* values in this layer range from -3 to $-10 \text{ } \mu\text{mol L}^{-1}$, indicative of waters of Pacific-origin. The depth of this low N^* layer shoals from 250 m in the Canada Basin to 80 m in Davis Strait and corresponds well with the depth of the 26.6 kg m^{-3} isopycnal and core of the cold-water tongue that extends from the Chukchi Shelf. In the Labrador Sea, N^* was relatively uniform with values of $\sim 2 \text{ } \mu\text{mol L}^{-1}$. Given the similarity to the N^* in the Labrador Sea, the subsurface maximum in N^* of $\sim 2 \text{ } \mu\text{mol L}^{-1}$ observed in the warm,

saline layer surface from the BS-CB to BB domains indicates waters of Atlantic-origin, although in BB this signal could also be driven by local denitrification.

5.4.2 Dissolved and Particulate Silica Concentrations

Silicic acid concentrations ranged from undetectable up to $102 \mu\text{mol L}^{-1}$ along our sampling transect, although concentrations mostly fell between $10\text{--}20 \mu\text{mol L}^{-1}$, with a median value of $15 \mu\text{mol L}^{-1}$ (Figures 5.4e and 5.5). Similar to that observed for temperature, a subsurface tongue of high $[\text{Si}(\text{OH})_4]$ water associated with the 26.6 kg m^{-3} isopycnal was observed to extend from the bottom waters of the Chukchi Sea, through the BS-CB and CAA, but is lost within the BB domain. The $[\text{Si}(\text{OH})_4]$ of this mid-depth maximum decreased from $\sim 35 \mu\text{mol L}^{-1}$ in the bottom waters of the BE-CH, to $\sim 15 \mu\text{mol L}^{-1}$ in the eastern CAA. Below this subsurface maximum, $[\text{Si}(\text{OH})_4]$ decreased to a minimum of $\sim 8 \mu\text{mol L}^{-1}$ in the BS-CB domain, which was associated with the layer of warm, saline waters. In the BS-CB, BB and LS domains, $[\text{Si}(\text{OH})_4]$ in waters $>600 \text{ m}$ increased with depth to a maximum in the bottom waters; however, while bottom water $[\text{Si}(\text{OH})_4]$ in the Canada Basin and Labrador Sea were similar around $12 \mu\text{mol L}^{-1}$, $[\text{Si}(\text{OH})_4]$ in Baffin Bay was nearly an order of magnitude higher, reaching a maximum value of $\sim 100 \mu\text{mol L}^{-1}$.

Biogenic SiO_2 concentrations were highly variable along our sampling transect, although subsurface maxima between $10\text{--}80 \text{ m}$ were observed in all domains (Figure 5.4g). Concentrations of $[\text{bSiO}_2]$ at the subsurface maxima were lowest in the BS-CB at $<0.1 \mu\text{mol L}^{-1}$. The highest subsurface maxima in $[\text{bSiO}_2]$ were observed in the BE-CH, reaching concentrations of up to $9 \mu\text{mol L}^{-1}$. Concentrations of bSiO_2 were also relatively high near the ice-edge in Barrow Strait, decreasing eastwards to a minimum of $0.2 \mu\text{mol L}^{-1}$ in Davis Strait.

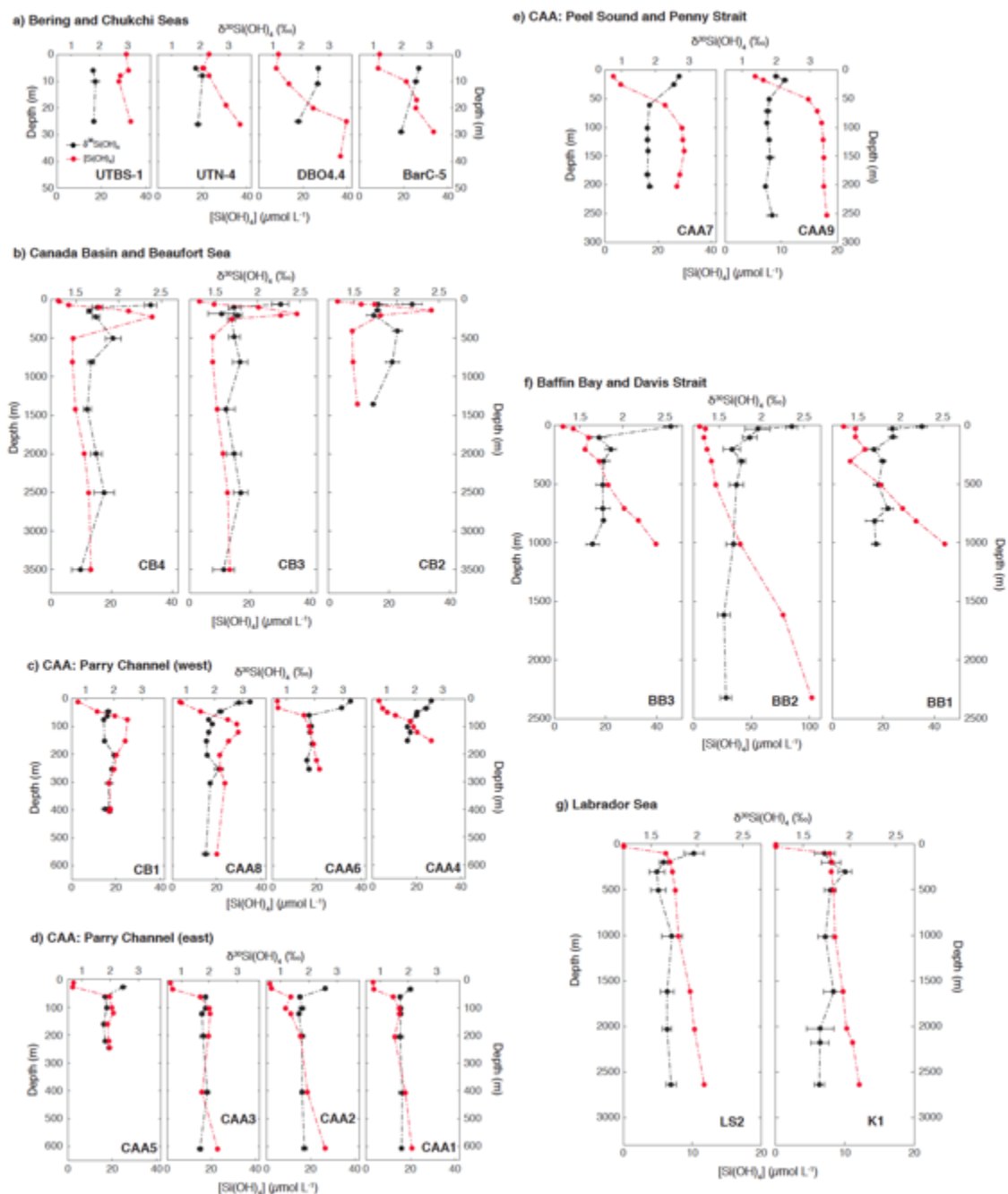


Figure 5.5. Silicic acid concentration, $[\text{Si}(\text{OH})_4]$ (red dots), and silicic acid isotopic composition, $\delta^{30}\text{Si}(\text{OH})_4$ (black dots), for all twenty-two stations sampled as part of the DBO and GEOTRACES cruises. Symbols represent the mean ± 2 SEM of at least 5 SSB measurements of the same field sample. Data are separated into major oceanographic domains as in Figure 5.6. (a) Bering and Chukchi Seas, (b) Canada Basin and Beaufort Sea, (c) western side and (d) eastern side of Parry Channel in the CAA, (e) Peel Sound and Penny Strait in the CAA, (f) Baffin Bay and Davis Strait, and (g) Labrador Sea.

Deep water $[\text{bSiO}_2]$ were generally $<0.08 \mu\text{mol L}^{-1}$ in waters $>500 \text{ m}$ deep. In the CAA, $[\text{bSiO}_2]$ below 100 m in were also $<0.08 \mu\text{mol L}^{-1}$, but only on the western side of Parry Channel. From Barrow Strait to Lancaster Sound, $[\text{bSiO}_2]$ below 100 m were much higher, averaging $0.4 \mu\text{mol L}^{-1}$.

Lithogenic SiO_2 concentrations were also variable along our sampling transect, with higher values usually being observed near the bottom of the water column within each domain (Figure 5.4h). The highest $[\text{lSiO}_2]$ were observed throughout the water column in the BE-CH domain and in the near bottom waters of the CAA domain ($0.2 - 6 \mu\text{mol L}^{-1}$) and lowest in the BS-CB and LS domains ($<0.1 \mu\text{mol L}^{-1}$). Bottom waters in the BB domain for the deep basin and near Davis Strait also had relatively high $[\text{lSiO}_2]$ ($\sim 0.4 \mu\text{mol L}^{-1}$). Higher $[\text{lSiO}_2]$ concentrations of $0.1\text{-}0.2 \mu\text{mol L}^{-1}$ were also observed in the top 100 m of the eastern sector of the CAA, from Barrow Strait to Lancaster Sound.

5.4.3 Distribution of Silicon Isotopes

Depth profiles of $\delta^{30}\text{Si}(\text{OH})_4$ exhibited the commonly observed inverse correlation between $\delta^{30}\text{Si}(\text{OH})_4$ and $[\text{Si}(\text{OH})_4]$, with higher $\delta^{30}\text{Si}(\text{OH})_4$ when $[\text{Si}(\text{OH})_4]$ is low (Figures 5.4e-f and 5.5). We observed an increase in $\delta^{30}\text{Si}(\text{OH})_4$ values towards the surface, with values ranging from $+1.78$ to $+3.27\text{‰}$ in the upper 60 m all along our sampling transect (note the lack of data for waters $<100 \text{ m}$ in the LS domain, Figure 5.5g). A subsurface minimum in $\delta^{30}\text{Si}(\text{OH})_4$ associated with the subsurface maximum in $[\text{Si}(\text{OH})_4]$ and the 26.6 kg m^{-3} isopycnal was observed most strongly in the BE-CH, BS-CB and into the CAA, but becomes less pronounced towards the eastern side of the CAA and into BB (Figures 5.4f and 5.5a-f). In the BS-CB and western side of the CAA, $\delta^{30}\text{Si}(\text{OH})_4$ values increased to a subsurface maximum around 250 to 500 m , which was

associated with a local minimum in $[\text{Si}(\text{OH})_4]$ and maximum in temperature. A similar feature in the same depth range was also observed on the eastern side of the CAA and in BB, although the corresponding minimum in $[\text{Si}(\text{OH})_4]$ was much less distinct (Figure 5.5d,f). In the northern part of the LS domain (station LS2), $\delta^{30}\text{Si}(\text{OH})_4$ decreased to a subsurface minimum around 300 m, while a subsurface maximum was observed at the same depth at the southern station (K1). Deep subsurface maxima between 1000 to 1500 m were observed at both stations. Isotope values in waters below this subsurface maximum showed little vertical variation. Isotope values below ~ 1000 m in the two isolated deep basins along our study transect (Canada Basin and Baffin Bay) exhibited different vertical trends (Figures 5.4f and 5.5b,f). In the Canada Basin, $\delta^{30}\text{Si}(\text{OH})_4$ increased by $\sim 0.2\text{‰}$ from 1500 to 2500 m, but then decreased by the same amount from 2500 to 3500 m. In Baffin Bay, values of $\delta^{30}\text{Si}(\text{OH})_4$ from 1000 to 2300 m decreased by $\sim 0.2\text{‰}$. Note that, while systematic, the differences of $\sim 0.2\text{‰}$ observed in bottom water $\delta^{30}\text{Si}(\text{OH})_4$ are very similar to the uncertainty of the $\delta^{30}\text{Si}(\text{OH})_4$ measurements.

5.4.4 Water mass distributions

Using T-S plots in conjunction with N^* values, we identified fourteen distinct water masses: Bering Chukchi Summer Water (BCSW), Bering Chukchi Winter Water (BCWW), NE Atlantic-origin water entering the Arctic through Fram Strait and the Barents Sea (ATW), surface waters of the Summer Mixed Layer (SML), the Polar Mixed Layer (PML), Pacific-origin Upper Halocline Water (UHL), Canada Basin Deep Water (CBDW), West Greenland Irminger Water (WGIW), Baffin Bay Arctic Water (BBAW), Baffin Bay Deep Water (BBDW), Modified Irminger Water (MIW), Labrador Sea Water

(LSW), Icelandic Slope Water (ISW), and Northeast Atlantic Deep Water (NEADW) (Table 5.4; Figure 5.6).

Two main water masses were identified in the BE-CH domain: BCSW and BCWW (Table 5.4; Figure 5.6a). Waters in the southeastern Chukchi Sea and Bering Strait were composed entirely of BCSW, while in the northeastern Chukchi Sea, BCSW was observed above 20 m, and BCWW below. The core of the BCWW (below ~20 m) has the characteristic salinity of 33.1 and temperature of -1.4°C of the Upper Halocline Layer (UHL) found in BS-CB and CAA domains. Values for N^* were lowest in BCWW, but less than -4 $\mu\text{mol L}^{-1}$ for all waters in the BE-CH domain.

In the BS-CB domain, waters of Pacific-origin (low N^* , Figure 5.4d) occupy the upper ~250 m of the water column due to their relatively low S compared to that of the underlying Atlantic-origin waters (Table 5.4; Figure 5.6b). The surface layer (0 – 100 m) was characterized by variable T-S properties and composed of SML and PML. We consider the PML to contain the remnants of the cold winter mixed layer, and the relatively warm BCSW, which forms a subsurface temperature maximum near a salinity of ~31 (McLaughlin et al., 2004; Steele et al., 2004; Jackson et al., 2010; Lansard et al., 2012). Below 100 m, T and S converged to values characteristic BCWW, which we identify as UHL (Table 5.4). Below the UHL lies the relatively warm and saline layer of ATW, composed of Atlantic-origin waters from Fram Strait or the Barents Sea. The final and deepest water mass found in the BS-CB is relatively old waters of CBDW, found below ~1500 m.

Table 5.4. Water mass T, S and N* signatures, and defining characteristics within each domain along our study transect. Abbreviations include BCSW = Bering-Chukchi Summer Water, BCWW = Bering-Chukchi Winter Water, SML = Summer Mixed Layer, PML = Polar Mixed Layer, UHL = Upper Halocline Layer, ATW = Atlantic Water from Fram Strait and the Barents Sea, CBDW = Canada Basin Deep Water, WGIW = West Greenland Irminger Water, BBAW = Baffin Bay Arctic Water, BBDW = Baffin Bay Deep Water, MIW = Modified Irminger Water, LSW = Labrador Sea Water, ISW = Icelandic Slope Water, NEADW = Northeast Atlantic Deep Water.

Water Mass	Temp. (°C)	Salinity (psu)	Depth Range (m)	N* ($\mu\text{mol L}^{-1}$)	Characteristics
<i>Bering and Chukchi Seas (BE-CH)</i>					
BCSW ^a	>0	30 to 33.5	0 – 50	-4	Pacific-origin waters either warmed from previous winter or advected from the Bering Sea continental slope and/or Gulf of Anadyr.
BCWW ^b	<0	30 to 33.5	>20	-8	Pacific-origin waters cooled during winter by low air temperatures, sea-ice formation, and brine rejection
References: Danielson et al. (2017)					
<i>Beaufort Sea and Canada Basin (BS-CB)</i>					
SML	<0	<29	0 – 20	-4	Low salinity surface water modified by addition of sea-ice melt, river runoff and precipitation. Extremely low nutrient content. Low N* indicates Pacific-origin from BE-CH
PML	-1 to 0	29 to 32	30 – 80	-4	Found immediately below SML. Contains remnants of the winter mixed layer, and modified BCSW. Moderate nutrient content. Low N* indicates of Pacific-origin from BE-CH
UHL	-1.4	33.1	120 – 250	-8	Modified BCWW. High-nutrient content. Lowest N* values indicative of Pacific-origin from BE-CH
ATW	+0.8	34.8	300 – 600	2.5	Warm, saline waters of NE Atlantic-origin. Waters entered Arctic through Fram Strait and Barents Sea, mixing together before transiting along the Siberian and North American shelves into the Canada Basin.
CBDW	-0.4	34.8	>1500	-	Cold and saline deep waters of the Canada Basin with restricted circulation due to shallow sill depths. Residence time of 500-1000 years ^d
References: McLaughlin et al. (1996), Steele et al. (2004), Rudels et al., (2013), Varela et al. (2016)					
<i>Canadian Arctic Archipelago (CAA)</i>					
Parry Channel (west), Penny Strait and Peel Sound					
SML	-0.5 to +2	<29	0 – 15	-4	See description above.
PML	-1.4 to +1	29 to 32	20 – 50	-4	See description above.
UHL	-1.4	33.1	50 – 200	-8 to -4	See description above.
ATW	+0.4	34.8	>250	2.5	See description above.
Parry Channel (east)					
PML	-1.4 to +4	30 to 33	0 - 60	-4	See descriptions above. Water masses become difficult to distinguish due to intense mixing in Barrow Strait
UHL	-1.4	33.1	80 – 150		

Water Mass	Temp. (°C)	Salinity (psu)	Depth Range (m)	N* ($\mu\text{mol L}^{-1}$)	Characteristics
WGIW	+1.2	34.5	>250	2.5	Warmer, but slightly less saline waters of NE Atlantic-origin composed of MIW from the Labrador Sea via Davis Strait.
References: Muench (1970), Jones et al. (2003), McLaughlin et al. (2005), Yashayaev (2007), Curry et al. (2014)					
<i>Baffin Bay (BB)</i>					
BBAW	-1.4 to +5	30 to 33	0 – 50	-8 to -4	Mixture of PML and UHL from Lancaster Sound, and surface waters from eastern Davis Strait and Labrador Sea cooled during transport around the Bay. Low N* indicative of Pacific-origin from BE-CH.
BBAW (core)	-1.6	33 to 33.5	50 – 150	-6 to -3	Mixture of UHL from Lancaster Sound and waters from eastern Davis Strait and Labrador Sea cooled during transport around the Bay. Low N* indicative of Pacific-origin from BE-CH.
WGIW	+2 to +4	34.5	300 – 600	2.5	See description above
BBDW	<0	34.5	>1200	< 0	Cold and saline deep waters of Baffin Bay with restricted circulation due to shallow sill depths of the CAA and Davis Strait ^f . Residence time of 160-750 years ^g .
References: Muench (1970), Tang et al. (2004), Curry et al. (2014)					
<i>Labrador Sea (LS)</i>					
SML	+2 to +6	<34.5	0 – 60	> 0	Low salinity surface water. On the western side of the Labrador Sea, SML will include BBAW modified by river runoff and sea-ice melt as waters transit south.
MIW^h	+4	34.85	200 – 400		Modified Irminger Sea-origin waters transported around the Labrador Sea by the West Greenland and Labrador Sea boundary currents.
LSWⁱ	+3.4 to +3.6	34.85	500 – 1600		Waters recently ventilated/formed during intense winter mixing events. For our study, this water mass was formed during the winters of 2014 and early 2015
ISWⁱ	+3	34.92	1700 – 2300		Waters formed through mixing of Atlantic Waters and the fresher and colder waters from the Icelandic shelf and slope.
NEADW	+2.5	34.92	2500 – 3000		NE Atlantic-origin waters that cycle around the Irminger and Labrador Seas before transiting south.
References: Lazier et al. (1993), Yashayaev (2007), Yashayaev and Clarke (2008), Hamme et al. (2017), García-Ibáñez et al. (2018)					

^a Waters also referred to as Anadyr Water (AW) and Bering Sea Water (BSW)

^b Waters also referred to as Bering Sea Winter Water (BSWW) and Chukchi Sea Winter Water (CSWW)

^c Sill depths of Alpha Ridge, Lomonosov Ridge, and Mendeleev Ridge: 400 – 1500 m

^d Östlund et al. (1987); Macdonald and Carmack (1991)

^e Waters also referred to as West Greenland Intermediate Water or West Greenland Irminger Water (WGIW)

^f Sill depths of Davis Strait and CAA: <700 m

^g Top et al., (1980); Bourke and Pacquette (1991)

^h observed at northernmost LS station only (LS2)

ⁱ LSW and ISW sometimes referred to as LSW_{upper} and LSW_{lower} in the literature (e.g. Sutton et al., 2018a), with LSW_{upper} being more recently ventilated (2014-2015) than LSW_{lower} (1987-1994); however, at the time of our sampling, the LSW_{lower} water mass was completely replaced by ISW

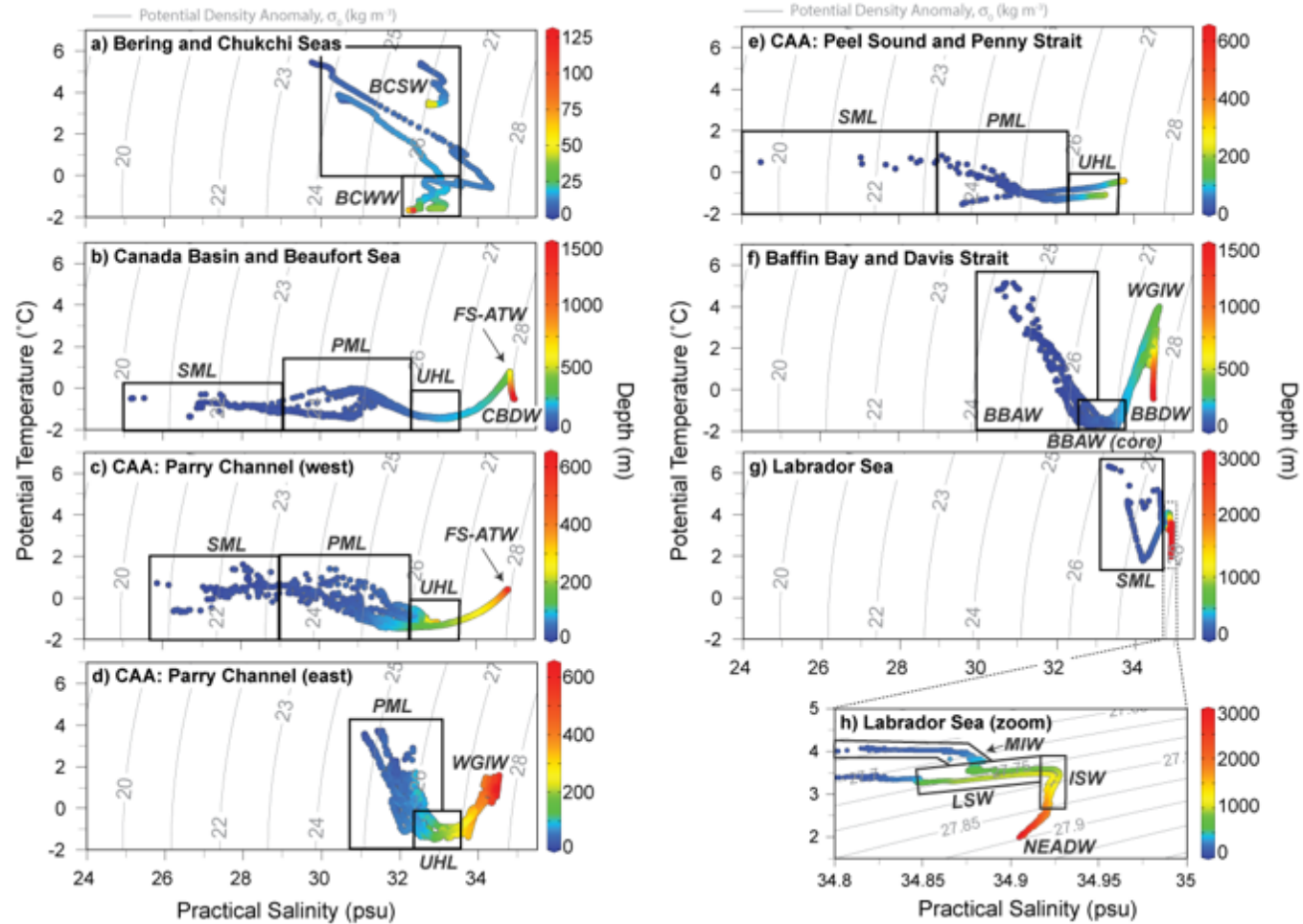


Figure 5.6. Potential temperature (°C) versus practical salinity diagrams for the major oceanographic domains along our study transect. (a) Bering and Chukchi Seas, (b) Canada Basin and Beaufort Sea, (c) western side and (d) eastern side of Parry Channel in the CAA, (e) Peel Sound and Penny Strait in the CAA, (f) Baffin Bay and Davis Strait, (g) Labrador Sea and (h) a finer scale diagram of the Labrador Sea T-S data from (g). Major water masses are noted as described in Table 5.4. Data from full CTD profiles were used. Colour of symbols indicates depth. Grey contour lines denote lines of constant potential density anomalies ($\sigma_\theta = \rho_\theta - 1000$, kg m^{-3} ; ρ_θ = constant potential density).

T-S relationships in the CAA domain were mainly influenced by waters inflowing from the BS-CB, which are then transformed as waters transit from west to east (Table 5.4; Figure 5.6c-e). The Pacific-influenced SML, PML and UHL water masses were observed in the upper 200 m, although the mixing that occurs during the east-west transit of these waters meant we found no evidence of SML on the eastern side of Parry Channel, and that PML and UHL in this area became difficult to differentiate. The relatively warm and saline NE Atlantic-origin waters were observed at depths deeper than 200 m, though the core of these waters was only found at stations where the water depth was deeper than 350 m. Warmer and less saline WGIW was found on the eastern side of Parry Channel, while the slightly cooler and more saline ATW was found on the western side. The very shallow Barrow Strait restricts the flow of ATW from the western CAA, such that waters east of Barrow Strait would not be influenced by this water mass. Instead, Atlantic-origin waters from the Labrador Sea and Baffin Bay influence the deeper waters of the CAA west of Barrow Strait. The different T-S properties of WGIW and ATW indicate they followed different pathways into the Arctic.

Both Pacific- and Atlantic-origin water masses are evident in the BB domain (Table 5.4; Figure 5.6f). The influence of Pacific-origin waters flowing from Lancaster Sound were found in the upper 120 m, although the SML, PML and UHL water masses were modified enough to identify the new water mass BBAW (Table 5.4). The temperature maximum in the underlying waters (300-500 m) represents the core of WGIW. Baffin Bay Deep Water (BBDW) found below ~800 m underlies all other water masses, with the core of these waters being identified by the temperature minimum of $<0^{\circ}\text{C}$ at a salinity of 34.5.

Waters in the Labrador Sea were the warmest and most saline of all of our study domains (Table 5.4; Figure 5.6g). Surface waters (0 – 60 m) of SML were the freshest and are influenced by BBAW that has been modified by warming and fresh water inputs. Underlying the SML at our northernmost station (LS2) is the relatively warm MIW, which originates in the Irminger Sea and is modified and transported around the Labrador Sea by the West Greenland and Labrador Sea boundary currents. Below MIW (or below SML if MIW is not present) is the well mixed layer of LSW, formed during extreme winter mixing events to depths often deeper than 500 m. This water mass was formed during the extremely deep winter convection events of 2014 and early 2015 (Yashayaev et al., 2016). Below LSW is Icelandic Slope Water (ISW), which is ventilated outside of the Labrador Sea (Yashayaev, 2007; Hamme et al., 2017). The deepest water mass we observe is the relatively cold NEADW. Unlike CBDW and BBDW, this water mass much more recently ventilated as the deep Labrador Sea is not isolated from its surrounding basins (e.g. Yashayaev, 2007).

5.5 Discussion

5.5.1 Relationship between $\delta^{30}\text{Si}(\text{OH})_4$ and Water Mass Distributions

The distributions of $\delta^{30}\text{Si}(\text{OH})_4$ show close associations with the water masses identified within each domain (Table 5.4; Figure 5.6). The high $\delta^{30}\text{Si}(\text{OH})_4$ in surface waters made up of BCSW, SML, PML and BBAW are the result of the preferential uptake of light isotopes of Si by diatoms, which is supported by our findings of high bSiO_2 production rates in the BE-CH, CAA and BB domains from Chapters 2 and 4. The minimum in $\delta^{30}\text{Si}(\text{OH})_4$ between 100 to 200 m from the BS-CB to BB domains is associated with UHL and the core of BBAW, which are composed of Pacific-origin BCWW (e.g. Steele et al., 2004; Shimada et al., 2005). The subsurface maximum in

$\delta^{30}\text{Si}(\text{OH})_4$ found below the $\delta^{30}\text{Si}(\text{OH})_4$ minimum is found within the warm, saline waters of Atlantic-origin (ATW or WGIW). Relatively low $\delta^{30}\text{Si}(\text{OH})_4$ found in CBDW and BBDW show different trends with depth that are likely the result of differences in the surface $\delta^{30}\text{Si}$ compositions of $[\text{Si}(\text{OH})_4]$ and bSiO_2 (see section 4.3). Undetectable $[\text{Si}(\text{OH})_4]$ in the surface waters of the LS domain meant that we were unable to identify a signal for SML that would include the outflow of BBAW. The subsurface $\delta^{30}\text{Si}(\text{OH})_4$ minimum at LS2 was associated with the subsurface T maximum that we identified as MIW. The deep subsurface maximum in $\delta^{30}\text{Si}(\text{OH})_4$ in the LS domain was associated with $\text{LSW}_{\text{upper}}$. The $\delta^{30}\text{Si}(\text{OH})_4$ within NEADW were relatively similar to values found in $\text{LSW}_{\text{lower}}$, likely due to the mixing that has occurred between these water masses (e.g. Yashayaev, 2007; Yashayaev et al., 2016).

5.5.1.1 Estimates of the $\delta^{30}\text{Si}(\text{OH})_4$ of Dominant Water Masses in the Arctic

We estimated the average $\delta^{30}\text{Si}(\text{OH})_4$ compositions for each of the identified water masses within our study domains using $\delta^{30}\text{Si}(\text{OH})_4$ measurements taken within the ‘core’ of each water mass (identified as where the T and S values of a sample were within approx. ± 0.1 of those reported in Table 5.4) (Table 5.5). We also used the results of a preliminary Optimum Multiparameter (OMP) analysis conducted for a subset of our study domains (Mucci and Lapierre, pers. comm.) to identify and average $\delta^{30}\text{Si}(\text{OH})_4$ samples where the relative contribution of a specific water mass was $>90\%$. While OMP analyses are an effective tool used to identify and quantify water mass distributions (e.g. Lansard et al., 2012; Varela et al., 2016; García-Ibáñez et al., 2018), the analysis available for our study area is only preliminary, and only available for a subset of our domains (BS-CB, CAA and BB).

Table 5.5. Water mass $\delta^{30}\text{Si}(\text{OH})_4$ signatures for all domains along our sampling transect. Values are obtained from literature results, T-S analysis of this dataset, and, for the BS-CB, CAA and BB domains, compared to $\delta^{30}\text{Si}(\text{OH})_4$ values measured from samples obtained at depths where $\geq 90\%$ of a single water mass existed according to the preliminary OMP-derived water mass distributions (Mucci and Lapierre, pers. comm.).

Water Mass ^a	Water mass values derived from:				
	Literature	Measured parameters (this study, T-S analysis)		Measured parameters ^a (this study, OMP analysis ^b)	
	$\delta^{30}\text{Si}(\text{OH})_4$ (‰)	$\delta^{30}\text{Si}(\text{OH})_4$ (‰)	n	$\delta^{30}\text{Si}(\text{OH})_4$ (‰)	n
<i>Bering and Chukchi Seas (BE-CH)</i>					
BCSW	-	$+2.12 \pm 0.38$	9	-	-
BCWW	-	$+1.94 \pm 0.06$	2	-	-
<i>Beaufort Sea and Canada Basin (BS-CB)</i>					
PML	$+2.26 \pm 0.39^c$	$+2.27 \pm 0.09$	3	$+2.32 \pm 0.02$	2
UHL	$+1.84 \pm 0.10^c$	$+1.71 \pm 0.08$	6	$+1.70 \pm 0.11$	3
ATW	$+2.04 \pm 0.11^c$	$+1.85 \pm 0.14$	6	$+1.89 \pm 0.14$	3
CBDW	$+1.88 \pm 0.12^c$	$+1.70 \pm 0.10$	8	$+1.70 \pm 0.11^i$	7
<i>Canadian Arctic Archipelago (CAA)</i>					
PML	-	$+2.25 \pm 0.40$	14	$+2.53 \pm 0.50$	10
UHL	-	$+1.77 \pm 0.07$	21	$+1.80 \pm 0.08$	10
ATW	-	$+1.83 \pm 0.01$	4	$+1.84 \pm 0.01$	3
WGIW	-	$+1.75 \pm 0.04$	5	$+1.78 \pm 0.11$	4
<i>Baffin Bay (BB)</i>					
BBAW (core)	-	$+1.84 \pm 0.11$	6	$+1.83 \pm 0.10$	3
WGIW	-	$+1.75 \pm 0.05$	8	$+1.76 \pm 0.03$	5
BBDW	-	$+1.61 \pm 0.07$	3	$+1.61 \pm 0.07$	3
<i>Labrador Sea (LS)</i>					
MIW	-	$+1.59 \pm 0.04$	3	-	-
LSW	$+2^{e,f}$ $+1.79 \pm 0.06^{f,g}$	$+1.78 \pm 0.07$	6	-	-
ISW	$+1.5^{e,h}$	$+1.68 \pm 0.01$	4	-	-
NEADW	$+1.5^c$	$+1.68 \pm 0.00$	2	-	-

^a Water mass names for the OMP analysis are the same as our own except for the two ATW water masses, which Mucci and Lapierre call N-ATW (for ATW) and S-ATW (for WGIW).

^b All values are the mean ($\pm$ SD) of each parameter from all sampling depths where $\geq 90\%$ of a single water mass existed according to the OMP-derived water mass distributions (Mucci and Lapierre, pers. Comm.).

^c Value from Varela et al. (2016).

^d Significant difference from literature value at $p < 0.05$.

^e Value from Sutton et al. (2018); Samples collected in May-June 2014.

^f Value for 'upper LSW' between 400 – 1200 m.

^g Value from de Souza et al. (2012); Samples collected in April-May 2010.

^h Value for 'lower LSW' between 1500 – 2300 m from Sutton et al. (2018).

Thus, in order to calculate $\delta^{30}\text{Si}(\text{OH})_4$ signatures for all our water masses identified via T-S analysis, we only use the OMP-derived $\delta^{30}\text{Si}(\text{OH})_4$ water mass signatures to validate our estimates based on the T-S water mass analysis. Estimates of $\delta^{30}\text{Si}(\text{OH})_4$ water mass

signatures derived from both methods agree well, indicating that the values we report for the water masses are robust.

We find evidence of the diatom utilization of Si on our $\delta^{30}\text{Si}(\text{OH})_4$ water mass signatures for several of our identified water masses (Table 5.5). Our water mass $\delta^{30}\text{Si}(\text{OH})_4$ estimates for BCSW and PML were the highest and most variable. Given that these water masses reside within the euphotic zone, this is consistent with the fractionation of Si isotopes by biosilicification. We also observed higher $\delta^{30}\text{Si}(\text{OH})_4$ for BCWW than for UHL despite BCWW being the source for UHL. This is likely due to our samples for BCWW being located within the euphotic zone, albeit near the bottom of the euphotic zone. However, as we show in Chapter 2, diatom utilization rates of Si are very high at the depths and stations where these samples were collected, such that we would expect $\delta^{30}\text{Si}(\text{OH})_4$ to be heavier as a result of this utilization. Although we do not have samples from below the euphotic zone at these stations, we would expect the $\delta^{30}\text{Si}(\text{OH})_4$ compositions to be lighter, and more comparable to those found in the UHL in the Canada Basin. The increase we see in the $\delta^{30}\text{Si}(\text{OH})_4$ signatures of UHL from BS-CB to the CAA and in the core of BBAW, which is mostly composed of UHL exiting Lancaster Sound (Table 5.5), is also indicative of diatom utilization of Si as this water mass shoals into the euphotic zone and $[\text{Si}(\text{OH})_4]$ in these water masses decrease along our sampling transect (Tables 5.4-5.5; Figures 5.4e,f and 5.6).

We also observed differences in the $\delta^{30}\text{Si}(\text{OH})_4$ signatures of the two types of Atlantic-origin waters found in the CAA, with ATW being $\sim 0.1\text{‰}$ heavier than WGIW. Although both of these water masses ultimately originate in the NE Atlantic (e.g. Buch et al., 2000, 2005; Yashayaev and Seidov, 2015), their pathways into and through the Arctic are very

different. The ATW follows a long pathway through the Eurasian Basin and along the Siberian and North American shelves, undergoing significant modification prior to circulating through the Canada Basin and CAA (Figure 5.1b; Table 5.5; e.g. McLaughlin et al., 2002; Rudels et al., 2013; 2015). In contrast, WGIW is primarily composed of MIW, which is formed in the Irminger Sea and transported through Davis Strait and into Baffin Bay and the eastern CAA via the East and West Greenland Slope Currents (Figure 5.1b; Yashayaev, 2007; Curry et al., 2014). While this pathway is ultimately shorter than that for ATW, we do see evidence of modification of this water mass given that our estimate for MIW in the Labrador Sea is $\sim 0.15\text{‰}$ lighter and the T-S properties are different (Tables 5.4-5.5). This difference between ATW and WGIW is not entirely unexpected given the cyclonic circulation of waters in Baffin Bay (e.g. Curry et al., 2014), and that our sampling of the WGIW occurred on the more western side of the bay (Figure 5.2b), thus leaving greater opportunity for waters to be modified prior to our sampling.

In the LS domain, our $\delta^{30}\text{Si}(\text{OH})_4$ estimates for LSW were heavier than those for ISW and NEADW, which is consistent with the trends observed by Sutton et al. (2018a) for these water masses (although note that Sutton et al. (2018a) identify LSW as ‘ $\text{LSW}_{\text{upper}}$ ’ and ISW as ‘ $\text{LSW}_{\text{lower}}$ ’ in their study). Given the increase in $[\text{Si}(\text{OH})_4]$ with depth, the differences between LSW and ISW could be driven by bSiO_2 dissolution through the water column given that the $\delta^{30}\text{Si}$ of bSiO_2 dissolved would likely have a different value from that of ambient $\delta^{30}\text{Si}(\text{OH})_4$ and thus be contributing a different value for $\delta^{30}\text{Si}(\text{OH})_4$ to these waters. Any isotopic fractionation occurring as a result of bSiO_2 dissolution would likely only exacerbate this difference. However, it is also possible that the

differences simply arise from differences in the preformed $\delta^{30}\text{Si}(\text{OH})_4$ values for each water mass when they were formed, as ISW is ventilated outside of the Labrador Sea (Table 5.4). It is also possible that the differences could be driven by the continued mixing between ISW and NEADW (Yashayaev, 2007; Yashayaev et al., 2016), especially considering the similarity between $\delta^{30}\text{Si}(\text{OH})_4$ signatures of these two water masses (Table 5.5) and the invariance in the depth profiles of $\delta^{30}\text{Si}(\text{OH})_4$ below 2000 m. In addition, the remarkably good agreement between LSW from our study with that of de Souza et al. (2012) suggests that renewal of LSW from deep convection produces a similar $\delta^{30}\text{Si}(\text{OH})_4$ signature each year that is not modified heavily in the intervening years. This is taking into account that the LSW sampled in 2010 as part of the de Souza et al. (2012) study would have been formed prior to 2010 (likely in 2008 or 2009, Yashayaev et al., 2016) while the LSW we sampled in 2015 had been recently ventilated in the preceding winter (2014-2015; Table 5.4; Yashayaev et al., 2016).

Our $\delta^{30}\text{Si}(\text{OH})_4$ estimates compare well to those made previously within the same laboratory (LSW from de Souza et al., 2012; Table 5.5); however, we find $\sim 0.2\%$ offsets between our measurements in BS-CB and those of Varela et al. (2016) and between our measurements in LS and Sutton et al. (2018a). The $\delta^{30}\text{Si}(\text{OH})_4$ measurements for these studies were conducted in three different laboratories: UCSB (USA) for Varela et al. (2016), Plouzané (France) for Sutton et al. (2018a), and ETH Zürich (Switzerland) for this study. Offsets between these three laboratories have been previously recognized and discussed (Brzezinski and Jones, 2015; Sutton et al., 2018a) and are generally consistent with the observed offsets between the each laboratory's reported $\delta^{30}\text{Si}(\text{OH})_4$ for the seawater reference standard ALOHA₁₀₀₀ (Grasse et al., 2017). Despite these biases, we

observe the same trends in $\delta^{30}\text{Si}(\text{OH})_4$ between water masses as previously reported, indicating that our interpretation of the overall isotope systematics is not compromised, although caution must be taken to ensure these offsets are accounted for during any future compilations of $\delta^{30}\text{Si}(\text{OH})_4$ datasets from multiple laboratories.

5.5.2 Estimating the Biogenic ^{30}Si Fractionation Factor, $^{30}\epsilon$

The fractionation of Si isotopes during biological production can be characterized using two simple models. The first model, described by the Rayleigh distillation equation, assumes a closed system where nutrient consumption is not replenished by external sources:

$$\delta^{30}\text{Si}(\text{OH})_{4, \text{ observed}} = \delta^{30}\text{Si}(\text{OH})_{4, \text{ source}} + ^{30}\epsilon \ln f \quad (2)$$

The second model assumes an open or steady-state system, where the overall concentration of nutrients is constant (i.e. inputs = outputs). This means there is a continuous supply of nutrients from external sources combined with a continuous removal of nutrients via biological consumption, which is described by the following equation:

$$\delta^{30}\text{Si}(\text{OH})_{4, \text{ observed}} = \delta^{30}\text{Si}(\text{OH})_{4, \text{ source}} - ^{30}\epsilon (1 - f) \quad (3)$$

In equations (2) and (3), $\delta^{30}\text{Si}(\text{OH})_{4, \text{ observed}}$ is equal to the measured $\delta^{30}\text{Si}(\text{OH})_4$, $\delta^{30}\text{Si}(\text{OH})_{4, \text{ source}}$ is equal to the source water $\delta^{30}\text{Si}(\text{OH})_4$, and f can be described by

$$f = [\text{Si}(\text{OH})_4]_{\text{observed}} / [\text{Si}(\text{OH})_4]_{\text{source}} \quad (4)$$

where $[\text{Si}(\text{OH})_4]_{\text{observed}}$ is equal to the measured $[\text{Si}(\text{OH})_4]$ and $[\text{Si}(\text{OH})_4]_{\text{source}}$ is equal to the expected source water $[\text{Si}(\text{OH})_4]$ before any localized Si consumption.

Varela et al. (2004) showed that equation (2) can be rearranged to:

$$\delta^{30}\text{Si}(\text{OH})_{4, \text{ observed}} = \text{Y-intercept} + ^{30}\epsilon \ln [\text{Si}(\text{OH})_4]_{\text{observed}} \quad (5)$$

where the Y-intercept = $\delta^{30}\text{Si}(\text{OH})_{4,\text{source}} - {}^{30}\epsilon \ln [\text{Si}(\text{OH})_4]_{\text{source}}$. Thus, the value for ${}^{30}\epsilon$ can be estimated from the slope of a linear regression between $\delta^{30}\text{Si}(\text{OH})_{4,\text{observed}}$ and $\ln [\text{Si}(\text{OH})_4]_{\text{observed}}$. Similarly, equation (3) can be rearranged to:

$$\delta^{30}\text{Si}(\text{OH})_{4,\text{observed}} = (\delta^{30}\text{Si}(\text{OH})_{4,\text{source}} - {}^{30}\epsilon) + {}^{30}\epsilon f \quad (6)$$

such that the slope of the linear regression between $\delta^{30}\text{Si}(\text{OH})_{4,\text{observed}}$ and f will give an estimate of ${}^{30}\epsilon$.

To estimate ${}^{30}\epsilon$ based on an closed-system model from equation (5), we only need our measurements of $\delta^{30}\text{Si}(\text{OH})_4$ and $[\text{Si}(\text{OH})_4]$. For an estimate of ${}^{30}\epsilon$ based on the open-system model, equation (6) requires an estimate of the ‘source water’ $[\text{Si}(\text{OH})_4]$ for each domain such that the values for f can be constrained. In the BE-CH domain, we use $[\text{Si}(\text{OH})_4]_{\text{source}} = 41 \mu\text{mol L}^{-1}$ based on an average $[\text{Si}(\text{OH})_4]$ for depths >40 m at our sampling stations ($[\text{Si}(\text{OH})_4]$ from Chapter 2 and Cooper et al., 2016), which we assume represents the ‘pre-bloom’ concentration of $[\text{Si}(\text{OH})_4]$ in this domain. In the BS-CB domain, surface waters are primarily composed of PML (Table 5.5). Thus, we use the ‘winter’ $[\text{Si}(\text{OH})_4]$ of $20 \mu\text{mol L}^{-1}$ reported by Carmack et al. (2004) as our source value the BS-CB domain. Given the shoaling of the UHL water mass we observe through the CAA domain, we assume that surface waters in the CAA are made up of a mixture of UHL and PML, which is also supported by our T-S analysis (Table 5.5; Figure 5.6) and the findings of the preliminary OMP water mass analysis (Mucci and Lapierre, pers. comm.). We estimate $[\text{Si}(\text{OH})_4]_{\text{UHL}} = 30 \mu\text{mol L}^{-1}$ based on an average of our $[\text{Si}(\text{OH})_4]$ measurements at ~ 200 m in the Canada Basin, which represent the core of the UHL water mass based on T-S properties. We then assume the $[\text{Si}(\text{OH})_4]_{\text{source}}$ for the CAA is 25

$\mu\text{mol L}^{-1}$, which is an average of $[\text{Si}(\text{OH})_4]_{\text{source}}$ for the UHL and PML. Finally, for the BB domain, we use a source water $[\text{Si}(\text{OH})_4] = 12.4 \mu\text{mol L}^{-1}$, based on an average of the $[\text{Si}(\text{OH})_4]$ for the four source waters in northern Baffin Bay, as reported by Tremblay et al. (2002). This is also consistent with our own measurements of $[\text{Si}(\text{OH})_4]$ of $\sim 12 \mu\text{mol L}^{-1}$ that we observe near the bottom of the surface layer ($\sim 100 \text{ m}$) at our BB stations.

Our fractionation factor estimates for the surface waters of each domain from BE-CH to BB ranged from -0.44 to -0.59‰ for the closed-system model and from -1.08 to -1.20‰ for the open-system model (Table 5.6).

Table 5.6. Estimates of the fractionation factor for the four study domains where $\delta^{30}\text{Si}(\text{OH})_4$ signals in the upper 100 m of the water column were measured.

Domain	$[\text{Si}(\text{OH})_4]_{\text{source}}$ ($\mu\text{mol L}^{-1}$)	Fractionation factor, $^{30}\epsilon$		n
		Closed system (Rayleigh)	Open-system (Steady state)	
BE-CH	41	-0.53 ± 0.10	-1.09 ± 0.22	12
BS-CB	20	-0.57 ± 0.09	-1.20 ± 0.25	6
CAA	25	-0.44 ± 0.05	-1.10 ± 0.17	34
BB	12.4	-0.59 ± 0.06	-1.08 ± 0.13	8
<i>All domains</i>	-	-0.37 ± 0.04	-1.07 ± 0.11	60
<i>BE-CH and CAA</i>	-	-	-1.07 ± 0.14	46
<i>BS-CB and BB</i>	-	-0.46 ± 0.07	-	14

When data from all domains were combined, we calculated a mean ($\pm 1\text{SE}$, $n = 60$) $^{30}\epsilon$ of $-0.37 \pm 0.04\text{‰}$ using the closed-system model (equations 2 and 5) and $-1.07 \pm 0.11\text{‰}$ using the open-system model (equations 3 and 6) (Table 5.6; Figure 5.7). These estimates are not significantly different from values of $-0.47 \pm 0.04\text{‰}$ and $-1.08 \pm 0.15\text{‰}$ we calculate for the closed- and open-system models based on the relative water mass contributions determined from a preliminary OMP analysis and following equations (4) and (6) from Varela et al. (2016) (see Appendix E details on this calculation). The similarity between our estimates with and without using the relative mass fractions from the OMP analysis also validates our assumptions regarding the contributions of different water masses to the ‘source’ water $[\text{Si}(\text{OH})_4]$ for each domain.

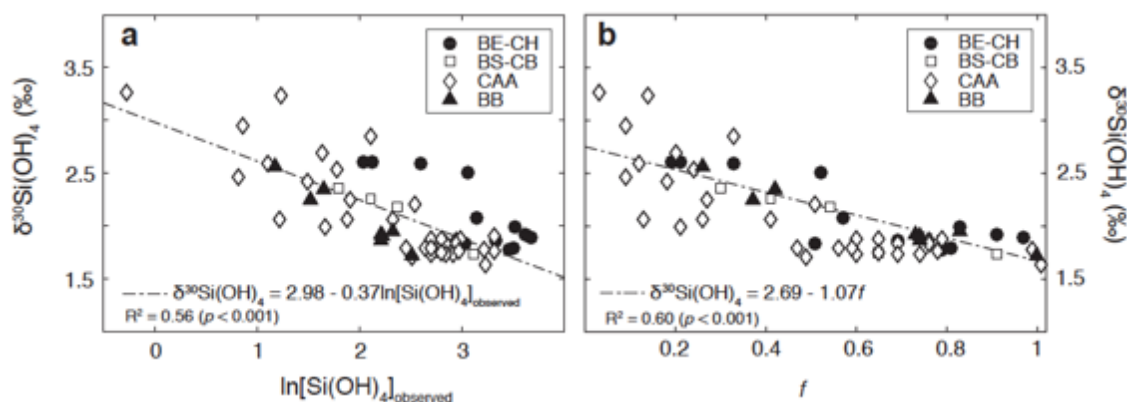


Figure 5.7. Estimates of the Si isotope fractionation factor ($^{30}\epsilon$) during summer in Arctic surface waters for all major oceanographic domains sampled. The lines and equations are the result of linear regression of (a) $\delta^{30}\text{Si}(\text{OH})_4$ versus the natural logarithm of $[\text{Si}(\text{OH})_4]$ assuming closed-system dynamics, and (b) $\delta^{30}\text{Si}(\text{OH})_4$ versus f assuming open-system dynamics. Symbols denote major oceanographic domains: solid circle, Bering and Chukchi Seas; open square, Beaufort Sea and Canada Basin; open diamond, Canadian Arctic Archipelago; closed triangle, Baffin Bay. Measurements of $\delta^{30}\text{Si}(\text{OH})_4$ for surface waters of the Labrador Sea were not possible as $[\text{Si}(\text{OH})_4]$ was below the limit of detection.

Culture-based estimates of the isotope fractionation of Si by 12 different diatom strains range from -0.56‰ to -2.09‰, with an overall mean ($\pm\text{SE}$) of -1.02 ± 0.11 (De La Rocha et al., 1997; Sutton et al., 2013). Field-based estimates of $^{30}\epsilon$ in the Beaufort Sea and Canada Basin vary between -0.33‰ (closed system) and -0.97‰ (open system) (Varela et al., 2016). An average for all field-based studies in the global ocean gives $^{30}\epsilon$ ($\pm 1\text{SE}$, $n = 9$) = -1.14 ± 0.05 ‰ with the open-system estimate from Varela et al. (2016) included, or $^{30}\epsilon = -1.07 \pm 0.10$ ‰ with the closed-system estimate (De La Rocha et al., 2000, 2011; Varela et al., 2004; Cardinal et al., 2005; Reynolds et al., 2006; Beucher et al., 2008; Cavagna et al., 2011; Fripiat et al., 2011, Varela et al., 2016). Our estimates of $^{30}\epsilon$ are not significantly different from those reported for each model by Varela et al. (2016), and our open-system estimates are not significantly different from culture- or field-based studies. However, similar to Varela et al. (2016), we find that our closed-system estimates of $^{30}\epsilon$ are significantly different from culture-based studies and field-based estimates in other

parts of the global ocean, which highlights the caution that is required when choosing open- versus closed-system isotope models in different marine systems.

The good agreement between our open-system estimates of $^{30}\epsilon$ and those values reported by previous studies suggests that the steady-state dynamics approximated by an open-system model are the most applicable to our study domains. This is likely the case in the BE-CH domain, as previous studies have shown that the advective supply of nutrients to the Bering-Chukchi shelves maintains a diatom bloom in these shelf waters throughout the summer (e.g. Springer and McRoy, 1993). This is likely also the case for the CAA domain, although the dynamics of this region are more complicated. Welch and Bergmann (1989) found limited evidence of a drawdown of Si(OH)_4 in the upper 100 m of the water column from March to August in Barrow Strait, which would indicate that a closed-system isotope model may be a better representation of the isotope dynamics. However, this drawdown was not sufficient to support the high algal biomass observed, and the $[\text{Si(OH)}_4]$ in these waters exhibited high temporal variability with concentrations in the upper 100 m remaining relatively high ($10 - 20 \mu\text{mol L}^{-1}$) until late August. In the same location, Cota et al. (1987) found that the fortnightly tidal cycle was able to deliver $2\text{-}6 \text{ mmol m}^{-2} \text{ d}^{-1}$ of Si(OH)_4 to surface waters via mixing across the pycnocline, which is on the order of the euphotic zone bSiO_2 production rates we measured for this region in Chapter 3. Finally, Prinsenberg and Bennett (1987) showed that transport through Barrow Strait occurred in summer and was on the order of 1 Sv ($10^6 \text{ m}^3 \text{ s}^{-1}$), which is the same as that observed for the Bering Strait (e.g. Woodgate, 2018). Thus, the combination of a strong advective flow and tidally driven vertical mixing observed in the CAA (e.g. Cota et al., 1987; Prinsenberg and Bennett, 1987; Cota and Horne, 1989; McLaughlin et al.,

2005) is likely most appropriately represented by a steady-state open system model for the isotope dynamics.

Given the seasonal drawdowns of Si(OH)_4 observed within the BS-CB and BB domains (e.g. Simpson et al., 2008; Tremblay et al., 2002, 2008; Matrai and Apollonio, 2013; Bergeron and Tremblay, 2014), the $\delta^{30}\text{Si}$ dynamics in these regions are likely better characterized by a closed-system model. However, our closed-system estimates of $^{30}\epsilon$ in these regions are significantly lower than the average estimates of $^{30}\epsilon$ measured in culture or in the field. Varela et al. (2016) found a similar discrepancy in their closed-system estimates of $^{30}\epsilon$ for the BS-CB domain, which they attribute to the effects of sea-ice diatoms on the overall expression of $^{30}\epsilon$ for a closed-system model. They hypothesize that limited diffusion between sea-ice and the underlying ocean drives this trend such that the apparent isotope effect for Si utilization, $^{30}\epsilon_{\text{app}}$, would be much smaller than the cellular isotope effect because a significant portion of the Si(OH)_4 drawdown occurs in sea ice. Essentially this means that sea-ice diatoms are completely using all of the Si(OH)_4 available to them within the ice. On the Beaufort Shelf, Tremblay et al. (2008) reported a strong drawdown of Si(OH)_4 in the upper ~30 m of the water column that occurred during the ice-algal bloom, and they observed no subsequent replenishment of Si(OH)_4 to these waters. Their observations support that ice-algae can contribute to a large proportion of the seasonal Si(OH)_4 drawdown in the water column. Varela et al. (2016) assumed that 60% of primary production in the BS-CB occurred in sea-ice with no apparent fractionation factor ($^{30}\epsilon_{\text{app}} = 0\text{‰}$), while that in the pelagic system occurs with a $^{30}\epsilon_{\text{app}} = -1.02\text{‰}$ and calculated an overall $^{30}\epsilon_{\text{total}} = -0.41\text{‰}$ based on these relative

proportions of sea-ice and pelagic primary production and estimates of the apparent $^{30}\epsilon$ for each system (i.e. $^{30}\epsilon = 0.6 \times 0.0\text{‰} + 0.4 \times -1.02\text{‰}$).

If we assume the proposed sea-ice/water column systematics are correct, we can alternatively use our closed system estimates of $^{30}\epsilon$ for the BS-CB and BB domains to calculate the relative proportions of pelagic and sea-ice diatom production. Doing so, we find that sea-ice primary production (PP) would account for $44 \pm 12\%$ of the total PP in BS-CB domain (i.e. $\% \text{ sea-ice PP} = 1 - (^{30}\epsilon_{\text{total}}/^{30}\epsilon_{\text{pelagic}}) = 1 - (-0.57\text{‰}/-1.02\text{‰})$) and $42 \pm 10\%$ in the BB domain. Although we could find no reports of the contribution of sea-ice algae to total PP in Baffin Bay, our estimate for the BS-CB domain is within the range of those reported for the central Arctic basin (50-62%; Gosselin et al., 1997; Fernandez-Mendez et al., 2015), suggesting that this may be a suitable method for estimating the sea-ice algae contribution to total PP over broad spatial scales in regions of the Arctic where a closed-system model can adequately describe the isotope dynamics.

Although we find that $\delta^{30}\text{Si}(\text{OH})_4$ and $[\text{Si}(\text{OH})_4]$ are highly correlated in the surface waters of the Arctic, our results emphasize the need to account for the localized hydrography and nutrient dynamics, which can vary widely between regions, especially in the Arctic. While our open-system model estimates of $^{30}\epsilon$ in all domains were similar to those estimated in culture and from other parts of the global ocean, we found that not all of the domains along our study transect were appropriately described by such a model. The discrepancy between our closed-system model estimates of $^{30}\epsilon$ and those previously reported in the literature can be explained if the additional influence of sea-ice and the contribution of sea-ice diatoms to the overall drawdown of $\text{Si}(\text{OH})_4$ is considered. A potential application of such closed-system dynamics where the contributions of and sea-

ice and sea-ice algae are added factors is to use estimates of the overall fractionation factor from water column $\delta^{30}\text{Si}(\text{OH})_4$ measurements to determine the contribution of sea-ice algae to total PP, something we are not able to do with open-system models.

5.5.3 Influence of biogenic silica dissolution on deep water $\delta^{30}\text{Si}(\text{OH})_4$ in Baffin Bay and the Canada Basin

5.5.3.1 Baffin Bay

The $[\text{Si}(\text{OH})_4]$ of the deep waters of Baffin Bay are nearly ten times higher than those observed at similar depths in the Canada Basin or Labrador Sea. This ‘silicate anomaly’ has been linked to high sinking fluxes and low dissolution rates of bSiO_2 in the upper water column (<150 m), with subsequent contributions from SiO_2 dissolution deeper in the water column and potentially also diffusion from sediment pore water at depth (Jones et al., 1984; Michel et al., 2002; Tremblay et al., 2002).

Our measurements of bSiO_2 production for Baffin Bay were $4.6 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Chapter 4). Assuming a growing season length of 150 d, this corresponds to $690 \text{ mmol bSiO}_2 \text{ m}^{-2}$ produced each year. Approximately $400 \text{ mmol m}^{-2} \text{ yr}^{-1}$ of bSiO_2 is available for export to depth, which we determine by multiplying the annual bSiO_2 production by $1 - 0.6$ (i.e., our average measurement of the euphotic-zone bSiO_2 dissolution to production ratio of 0.6 for BB; Appendix D), or 0.4. Although the source of the deep waters to Baffin Bay has not been explicitly identified, a number of studies argue it is saline Atlantic-origin water that cools at irregular intervals in Nares Strait in winter (e.g. Muench, 1971; Bourke et al., 1989; Tang et al., 2004). If we assume that our $[\text{Si}(\text{OH})_4]$ measurements of $\sim 20 \mu\text{mol L}^{-1}$ between 300 – 500 m at our BB stations represent $[\text{Si}(\text{OH})_4]_{\text{source}}$, then we can calculate the ‘excess’ of Si ($[\text{Si}(\text{OH})_4]_{\text{excess}}$) for the deep waters of Baffin Bay as the difference between our measured $[\text{Si}(\text{OH})_4]$ and $[\text{Si}(\text{OH})_4]_{\text{source}}$. Integrating $[\text{Si}(\text{OH})_4]_{\text{excess}}$

from 500 to 2300 m gives an overall $[\text{Si}(\text{OH})_4]_{\text{excess}}$ inventory of $80 \times 10^3 \text{ mmol m}^{-2}$. If all of the bSiO_2 available for export from the surface waters was exported and subsequently dissolved, it would take ~ 290 years ($80,000 \text{ mmol m}^{-2} / 276 \text{ mmol m}^{-2} \text{ yr}^{-1}$) to produce the deep $\text{Si}(\text{OH})_4$ anomaly observed in Baffin Bay. This is within the range of the ages estimated for BBDW (160 – 750 yr; Top et al., 1980; Bourke and Paquette, 1991), indicating that it is possible for only dissolution of bSiO_2 in the water column to produce the silicate anomaly in Baffin Bay.

The $\sim 0.2\text{‰}$ decrease in $\delta^{30}\text{Si}(\text{OH})_4$ we observe from 500 to 2300 m at our deep BB station (BB2) lends further support for this theory. Simultaneous measurements of $\delta^{30}\text{Si}$ - bSiO_2 and $\delta^{30}\text{Si}(\text{OH})_4$ in the field have shown that fractionation of Si isotopes during diatom growth produces $\delta^{30}\text{Si}$ - bSiO_2 that is systematically lighter than that of the ambient seawater (e.g. Varela et al., 2004; Fripiat et al., 2011). Thus, dissolution of bSiO_2 at depth could contribute $[\text{Si}(\text{OH})_4]$ with a lighter $\delta^{30}\text{Si}$ composition compared to that of the ambient seawater. We estimated the $\delta^{30}\text{Si}$ - bSiO_2 expected in surface waters using the closed-system isotope model described in section 5.5.2. From this model, the isotopic composition of bSiO_2 can describe either the accumulated ($\delta^{30}\text{Si}$ - $\text{bSiO}_{2,\text{acc}}$) or instantaneous ($\delta^{30}\text{Si}$ - $\text{bSiO}_{2,\text{inst}}$) isotopic composition of bSiO_2 in the system. The calculation for accumulated $\delta^{30}\text{Si}$ - bSiO_2 assumes no export of bSiO_2 from the system:

$$\delta^{30}\text{Si-bSiO}_{2,\text{acc}} = \delta^{30}\text{Si}(\text{OH})_{4,\text{source}} - {}^{30}\epsilon f \ln(f)/(1-f) \quad (7)$$

In contrast, the instantaneous $\delta^{30}\text{Si}$ - bSiO_2 assumes immediate export of bSiO_2 from the system:

$$\delta^{30}\text{Si-bSiO}_{2,\text{inst}} = \delta^{30}\text{Si}(\text{OH})_{4,\text{observed}} + {}^{30}\epsilon \quad (8)$$

Equations 7 and 8 represent the two extremes of bSiO₂ production and export in surface waters, with the actual bSiO₂ dynamics likely lying somewhere in-between.

To calculate $\delta^{30}\text{Si-bSiO}_2$, we use our estimates of $^{30}\epsilon$ for the closed-system model in Baffin Bay, values for f as determined in section 5.5.2, and a $\delta^{30}\text{Si(OH)}_4, \text{source} = 1.74\text{‰}$, which is an average of the $\delta^{30}\text{Si(OH)}_4$ between 100 to 200 m, i.e. where $[\text{Si(OH)}_4]$ are approximately equal to the expected source water $[\text{Si(OH)}_4]$ for surface waters of Baffin Bay from Table 5.6. Using these values in equations 7 and 8, we calculated an expected $\delta^{30}\text{Si-bSiO}_2$ for surface waters (<100 m) of 1.3 to 1.5‰. The $[\text{Si(OH)}_4]$ in the bottom waters (~2300 m) of Baffin Bay is $\sim 100 \mu\text{mol L}^{-1}$, which is equivalent to an $[\text{Si(OH)}_4]_{\text{excess}} = 80 \mu\text{mol L}^{-1}$. Assuming the entirety of the $[\text{Si(OH)}_4]_{\text{excess}}$ results from bSiO₂ dissolution with a $\delta^{30}\text{Si(OH)}_4$ equal to our estimate $\delta^{30}\text{Si-bSiO}_2$, this would represent 80% ($80/100 \mu\text{mol L}^{-1}$) of the measured $[\text{Si(OH)}_4]$. We assume that the $\delta^{30}\text{Si(OH)}_4$ of waters between 300 – 500 m represent the source water $\delta^{30}\text{Si(OH)}_4$ for deep Baffin Bay (+1.8‰), and that these water contribute 20% of the total $[\text{Si(OH)}_4]$ at depth. Using a $\delta^{30}\text{Si-bSiO}_2$ of 1.5‰ gives an estimate for $\delta^{30}\text{Si(OH)}_4$ at 2300 m of 1.56‰ (i.e. $0.2 \times 1.8\text{‰} + 0.8 \times 1.5\text{‰}$), which is remarkably consistent with our measured $\delta^{30}\text{Si(OH)}_4$ of $1.58 \pm 0.07\text{‰}$ ($\pm 2\text{SE}$). Indeed, we find our estimated $\delta^{30}\text{Si(OH)}_4$ for all sampling depths >1000 m agree within 0.05‰ of our in situ $\delta^{30}\text{Si(OH)}_4$ measurements if we use a $\delta^{30}\text{Si-bSiO}_2$ of 1.5‰, further supporting the theory that bSiO₂ dissolution is the main process contributing to the BB silicate anomaly.

Although the evidence for the fractionation of Si isotopes during bSiO₂ dissolution is mixed, a caveat to this analysis is that our estimated $\delta^{30}\text{Si(OH)}_4$ values for the deep waters of Baffin Bay do not account for any fractionation of Si isotopes during

dissolution (Demarest et al., 2009; Sun et al., 2014; Frings et al., 2014; Wetzel et al., 2014). If bSiO₂ dissolution were incomplete and a preferential release of the lighter isotopes of Si occurred (e.g. Demarest et al., 2009), our estimates of $\delta^{30}\text{Si}(\text{OH})_4$ for the deep waters of Baffin Bay would be much lower. However, the [bSiO₂] we observe at depths >500 m ranged from 0.04 – 0.07 $\mu\text{mol L}^{-1}$, which is within the analytical uncertainty of these measurements ($\pm 0.07 \mu\text{mol L}^{-1}$), leaving us reasonably confident that bSiO₂ dissolution in the water column has proceeded to completion.

It is also possible that a portion of the [Si(OH)₄] and $\delta^{30}\text{Si}(\text{OH})_4$ signals are driven by a sedimentary flux of Si(OH)₄. Only two studies have reported sedimentary Si(OH)₄ flux measurements for Baffin Bay. Darnis et al. (2012) reported a sedimentary Si(OH)₄ flux of $\sim 300 \text{ mmol Si m}^{-2} \text{ yr}^{-1}$ for shallow stations located near edges of Baffin Bay, which is on the same order of magnitude as our calculated bSiO₂ flux from surface waters; however, it is likely that sedimentary Si(OH)₄ fluxes in central Baffin Bay are much smaller. Jones et al. (1984) report an approximate Si(OH)₄ sediment porewater gradient of $\sim 20 \mu\text{mol Si L}^{-1} \text{ cm}^{-1}$. Using this gradient, we calculate an approximate sedimentary Si(OH)₄ flux using the same calculations and assumptions presented in Marz et al. (2015) to estimate Si(OH)₄ fluxes from sediment porewater gradients in the central Arctic Ocean. Doing so results in a flux of $\sim 17 \text{ mmol Si m}^{-2} \text{ yr}^{-1}$ to the deep waters of central Baffin Bay, which is more than 20 times smaller than the potential bSiO₂ export flux we estimated. Only one study in the global ocean has reported the $\delta^{30}\text{Si}$ dynamics of a seawater-sediment porewater system, showing that porewater $\delta^{30}\text{Si}(\text{OH})_4$ from the Peruvian upwelling system were similar to, or slightly heavier than $\delta^{30}\text{Si}(\text{OH})_4$ of the overlying seawater (Ehlert et al., 2016). Whether these results are representative of the Si isotope dynamics

in all marine sediment porewaters requires much further study. Nevertheless, if we assume that porewater $\delta^{30}\text{Si}(\text{OH})_4$ had values heavier than the overlying seawater, extrapolating their observations to our location suggests that sedimentary fluxes of $\text{Si}(\text{OH})_4$ could not be driving the majority of the silicate anomaly, as we would expect a gradient in $\delta^{30}\text{Si}(\text{OH})_4$ opposite to what we observe. A caveat to this is that if porewater $\delta^{30}\text{Si}(\text{OH})_4$ was indistinguishable from the overlying seawater $\delta^{30}\text{Si}(\text{OH})_4$, we would not be able to use $\delta^{30}\text{Si}(\text{OH})_4$ signals to distinguish the source of the Si flux. However, the estimated sedimentary fluxes indicate that the $\text{Si}(\text{OH})_4$ anomaly in Baffin Bay is not caused by sedimentary diffusion of $\text{Si}(\text{OH})_4$ to the water column, and the depth gradient we observe in our $\delta^{30}\text{Si}(\text{OH})_4$ measurements potentially also support this. Instead of sedimentary diffusion, the most likely source of the $\text{Si}(\text{OH})_4$ anomaly in the deep waters of Baffin Bay is bSiO_2 dissolution from surface waters, which is consistent with the suggestions of previous studies (Jones et al., 1984; Tremblay et al., 2002).

5.5.3.2 Canada Basin

Primary productivity in the Canada Basin is much lower than for other regions along our sampling transect (e.g. Varela et al., 2013) such that we would not expect to see such a strong $\text{Si}(\text{OH})_4$ anomaly as that observed in Baffin Bay, despite the deep waters of Canada Basin have a similar age (~500 years, Macdonald et al., 1993). Nevertheless, we still observed an increase in $[\text{Si}(\text{OH})_4]$ of $\sim 4 \mu\text{mol L}^{-1}$ from 1500 to 2500 m at our stations in the deep Canada Basin (stations CB-3 and CB-4), although this corresponded to an $\sim 0.2\text{‰}$ increase in $\delta^{30}\text{Si}(\text{OH})_4$, rather than a decrease as observed in Baffin Bay. Regardless, these trends in the Canada Basin are still likely due to bSiO_2 dissolution,

although it is likely that surface water bSiO_2 has a heavier isotopic composition than the ‘source’ $\delta^{30}\text{Si}(\text{OH})_4$ for deep waters in this domain.

To test this hypothesis, we estimated the $\delta^{30}\text{Si-bSiO}_2$ for the Canada Basin and used a simple mass balance as described in section 5.5.3.1. Using equations 7 and 8 and a $\delta^{30}\text{Si}(\text{OH})_{4,\text{source}}$ of 2.27‰ (i.e., the $\delta^{30}\text{Si}(\text{OH})_4$ for PML from BS-CB in Table 5.5) gives an expected $\delta^{30}\text{Si-bSiO}_2$ for surface waters of 1.7 to 2.0‰, which is higher than the range of values estimated for Baffin Bay, but relatively consistent with measurements of $\delta^{30}\text{Si-bSiO}_2$ between 75-100 m in the Canada Basin (2.0 to 2.9‰; Varela et al., 2016). For the mass balance, we calculate source water $[\text{Si}(\text{OH})_4]$ and $\delta^{30}\text{Si}(\text{OH})_4$ of the deep Canada Basin using our measurements of these parameters between 800 to 1500 m, giving values of $8 \mu\text{mol L}^{-1}$ and 1.7‰, respectively. If we use a $\delta^{30}\text{Si-bSiO}_2$ estimate of 2.0‰, our estimates of $\delta^{30}\text{Si}(\text{OH})_4$ for waters from 1500 to 2500 m are consistent with our measurements of $\delta^{30}\text{Si}(\text{OH})_4$ within 0.05‰. If we use $\delta^{30}\text{Si-bSiO}_2 = 2.5‰$ (75-100 m average $\delta^{30}\text{Si-bSiO}_2$ from Varela et al. 2016), our estimates are consistent within 0.02‰. Thus, as for Baffin Bay, we find that bSiO_2 dissolution for waters from 1500 to 2500 m is likely driving the trends in $\delta^{30}\text{Si}(\text{OH})_4$ that we measured.

We observed an $\sim 0.2‰$ decrease in $\delta^{30}\text{Si}(\text{OH})_4$ from 2500 to 3500 m in the Canada Basin, which is not consistent with the dissolution of relatively heavy bSiO_2 from surface waters. One possible explanation is dissolution of relatively fresh bSiO_2 that could have reached the seafloor via fast sinking aggregates of sea-ice diatoms, as has been observed in the Eurasian Basin (Boetius et al., 2013). However, sea-ice diatoms in the BS-CB likely have a $\delta^{30}\text{Si-bSiO}_2$ composition $\sim 0.5‰$ heavier than that of the suspended seawater $\delta^{30}\text{Si-bSiO}_2$ (Varela et al., 2016). Thus, even if bSiO_2 dissolution preferentially released

lighter isotopes of Si, the $\delta^{30}\text{Si-bSiO}_2$ would likely still be too heavy to drive the trend we observed (Demarest et al., 2009; Sun et al., 2014; Varela et al., 2016). Alternatively, the signal could be driven by a sedimentary flux of Si(OH)_4 with a low $\delta^{30}\text{Si(OH)}_4$ composition. Using our $\delta^{30}\text{Si(OH)}_4$ and $[\text{Si(OH)}_4]$ measurements at 2500 m to represent the source water signals, a mass balance for our measurements at 3500 m indicates that it would take an input of dissolved Si with a $\delta^{30}\text{Si(OH)}_4 = -2.5\text{‰}$ to generate our measured $\delta^{30}\text{Si(OH)}_4$. Although sedimentary/lithogenic SiO_2 has a $\delta^{30}\text{Si}$ that is generally lighter than the values observed in seawater ($+0.4\text{‰}$, Sutton et al., 2018b), this value is not light enough to drive the trend we observe. It is possible that Si isotope fractionation of particulate SiO_2 during dissolution in sediments could explain this discrepancy, although no consensus on the magnitude, or even existence, of this fractionation has yet been reached in the literature (e.g. Demarest et al., 2009; Sun et al., 2014; Frings et al., 2014; Wetzel et al., 2014).

Another possibility is that this signal is driven by the dissolution of bSiO₂ from siliceous sponge spicules transported from the surrounding shelves to the deep basin. The average $\delta^{30}\text{Si-bSiO}_2$ for sponges is much lighter and closer to the value we estimate from our mass balance calculation (-2.1‰ ; Sutton et al., 2018b). Van Wagoner et al. (1989) found widespread communities of siliceous sponges that form reef mounds up to 10 m high, along with extensive mats of sponge spicules in the sediments on the northern Beaufort Shelf. Honjo et al. (2010) found an extremely large flux of suspended material (including bSiO₂) to ~3100 m that was not consistent with the fluxes observed in shallower sediment traps in the Canada Basin. They hypothesize that this deep flux is driven by transport from the Beaufort Shelf via the benthic nepheloid layer, indicating

that it is possible that the signal we observed may be the result of dissolution of sponge spicules from the Beaufort Shelf. Regardless of what process is truly influencing our bottom water $\delta^{30}\text{Si}(\text{OH})_4$ in the Canada Basin, our results suggest that the $\delta^{30}\text{Si}(\text{OH})_4$ we observe cannot be attributed to the dissolution of bSiO_2 sinking from higher in the water column.

5.6 Conclusions

Since the first measurements of seawater $\delta^{30}\text{Si}(\text{OH})_4$ were reported almost 20 years ago (De La Rocha et al., 2000), the field of marine Si isotope geochemistry has primarily focussed on observational studies in the global ocean and investigating how large-scale patterns in ocean circulation and Si utilization influence the observed distributions (e.g. Beucher et al., 2008; de Souza et al., 2012; Brzezinski and Jones, 2015; Varela et al., 2016; Sutton et al., 2018a). Our study adds to this ever-growing body of literature, presenting the first measurements of the silicon isotopic composition of dissolved Si in seawater for the Bering and Chukchi Seas and the Eastern Canadian Arctic, from the Canadian Arctic Archipelago to Baffin Bay. We also build on previous datasets within the Beaufort Sea, Canada Basin and Labrador Sea (de Souza et al., 2012; Varela et al., 2016; Sutton et al., 2018a), presenting a complete transect along flow path of Pacific-origin waters from the Bering Sea to Baffin Bay.

Our results show that, like elsewhere in the global ocean, marine Si isotopes are a powerful tool that can track Si utilization, bSiO_2 dissolution, and the distribution and modification of water masses in the Arctic. In particular, $\delta^{30}\text{Si}(\text{OH})_4$ signals track how bSiO_2 production modifies the nutrient-rich Pacific-origin waters on their transit from west to east, and how bSiO_2 dissolution influences the $\delta^{30}\text{Si}(\text{OH})_4$ signatures of the

isolated deep waters of the Canada Basin and Baffin Bay. We also found evidence of modification in the two types of NE Atlantic-origin waters identified along our sampling transect, which is likely related to the different pathways these water masses follow through the Arctic. Elucidating the processes driving these modifications will require further study of the marine bSiO₂ and $\delta^{30}\text{Si}$ dynamics along these pathways, particularly around the eastern and western coasts of Greenland, and in Fram Strait and the Barents Sea.

As the marine Si isotope geochemistry field matures, the need for mechanistic studies investigating the processes and interactions between the water column and its surrounding environments (i.e. sea-ice, sediments) is becoming more apparent. We found that water column $\delta^{30}\text{Si}(\text{OH})_4$ measurements have the potential to be a simple and effective method to estimate the relative proportion of annual sea-ice algae production to total primary production, provided that our assumptions about the Si isotope systematics of the sea-ice/water column system are correct; however, such systematics have not yet been adequately investigated in the literature. Our results also highlighted the need to better understand the interactions between the sediment/water column system and the potential fractionation of Si isotopes during bSiO₂ dissolution as it remains unclear how and to what extent these processes and fluxes may affect the water column $\delta^{30}\text{Si}(\text{OH})_4$.

General Conclusions

1. Main Findings

This thesis has described the marine biogenic silica dynamics of the Arctic Ocean along the flow path of nutrient-rich Pacific-origin waters as they flow from the highly productive Bering and Chukchi Seas, through the Canada Basin and Canadian Arctic Archipelago, and out into Baffin Bay and the Labrador Sea. This was the first study to (a) simultaneously measure biogenic silica production and dissolution rates in Arctic waters (b) investigate the effect of silicic acid on biogenic silica production by natural diatom assemblages in the Arctic, and (c) report the natural isotopic composition of silicic acid for the Bering and Chukchi Seas, the Canadian Arctic Archipelago and Baffin Bay. The general conclusions of this thesis are best summarized by highlighting the main results from each chapter.

Chapter 1: A decade of summertime measurements of phytoplankton biomass, productivity and assemblage composition in the Pacific Arctic Region from 2006 – 2016.

- Diatoms dominated the phytoplankton assemblages throughout most of the Pacific Arctic Region, and phytoplankton biomass and productivity were highest under the influence of the nutrient rich Pacific-origin waters flowing through the Gulf of Anadyr.
- Differences in the nutrient content of water masses found in the southeastern Chukchi Sea resulted in an east to west gradient in phytoplankton assemblage composition, biomass, and productivity in this region. The western sector was characterized by high $[\text{NO}_3^-]$, a diatom-dominated phytoplankton assemblage, and high phytoplankton biomass and productivity. In contrast, the eastern sector was characterized by low euphotic zone $[\text{NO}_3^-]$, a phytoplankton assemblage dominated

by coccolithophores and small flagellated plankton, and low phytoplankton biomass and productivity.

- The presence or absence of sea-ice can impact the composition of phytoplankton assemblages, with pennate diatoms being more abundant than centric diatoms in the northeastern Chukchi Sea when sea-ice was present.
- The generally high $[\text{NO}_3^-]$ within the euphotic zone throughout most of the DBO regions suggests that light and/or grazing may exert a greater control on phytoplankton productivity than $[\text{NO}_3^-]$ in July
- There is significant interannual variability in phytoplankton biomass and productivity in the Pacific Arctic Region that cannot be attributed to differences in methodology. Instead, this may be the result of the highly dynamic nature of this region, which complicates the identification of long-term trends.

Chapter 2: A decade of diatoms: summertime silica dynamics in the Pacific Arctic Region from 20016 to 2016

- Rates of bSiO_2 production in the Pacific Arctic Region were high, and exhibited similar spatial trends to concurrent measurements of primary productivity and nitrate utilization rates that track the northward progression of the seasonal bloom.
- Diatoms drive most of the primary production and nitrate utilization in the PAR during July, but contribute a disproportionately large amount to the NO_3^- utilization ($87 \pm 6\%$), while their contribution to primary productivity ($61 \pm 8\%$) is proportionate to their contribution to autotrophic biomass ($65 \pm 4\%$).
- There was evidence of Si limitation of bSiO_2 production, and that light may also be affecting bSiO_2 production in the PAR.

- Light also appeared to modulate the response of silica production to changes in Si(OH)_4 availability and ambient irradiance in surface waters of the PAR may not be sufficient to maximize bSiO_2 production by diatoms.
- Differences in the $[\text{NO}_3^-]$ content of water masses in the southeastern Chukchi Sea, rather than the $[\text{Si(OH)}_4]$ content, likely drives the east to west gradient in diatom biomass and productivity in this region.
- Phytoplankton phenology responds to short-term environmental changes, with a shift in the timing of the spring bloom due to earlier sea-ice breakup resulting in a decrease in bSiO_2 production and the contribution of diatoms to primary production and nitrate utilization at the time of our sampling in July.

Chapter 3: Recycling of biogenic silica in the Pacific Arctic Region from 2013 – 2016

- Dissolution rates of bSiO_2 were interannually variable, and high compared to other parts of the world's oceans.
- The high bSiO_2 dissolution rates observed may be tied to lower water column Al:Si ratios, and/or increased heterotrophic bacterial activity, though there is a need for a better understanding of the links between the cycling of Al and Si, and the influence of heterotrophic bacteria on bSiO_2 dissolution in the PAR.
- There was a decrease in the ratio of bSiO_2 dissolution to production, and an increase in net bSiO_2 production in the western sector of the southeastern Chukchi Sea from 2013-2016. If sustained, this could significantly affect marine Si cycling and food web dynamics within the PAR and further into the Arctic.

Chapter 4: Diatoms in the Canadian Arctic Ocean: Silica production and diatom contributions to primary production and nitrogen uptake during the 2015 Canadian Arctic GEOTRACES

- Rates of bSiO_2 production in the Eastern Canadian Arctic and Labrador Sea were lower than those observed in the Bering and Chukchi Seas, but comparable to some areas of the Southern Ocean.
- Diatoms contributed to the majority of primary production and nitrate utilization, which is consistent with previous studies.
- A discrepancy in the specific and absolute bSiO_2 production rates implied the onset of a later, second diatom bloom in Baffin Bay, which may be linked to recent losses in Arctic sea-ice.
- There was widespread Si limitation that was intense enough in some areas to not only limit Si uptake, but also diatom growth.
- Diatom assemblages in the Eastern Canadian Arctic were inefficient at taking up Si at low concentrations compared to assemblages from more temperate ecosystems. This inefficiency appears to be ubiquitous in the polar oceans, and is likely driven by both lower temperatures and potentially also lower light levels.

Chapter 5: From the Pacific Arctic Region to the Labrador Sea: Natural Variations in dissolved silicon isotopes across Subarctic and Arctic Seas during 2015

- $\delta^{30}\text{Si}(\text{OH})_4$ signals track how bSiO_2 production modifies the nutrient-rich Pacific-origin waters on their transit from west to east through the Arctic.
- bSiO_2 dissolution influences the $\delta^{30}\text{Si}(\text{OH})_4$ signatures of the isolated deep waters of the Canada Basin and Baffin Bay, with the deep, high $[\text{Si}(\text{OH})_4]$ anomaly of

Baffin Bay potentially being entirely supplied by bSiO_2 dissolution rather than sediment remineralization. In the Canada Basin, it is possible that dissolution of sponge spicules may be contributing to the $\delta^{30}\text{Si}(\text{OH})_4$ signals measured near the bottom of the water column.

- $\delta^{30}\text{Si}(\text{OH})_4$ signals also reflect the modification that occurs in NE Atlantic-origin water masses as they follow different pathways through the Arctic.
- Water column $\delta^{30}\text{Si}(\text{OH})_4$ measurements have the potential to be a simple and effective method to estimate the relative proportion of annual sea-ice algae production to total primary production provided our assumptions about the Si isotope systematics of the sea-ice/water column system are correct.

Appendix A: Kinetics of Silicon Utilization: Silicon limitation and low kinetic efficiencies of diatom assemblages in the Pacific Arctic Region from 2013 – 2016

- Silicon limitation of bSiO_2 production was ubiquitous throughout the Pacific Arctic Region.
- Half-saturation constants ranged from 5.93 to 9.68 $\mu\text{mol L}^{-1}$, and V_{max} ranged from 0.053 to 0.404 d^{-1} .
- Depth profiles of the Si limitation index (Enh) exhibited differences in the vertical structure of limitation; however, Si limitation was observed throughout the water column southeastern Chukchi Sea.

Appendix B: Phytoplankton biomass and productivity on the 2015 Canadian Arctic GEOTRACES

- Vertical profiles of NO_3^- show depleted concentrations in the top ~20 m of the euphotic zone that increased with depth. Ammonium concentrations were more

spatially variable, though concentrations were generally highest at depths deeper than 20 m.

- Profiles of total Chl *a* exhibited subsurface maxima, and concentrations increased northwards to a maximum near the ice-edge station at CAA6. The greatest contribution of phytoplankton >20 μm to Chl *a* was found at stations in the CAA.
- Rates of ρC and ρNO_3 were highest in the upper 40 m of the water column, while the highest rates of ρNH_4 were observed at depths below 40 m except in Davis Strait and the Labrador Sea.
- Depth-integrated distributions of all nutrients and phytoplankton biomass and productivity were spatially variable, and not all parameters exhibited the same trends.

Appendix C: A comparison of collection and storage methods for dissolved silica samples

- For all samples collected for $[\text{Si}(\text{OH})_4]$ from 2014 to 2016 in the PAR, samples stored at 4°C and filtered through a 0.6 μm polycarbonate filter had a lower mean coefficient of variation (CV = 8%) compared to samples stored at -20°C and filtered through glass-fibre filters (CV = 16%).

Appendix D: Recycling of biogenic silica in the Canadian Arctic Ocean during the 2015 Canadian Arctic GEOTRACES

- No consistent spatial trends in ΔbSiO_2 or $\rho\text{Si}_{\text{diss}}$ were observed.
- The highest rates of $\rho\text{Si}_{\text{diss}}$ and ΔbSiO_2 were observed at stations in the CAA.
- The ratio of bSiO₂ dissolution to production ranged from 0.02 to 0.96, with an average of 0.51 for the entire sampling transect from the Labrador Sea to the CAA,

indicating that approximately 50% of the bSiO₂ production in the euphotic zone is recycled.

Appendix E: Estimating the biogenic ³⁰Si fractionation factor in surface waters from the Canada Basin to Baffin Bay using water mass composition data from a preliminary Optimum Multiparameter Analysis (OMP)

- The mean ($\pm 1\text{SE}$) biogenic ³⁰Si fractionation factor calculated for surface waters from the Canada Basin to Baffin Bay was $-0.47 \pm 0.04\text{‰}$ using the closed system model of Si isotope systematics, and $-1.08 \pm 0.15\text{‰}$ using the open system model.

2. Overall Conclusions and Implications

The research in this dissertation aimed to answer five specific questions, which are listed again here for ease of reference:

1. What is the contribution of diatoms to marine primary production and NO₃⁻ uptake in the Arctic?
2. What is the contribution of diatoms to the phytoplankton assemblages?
3. What spatial and temporal variations exist in the bSiO₂ dynamics of Arctic surface waters?
4. To what extent are diatoms limited by the availability of Si in the Arctic?
5. How do $\delta^{30}\text{Si}(\text{OH})_4$ signals change across Arctic ecosystem regimes and how do these variations relate to Si utilization and supply?

In response to questions (1) and (2), the research presented in this thesis has confirmed that diatoms dominate the phytoplankton assemblage and drive the productivity in regions influenced by the nutrient-rich Pacific-origin waters as they flow through the Arctic from the Bering Strait to Baffin Bay. Rates of bSiO₂ production increased from the

Bering Sea to a maximum in the Chukchi Sea (western sector), and then decreased through the Canadian Arctic Archipelago, Baffin Bay and finally into the Labrador Sea (eastern sector), answering question (3). Furthermore, simultaneous cruises within the western and eastern sectors of the North American Arctic in 2015 allowed for an unprecedented and methodologically consistent comparison of bSiO₂ production between these two regions. The highest rates of bSiO₂ production observed in the western ‘hotspot’ within the Chukchi Sea were ~5 times higher than the highest rates measured in the eastern ‘hotspot’ within the Canadian Arctic Archipelago (Figure 4).

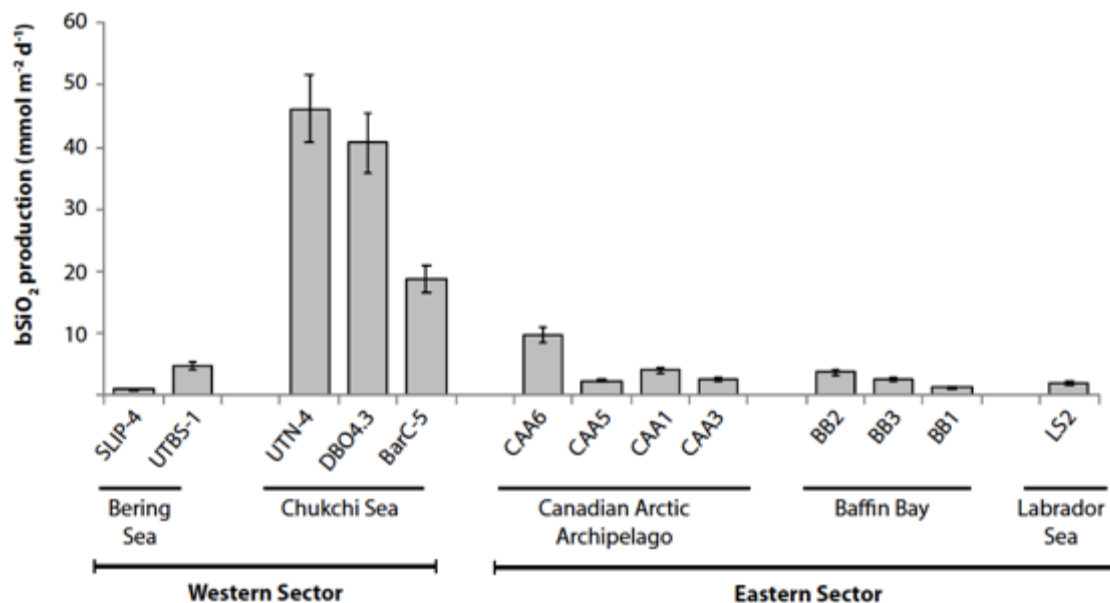


Figure 4. Depth-integrated rates of bSiO₂ production measured in the western and eastern sectors of the North American Arctic in July-August 2015. See Chapters 2 and 4 for sampling dates, station locations, and methodological details. The western sector contains stations within the Bering and Chukchi Seas. The eastern sector contains stations within the Canadian Arctic Archipelago, Baffin Bay and the Labrador Sea. Error bars represent ± 1 SD based on triplicate measurements.

This decrease in bSiO₂ production from west to east is consistent with the decrease in [Si(OH)₄] and increase in $\delta^{30}\text{Si}(\text{OH})_4$ observed within the Pacific-origin waters as they transit from the Bering Strait to Baffin Bay (Figure 5.4e), which provides insight to question (5). The observed spatial and interannual variability in bSiO₂ production is

consistent with the inherent heterogeneity expected of the marine ecosystems of the Arctic, but also indicates that the spatial variability observed can both influence and be influenced by the modification of water masses that transit through the Arctic (e.g. Sakshaug, 2004; Codispoti et al., 2013; Varela et al., 2013).

Chapters 2 and 4 discussed the influence of light and Si availability on bSiO_2 production, and the inefficiency of polar marine diatom assemblages in taking up Si(OH)_4 at low concentrations. These chapters provided a detailed answer to question (4), and further expanded on this question to also include the impact of light on bSiO_2 production. Although NO_3^- is believed to be the main limiting nutrient in Arctic marine waters, this work has shown that the influence of Si(OH)_4 on diatom growth should not be overlooked. Changes in relative distribution of NO_3^- or Si(OH)_4 could result in significant changes in the composition of phytoplankton assemblages, which could further impact food-web dynamics and biogeochemical cycling. The influence of light on bSiO_2 production seems to primarily affect the kinetic efficiency of diatom Si utilization, with increasing light making diatoms more efficient at taking up Si(OH)_4 at low concentrations. Increases in the amount of available light to the euphotic zone due to decreased sea-ice extent could thus result in diatoms becoming more kinetically efficient in utilizing Si. This could mitigate potential decreases in nutrient supply, but could also lead to changes in the Si:C:N ratios as the metabolisms of C and N become decoupled from that of Si under low light conditions. Such changes could subsequently impact the diatom contribution to the biological carbon pump and downward fluxes of bSiO_2 and N in the Arctic.

In answering questions (1) through (3), this research also provided evidence of how changing sea-ice conditions are driving changes in phytoplankton phenology throughout the Arctic. A decrease in the contribution of diatoms and in bSiO_2 production in the northern Bering Sea suggests that the timing of the seasonal bloom in this region is shifting to earlier in the season due to earlier sea-ice break-up. In Baffin Bay, the high specific rates of bSiO_2 production observed compared to other regions in the Eastern Canadian Arctic indicate that a second, later diatom bloom may have been forming at the time of our sampling in August. This is consistent with previous studies in the region which link the appearance of fall blooms with changes in sea-ice. We also found evidence of changes in the dissolution and recycling of bSiO_2 within the euphotic zone of the southeastern Chukchi Sea, which may indicate an increase in the export of bSiO_2 to the benthos. The Arctic is an important link between the two ends of the global thermohaline circulation, exporting nutrients from the Pacific to the NE Atlantic Ocean. The north Bering Sea and the Bering Strait act as the main import gateway for Si(OH)_4 to the Arctic, while Baffin Bay and Davis Strait act as the main export gateway (Torres-Valdez et al., 2013). As such, changes in the contribution of diatoms to the phytoplankton assemblage, in rates of bSiO_2 production, or in the recycling of Si(OH)_4 from these nutrient-rich waters as they transit through the Arctic could have far reaching effects on biogeochemical fluxes not only within the Arctic, but also on a global scale.

3. Future Studies

A number of additional research questions arose from the work presented in this thesis. Future studies that would complement the results of this thesis include:

- i. Seasonality of phytoplankton and marine bSiO_2 dynamics in the PAR. While the research presented in this thesis focussed on interannual variability in the PAR,

little is known about the seasonality of these processes. Field studies focussing on the periods earlier and later in the growing season would provide a broader picture of annual Si cycling in the PAR and how representative the summertime measurements presented in Chapters 1 and 2 are of these processes.

- ii. The interacting effects of light and Si(OH)_4 on bSiO_2 production. Controlled field experiments where a single diatom assemblage is exposed to a series of light levels and Si(OH)_4 concentrations would help to confirm and better understand the interacting effects of light and Si(OH)_4 on bSiO_2 production that were observed for the ‘regional diatom assemblage’ in the PAR in Chapter 2.
- iii. Links between Al and Si with respect to bSiO_2 dissolution in the PAR.
Measurements of dissolved seawater [Al] in the PAR, and the Al content of bSiO_2 may help to explain the high bSiO_2 dissolution rates we observed in these waters in Chapter 3.
- iv. Heterotrophic bacterial activity and its impact on bSiO_2 dissolution in the PAR.
Heterotrophic bacteria are known to break down the organic coating on diatoms, thus enhancing bSiO_2 dissolution. Better understanding of the distribution and activity of heterotrophic bacteria in the PAR, and how these measurements correlate to bSiO_2 dissolution rates could also help to understand the high bSiO_2 dissolution rates we observed in these waters in Chapter 3.
- v. Light and temperature effects on the kinetic efficiencies of polar and temperate marine diatoms. Laboratory culture experiments producing Si kinetic curves at different light and temperature levels may clarify why polar marine diatoms are

more inefficient at taking up Si(OH)_4 at low concentrations compared to temperate diatoms as observed in Chapter 4.

- vi. Field and/or laboratory studies to investigate Si and NO_3^- co-limitation. Also to investigate whether other sources of N, i.e. NH_4^+ or urea, serve as a suitable N source for polar diatoms when seawater $[\text{NO}_3^-]$ is depleted. Results from such studies would complement our results in Chapter 4, which showed that addition of Si(OH)_4 enhanced bSiO_2 production despite very low $[\text{NO}_3^-]$.
- vii. Marine bSiO_2 and $\delta^{30}\text{Si}$ dynamics around the eastern and western coasts of Greenland, and in Fram Strait and the Barents Sea. Our work from Chapter 5 shows differences in the $\delta^{30}\text{Si(OH)}_4$ signatures of NE Atlantic-origin water that follows two different pathways through the Arctic. Further study of marine Si cycling along these pathways would help to elucidate the processes modifying the $\delta^{30}\text{Si(OH)}_4$ signals in these water masses as they flow into and through the Arctic.
- viii. Measuring the Si isotope fractionation factor in sea-ice diatoms and differentiating between the ‘apparent’ and observed fractionation factor for the sea-ice/water column system. In Chapter 5, we assume that bSiO_2 production in the sea-ice/water column system acts in a similar manner to that of denitrification in the sediment/water column system, such that the apparent fractionation factor for sea-ice diatoms is 0‰ when considering their impact on seawater $\delta^{30}\text{Si(OH)}_4$. Confirmation of this assumption would further support using $\delta^{30}\text{Si(OH)}_4$ measurements to estimate sea-ice algae production.
- ix. Fractionation of Si isotopes during bSiO_2 dissolution. The literature remains unclear on how and to what extent Si isotopes are potentially fractionated during

bSiO₂ dissolution in the water column or within sediments. Several studies have looked at Si fractionation during bSiO₂ dissolution, but experiments were conducted under different conditions using different types of bSiO₂ (e.g. ‘fresh’, recently exported, sediments) and dissolution methods (e.g. seawater, NaOH) with mixed results. A future study using consistent methods and a range of bSiO₂ ‘types’ and dissolution conditions would help to more definitively identify the extent of Si fractionation during bSiO₂ dissolution.

- x. $\delta^{30}\text{Si}$ dynamics in the sediment/pore-water system. Future studies looking at how $\delta^{30}\text{Si}$ -bSiO₂ signals in sediments translate into pore-water and overlying seawater $\delta^{30}\text{Si}(\text{OH})_4$ signals would help to elucidate the impact of sedimentary Si fluxes on seawater $\delta^{30}\text{Si}(\text{OH})_4$. Currently only one study in the highly productive Peruvian upwelling system has investigated these processes, and the applicability of these results on a broader scale is unclear.
- xi. Mechanistic modelling study to investigate the controls on diatom productivity in Arctic marine ecosystems. Such studies could include models to investigate the potential physiological basis for the interacting effects of light and Si(OH)₄ on bSiO₂ production. Another model study could look at the effect of light and temperature on the kinetic efficiencies of diatoms, and whether it is indeed these parameters that make polar diatoms less efficient at using lower concentrations of Si(OH)₄. These models might also help elucidate what effect climate-induced changes such as warming and increased light availability might have on Si:C:N ratios if models of diatom C and N metabolism are also incorporated.

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Appendix A.

Kinetics of Silicon Utilization: Silicon limitation and low kinetic efficiencies of diatom assemblages in the Pacific Arctic Region from 2013 – 2016

A.1 Objective

To assess the extent of Si limitation from summer field experiments conducted over a period of four years in the Pacific Arctic Region, evaluate any spatial or interannual variability in this limitation, and identify any temporal trends that could be linked to changes in environmental parameters such as sea-ice extent or temperature.

A.2 Introduction

The highly productive waters of the Pacific Arctic Region (PAR) are dominated by diatoms (Gosselin et al., 1997; Varela et al., 2013; Crawford et al., 2018; Chapter 1). Spanning from the northern Bering Sea to the Arctic Basin, the PAR encompasses areas influenced by the advection of Pacific waters into the Arctic. The northward flow of these waters brings nutrients, heat and freshwater to the shallow shelves of the Bering and Chukchi Seas, supporting a highly productive ecosystem with a strong degree of pelagic-benthic coupling (e.g. Grebmeier and McRoy, 1989; Grebmeier et al., 2006a; Serreze et al., 2006, Woodgate et al., 2010). The PAR is also one of the fastest changing marine environments, with climate-induced changes such as declining sea-ice and increasing ocean temperatures driving shifts in phytoplankton bloom timing and magnitude, which in turn affects marine species composition and carbon cycling (e.g. Overland and Stabeno, 2004; Grebmeier et al., 2010, 2012, 2015; Moore et al., 2014, 2015; Nelson et al., 2014). Although nutrient stocks are generally high within the PAR, water mass differences, biological utilization and interannual variability can result in low concentrations, especially in surface waters, which, in turn, can affect primary

productivity (Walsh et al., 1989; Lee et al., 2007, 2012, 2013; Chapter 1). One method for investigating how changing nutrient supply will affect primary productivity is through field-based nutrient kinetic experiments (e.g. Nelson et al., 2001), which can be used to assess and predict nutrient limitation of phytoplankton communities.

Diatoms have an obligate need for silicon (Si), which they convert to biogenic silica (bSiO_2) to form their siliceous cell walls (frustules). The main form of dissolved Si available at seawater pH is orthosilicic acid (Si(OH)_4), which diatoms actively transport immediately prior to silica polymerization and cell division (Brzezinski et al., 1990). Nutrient transport across the cell membrane can be thought of in a manner similar to Michaelis-Menten enzyme kinetics (Dugdale, 1967), where transport is saturable and the specific rate of nutrient uptake (V) into a cell is dependent on the ambient nutrient concentration ([nutrient]). For Si, this relationship is described by:

$$V = \frac{V_{\max}[\text{Si(OH)}_4]}{(K_s + [\text{Si(OH)}_4])} \quad (1)$$

where $V_{\max}$ represents the maximum uptake rate, or saturable limit of nutrient acquisition when the given nutrient is not limiting, and K_s the half-saturation constant, or the [nutrient] at which V is equal to $V_{\max}/2$. For Si, diatoms typically reach $V_{\max}$ when the $[\text{Si(OH)}_4]$ is above $0.2 - 8 \mu\text{mol L}^{-1}$, though this depends on the diatom species (Martin-Jézéquel et al., 2000). In the PAR, surface $[\text{Si(OH)}_4]$ can be significantly depleted by diatom utilization, to concentrations as low as $0.5 - 1 \mu\text{mol L}^{-1}$, which suggests that diatoms may experience Si limitation in this region.

Specific growth rate (μ) also responds to the ambient nutrient concentration, and can be described by a similar equation as shown above, but with V replaced with μ , $V_{\max}$ with $\mu_{\max}$ (the maximum specific growth rate) and K_s with K_μ (the [nutrient] where $\mu =$

$\mu_{\max}/2$). At steady state, these equations are equivalent (i.e. $V = \mu$); however, studies have shown that K_{μ} is often much smaller than K_S , which is a result of acclimation strategies of the organisms. In other words, ambient nutrient concentrations can limit uptake without limiting growth. When uptake is limited, phytoplankton can avoid growth limitation by changing both their internal nutrient quotas and their maximum short-term nutrient uptake rates in response to variability in ambient nutrient concentrations (Morel, 1987). For example, when Si uptake is limited in diatoms, cells produce less silicified frustules (Harrison et al., 1977; Martin-Jézéquel et al., 2000) and may increase their cellular C quotas resulting in decreased Si:C ratios (Flynn and Martin-Jézéquel, 2000). In turn, changes in the Si:C ratio may affect the export efficiency of diatom cells which account for a disproportionate amount of the biological export of carbon (Buesseler, 1998).

A.3 Methods

A.3.1 Sampling locations and seawater sampling

Sampling was conducted within the five identified Distributed Biological Observatory (DBO) hotspot regions in the northern Bering and Chukchi Seas for the stations and cruises from July 2013-2016 as described in Chapters 1-3. In 2013, seawater samples were collected at six depths corresponding to light levels of 100%, 55%, 30%, 15%, 1% and 0.1% of the surface incident irradiance (I_0). In 2014-2016, seawater samples were only collected at 55% I_0 . For each sampling depth, we measured $[\text{Si}(\text{OH})_4]$ and $[\text{bSiO}_2]$, and ambient and augmented bSiO_2 production rates using the radioisotope ^{32}Si (ρSi), where augmented samples received an addition of isotopically natural (non-radioactive) $\text{Si}(\text{OH})_4$ to increase the $[\text{Si}(\text{OH})_4]$ in the sample.

A.3.2 Dissolved and particulate silica concentrations

Water samples for dissolved and particulate silica concentrations (bSiO_2 and lSiO_2) were collected and processed as described in Chapter 2.

A.3.3 Kinetics of silicon utilization

Standard and two-point $[\text{Si}(\text{OH})_4]$ kinetic experiments were conducted to examine the response of the ambient diatom assemblage to increase $\text{Si}(\text{OH})_4$ availability. For the standard kinetic experiments, a single sample of near-surface seawater (55% I_0 , 4 – 8 m depth) was collected and divided into eight 300 mL subsamples contained in acid-cleaned polycarbonate bottles. Samples were then augmented with a non-radioactive $\text{Si}(\text{OH})_4$ solution to produce a final $[\text{Si}(\text{OH})_4]$ ranging from ambient to $20 \mu\text{mol Si L}^{-1}$ above the ambient concentration. Following this addition, samples were mixed and then 370 Bq of high specific activity $^{32}\text{Si}(\text{OH})_4$ ($\sim 25,000 \text{ MBq } \mu\text{mol Si}^{-1}$) was added, except for samples where $[\text{Si}(\text{OH})_4]$ additions were $> 8 \mu\text{mol L}^{-1}$. For these samples, 1110 Bq of $^{32}\text{Si}(\text{OH})_4$ was added to enhance the final specific activity of the tracer and ensure measurement sensitivity. Samples were then incubated for 24 h at 50% I_0 and processed as for ρSi as described in Chapter 2.

Specific uptake rates (V_{Si} , d^{-1}) were calculated as in Brzezinski and Phillips (1997) using the measured ^{32}Si activity in the samples, the final $[\text{Si}(\text{OH})_4]$ (ambient + added Si), and the ambient $[\text{bSiO}_2]$. This first type of experiment was conducted in all DBO regions sampled in 2013, and in DBO1 and DBO3E in 2014, for a total of seven experiments. Data from the experiments were fitted with the hyperbolic Michaelis-Menten function in equation (1), where V is the specific rate of $[\text{Si}(\text{OH})_4]$ utilization, $[\text{Si}(\text{OH})_4]$ the final concentration of silicic acid (ambient + added Si), V_{max} the maximum specific uptake rate, and K_s the half-saturation constant. Statistical outliers were identified by applying a linear

Woolf transformation of the Michaelis-Menten function and fitting a least squares regression. Any point where the residual was greater than twice the standard deviation of all the residuals of the experiment was considered an outlier and removed (Brzezinski et al., 2008). This resulted in the removal of no more than one point from any of the seven experiments. After removal of outliers, $V_{\max}$ and K_s were calculated using the least squares regression of the Woolf transformation.

The two-point kinetic experiments were similar to the standard experiments, except that ^{32}Si incubations were conducted at only two $\text{Si}(\text{OH})_4$ concentrations: ambient and $20 \mu\text{mol Si L}^{-1}$ above ambient. The experiments were performed at all stations sampled from 2013 – 2016. In 2013, experiments were conducted at all six light depths (100, 50, 30, 15, 1 and 0.1% I_0), while from 2014 onwards, samples were collected only from near-surface (either 100 or 50% I_0 , 2 – 11 m depth). The specific uptake rates from these experiments were used to determine the rate-enhancement statistic (Enh), which is defined as:

$$\text{Enh} = \frac{V_{\text{Si,enhanced}}}{V_{\text{Si,ambient}}} \quad (2)$$

where $V_{\text{Si,enhanced}}$ is the specific uptake rate at $20 \mu\text{mol Si L}^{-1}$ above ambient, and $V_{\text{Si,ambient}}$ is the specific uptake rate at ambient $[\text{Si}(\text{OH})_4]$ (Brzezinski et al., 1997). This statistic assumes that the addition of $20 \mu\text{mol L}^{-1}$ saturates the Si uptake, such that when $\text{Enh} \approx 1.0$, it indicates that the ambient $[\text{Si}(\text{OH})_4]$ was not limiting to the natural diatom assemblage. In contrast, $\text{Enh} > 1.0$ indicates that ambient $[\text{Si}(\text{OH})_4]$ was limiting the rate of Si uptake, with greater values of Enh indicating the severity of the limitation. Given the uncertainties associated with each estimate of V_{Si} (CV = 14%, from Chapter 2), Enh values must be above 1.2 to be indicative of Si limitation. Specific uptake rates from the two-point kinetic experiments can also be used to estimate $V_{\max}$ and K_s assuming that $V_{\text{Si,enhanced}}$ and $V_{\text{Si,ambient}}$

represent two points on a Michaelis-Menten hyperbola (Equation 1) and using the equations described by Nelson et al. (2001).

A.4 Results

A.4.1 Standard kinetic experiments

Silicon limitation of biogenic silica production was observed in six out of the seven standard kinetic experiments performed (Figure A1, Table A1). Three types of functional relationships between V_{Si} and increasing $[Si(OH)_4]$ were observed in the standard kinetic experiments: Michaelis-Menten, linear, and sigmoidal dose-response. Experiments in DBO1, DBO3W and DBO4-5 exhibited Michaelis-Menten kinetics, although in DBO1 in 2014, a Michaelis-Menten relationship was only observed up to $4 \mu\text{mol L}^{-1}$ (Figure A1a,c,e-f). Beyond $4 \mu\text{mol L}^{-1}$, the response of V_{Si} to increasing $[Si(OH)_4]$ in DBO1 in 2014 was linear, with no further indication of a saturation of V_{Si} and thus no information on V_{max} or K_s can be obtained (Figure A1a). In DBO2, V_{Si} exhibited no measurable increase in response to increasing $[Si(OH)_4]$ such that the only information on K_s that can be obtained is that $K_s < \text{ambient } [Si(OH)_4]$ (Figure A1b). In DBO3E, specific uptake rates exhibited a sigmoidal dose-response to increasing $[Si(OH)_4]$, with rates that did eventually saturate (Figure A1d). Both V_{max} and K_s can be estimated from the sigmoidal relationship found in DBO3E (e.g. Thamtrakoln and Hildebrand, 2008).

Half-saturation constants obtained from the standard kinetic experiments were between 5.93 and $9.68 \mu\text{mol L}^{-1}$, with V_{max} ranging from 0.053 to 0.404 d^{-1} (Table A1). The ratio of $V_{Si, \text{ambient}}/V_{max}$ indicates the degree to which ambient $[Si(OH)_4]$ has limited silica production rates from their maximum potential rates; however, given the uncertainties associated with estimates of $V_{Si, \text{ambient}}$ and V_{max} , only values below 80% can be considered indicative of significant Si limitation. For this study, $V_{Si, \text{ambient}}/V_{max}$ ranged

from 10 – 87%, with a mean ($\pm$ SE) of $47 \pm 11\%$ (Table A1). The efficiency of Si uptake at low concentration is indicated by the steepness of the initial slope of a Michaelis-Menten curve ($V_{\max}/K_s$; Healey, 1980), with higher values corresponding to steeper slopes and more efficient Si uptake. In this study, values ranged from 0.11 – 1.74 ($\text{mmol L}^{-1} \text{h}^{-1}$), with the most efficient uptake occurring in DBO3W, and least efficient uptake occurring in DBO3E (Table A1). Interannual variability in the kinetics of Si uptake was observed in DBO1, including a difference in the functional relationship between V_{Si} and increasing $[\text{Si}(\text{OH})_4]$.

A.4.2 Two-point kinetic experiments

A total of 44 two-point kinetic experiments were performed from 2013 – 2016 (Tables A2 and A3), with significant Si limitation ($\text{Enh} > 1.2$) observed in 33 experiments. Depth profiles of Enh conducted in 2013 exhibited differences in the vertical structure of limitation (Figure A2). Si limitation was observed throughout the water column in DBO3W, in the upper euphotic zone (100, 55 and 30% I_0) for DBO1 and DBO4, and in the lower euphotic zone in DBO2 and DBO5 (Table A3; Figure A2).

A.4.3 Estimating the kinetic parameters from two-point kinetic experiments

The accuracy of estimating $V_{\max}$ and K_s from the two-point kinetic experiments can be evaluated by comparing the parameters calculated from the standard experiments with two-points of data from those same experiments, i.e. using only the two points at ambient and $+20 \mu\text{mol L}^{-1} [\text{Si}(\text{OH})_4]$ (Figure A3). The experiment in DBO1 in 2014 showing linear kinetics was not included in the comparison. For DBO3E, $V_{\max}$ and K_s for the comparison were calculated from a Michaelis-Menten fit of the standard experiment. While this is not the best fit of the data from this experiment, it is more comparable to what is calculated from the two-point experiments, given that the parameters calculated

from the two-point experiments assume Michaelis-Menten kinetics. The $V_{\max}$ calculated using the two-point kinetic experiments was $133\% \pm 7\%$ ($\pm$ SE, $R^2 = 0.92$, $p < 0.01$) of the $V_{\max}$ determined from the standard kinetic experiments. Removing the one high value for $V_{\max}$ ($\sim 0.4 \text{ d}^{-1}$) reduces the slope of the regression between the $V_{\max}$ estimates to $106\% \pm 9\%$ ($\pm$ SE, $R^2 = 0.98$, $p < 0.01$). The K_s calculated using the two-point kinetic experiments was $110\% \pm 21\%$ ($\pm$ SE, $R^2 = 0.90$, $p = 0.014$) of the K_s calculated from the standard kinetic experiments. These results suggest that the $V_{\max}$ and K_s determined from the two-point kinetic experiments agree well with those from the standard experiments, although values are potentially slightly overestimated.

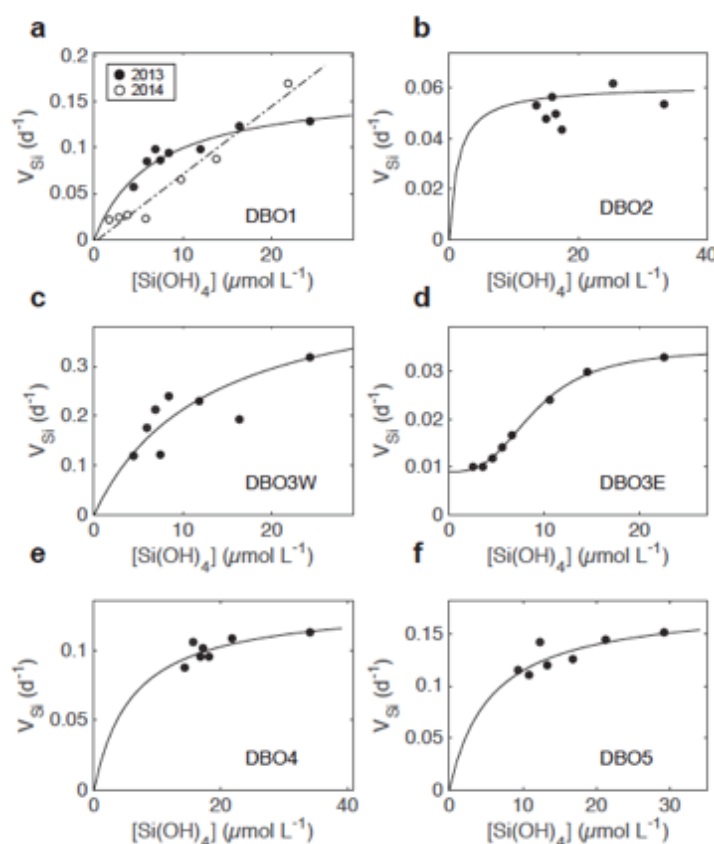


Figure A.1. Standard kinetics curves from 55% I_0 showing the response of specific uptake (V_{si}) to increasing $[\text{Si}(\text{OH})_4]$. (a) DBO1 for 2013 and 2014, (b) DBO2 for 2013, (c) DBO3W for 2013, (d) DBO3E for 2014, (e) DBO4 for 2013, and (f) DBO5 for 2013. The solid line curve fit is the Michaelis-Menten function for all panels except (d), which is a sigmoidal dose-response curve. The dashed line in (a) is linear regression through the 2014 data for DBO1. Note the different V_{si} and $[\text{Si}(\text{OH})_4]$ scales between regions.

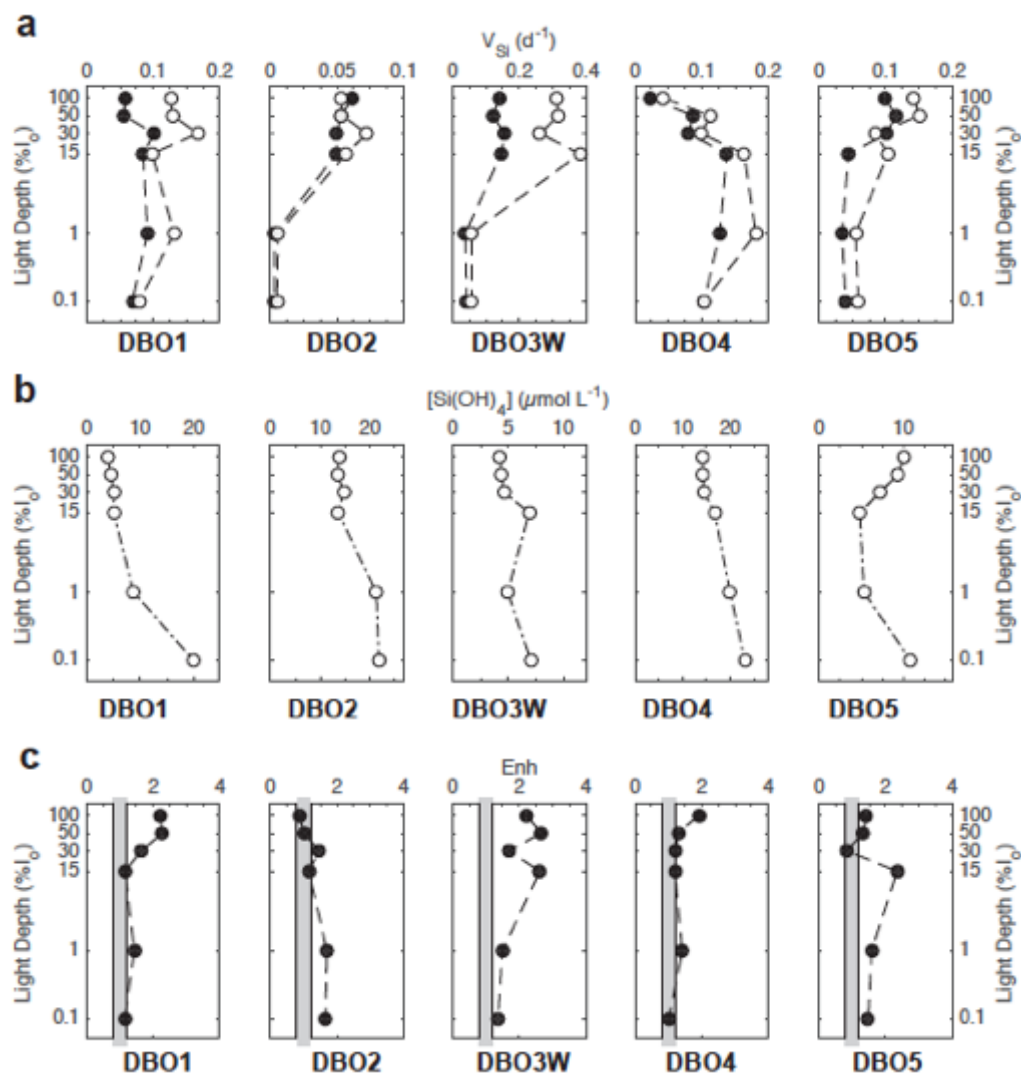


Figure A.2. Assessment of kinetic responses within the euphotic zone for the five DBO regions. Depth profiles of (a) $V_{Si,ambient}$ (black dots) and $V_{Si,enhanced}$ (white dots), (b) ambient silicic acid concentrations, and (c) the enhancement statistic, Enh. The grey shaded bar in (c) signifies the range of Enh values (0.8 – 1.2) where no Si limitation is observed. Note the different scales for V_{Si} and $[Si(OH)_4]$ between regions.

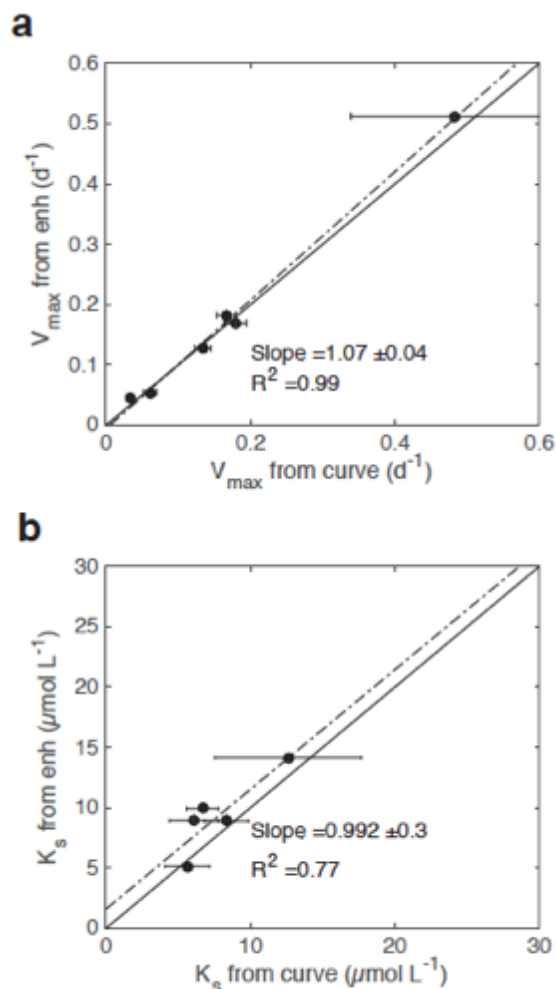


Figure A.3. Direct comparison of calculation methods for (a) $V_{\max}$, and (b) K_s . All standard kinetic experiments were used except for DBO1 in 2014, which exhibited linear kinetics and so K_s and $V_{\max}$ could not be calculated. Parameters $\pm$ SE (error bars) from the standard kinetic curves (x-axis) were determined using a nonlinear curve fitting algorithm (Matlab 2014b). Parameters on the y-axis were determined algebraically (Nelson et al., 2001) using the $V_{\text{Si,ambient}}$, $V_{\text{Si,enhanced}}$ and $[\text{Si}(\text{OH})_4]$ from the two-point enhancement (Enh) experiments. Solid lines are a 1:1 relationship. Dashed lines are a least-squares linear regression with the slope($\pm$ SE) and R^2 listed in each panel.

Table A.1. Results from the standard kinetic curve experiments conducted at 55%I₀ within each DBO region in 2013 and in DBO1 and DBO3E in 2014. Concentrations of dissolved ([Si(OH)₄] and biogenic silica ([bSiO₂]) are also shown. Error terms are standard error (SE). Error terms for V_{amb}:V_{max} and V_{max}:K_s and kinetic parameter means are derived using error propagation.

Year	Region	[Si(OH) ₄] (μmol L ⁻¹)	[bSiO ₂] (μmol L ⁻¹)	V _{Si,ambient} (d ⁻¹)	V _{max} (d ⁻¹)	K _s (μmol L ⁻¹)	V _{amb} :V _{max} (%)	V _{max} :K _s (mmol L ⁻¹ h) ⁻¹	Functional Relationship
2013	DBO1	4.5	0.4	0.057	0.166 ± 0.013	6.7 ± 1.1	34 ± 6	1.04 ± 0.19	Michaelis-Menten
	DBO2	13.5	3.3	0.053	0.061 ± 0.009	<13	87 ± 28	-	Michaelis-Menten
	DBO3W	4.4	8.7	0.120	0.482 ± 0.143	12.6 ± 5.1	25 ± 15	1.59 ± 0.80	Michaelis-Menten
	DBO4	14.2	10.3	0.088	0.134 ± 0.011	6.1 ± 1.7	65 ± 12	0.92 ± 0.27	Michaelis-Menten
	DBO5	9.3	4.8	0.115	0.179 ± 0.015	5.6 ± 1.5	64 ± 12	1.33 ± 0.38	Michaelis-Menten
2014	DBO1	1.8	0.04	0.001	-	-	-	-	Linear
	DBO3E	2.5	1.4	0.010	0.034 ± 0.002	8.3 ± 1.5	30 ± 4	0.17 ± 0.03	Sigmoidal
Mean ± SE		7.2 ± 2.0	4.1 ± 1.5	0.063 ± 0.018	0.176 ± 0.066	7.9 ± 1.3	51 ± 10	1.01 ± 0.24	

Table A.2. Results from the two-point kinetic experiments conducted at six depths in the euphotic zone within each DBO region in 2013. Concentrations of dissolved ($[\text{Si}(\text{OH})_4]$) and biogenic silica ($[\text{bSiO}_2]$) are also shown. Kinetic parameters V_{max} and K_s are derived algebraically (Nelson et al., 2001).

Region	Depth (%I ₀)	$[\text{Si}(\text{OH})_4]$ ($\mu\text{mol L}^{-1}$)	$[\text{bSiO}_2]$ ($\mu\text{mol L}^{-1}$)	$V_{\text{Si,ambient}}$ (d^{-1})	Enh	V_{max} (d^{-1})	K_s ($\mu\text{mol L}^{-1}$)	$V_{\text{amb}}:V_{\text{max}}$ (%)	$V_{\text{max}}:K_s$ ($\text{mmol L}^{-1} \text{ h}^{-1}$) ⁻¹
DBO1	100	0.39	0.39	0.0573	2.20	0.17	7.57	34%	0.92
	50	0.36	0.36	0.0567	2.28	0.18	9.92	31%	0.76
	30	0.30	0.30	0.1013	1.65	0.20	5.03	51%	1.66
	15	1.45	1.45	0.0850	1.16	0.10	-	83%	-
	1	11.05	11.05	0.0914	1.44	0.16	6.92	56%	0.98
	0.1	5.97	5.97	0.0691	1.15	0.09	-	74%	-
DBO2	100	3.28	3.28	0.0610	0.87	0.05	-	126%	-
	50	3.27	3.27	0.0532	1.01	0.05	-	99%	-
	30	2.78	2.78	0.0497	1.46	0.11	17.98	45%	0.26
	15	2.92	2.92	0.0496	1.15	0.06	-	79%	-
	1	6.76	6.76	0.0033	1.66	0.02	101.09	17%	0.01
	0.1	7.32	7.32	0.0029	1.65	0.02	102.37	18%	0.01
DBO3W	100	8.51	8.51	0.1407	2.22	0.42	8.52	33%	2.06
	50	8.69	8.69	0.1196	2.66	0.50	14.21	24%	1.48
	30	9.41	9.41	0.1559	1.68	0.31	4.57	50%	2.83
	15	11.60	11.60	0.1455	2.62	0.87	34.62	17%	1.05
	1	14.19	14.19	0.0376	1.48	0.06	3.39	59%	0.78
	0.1	14.28	14.28	0.0418	1.36	0.07	3.98	64%	0.68
DBO4	100	11.65	11.65	0.0224	1.91	0.12	64.87	18%	0.08
	50	10.26	10.26	0.0877	1.29	0.14	8.83	62%	0.67
	30	8.84	8.84	0.0803	1.24	0.12	7.14	67%	0.70
	15	6.08	6.08	0.1376	1.19	0.20	-	70%	-
	1	3.93	3.93	0.1273	1.42	0.32	29.62	40%	0.44
	0.1	12.14	12.14	0.1035	1.01	0.11	-	98%	-
DBO5	100	5.07	5.07	0.0999	1.43	0.18	8.20	55%	0.92
	50	4.81	4.81	0.1146	1.32	0.18	5.14	65%	1.44
	30	4.21	4.21	0.1020	0.83	0.08	-	128%	-
	15	7.50	7.50	0.0442	2.34	0.15	11.95	29%	0.54
	1	11.85	11.85	0.0347	1.58	0.06	4.59	54%	0.59
	0.1	9.69	9.69	0.0400	1.47	0.08	10.47	51%	0.31

Table A.3. Results from the two-point kinetic experiments conducted at 100% or 55% I_0 within each DBO region sampled from 2013 to 2016. Concentrations of dissolved ([Si(OH)₄] and biogenic silica ([bSiO₂]) are also shown. Kinetic parameters V_{max} and K_s are derived algebraically (Nelson et al., 2001).

Year	Region	Depth (% I_0)	[Si(OH) ₄] ($\mu\text{mol L}^{-1}$)	[bSiO ₂] ($\mu\text{mol L}^{-1}$)	$V_{Si,ambient}$ (d^{-1})	Enh	V_{max} (d^{-1})	K_s ($\mu\text{mol L}^{-1}$)	$V_{amb}:V_{max}$ (%)	$V_{max}:K_s$ ($\text{mmol L}^{-1} \text{ hr}^{-1}$)
2013	DBO1	55	4.49	0.36	0.057	2.28	0.18	9.92	31%	0.76
	DBO2	55	13.54	3.27	0.053	1.01	0.05	-	99%	-
	DBO3W	55	4.42	8.69	0.120	2.66	0.50	14.21	24%	1.48
	DBO4	55	14.22	10.26	0.088	1.29	0.14	8.83	62%	0.67
	DBO5	55	9.35	4.81	0.115	1.32	0.18	5.14	65%	1.44
2014	DBO1	55	1.75	0.04	0.022	7.74	0.41	31.08	5%	0.55
	DBO2	55	17.64	1.70	0.590	0.95	0.53	-	111%	-
	DBO3W	55	0.36	1.38	0.055	8.41	0.53	3.09	10%	7.20
	DBO3E	55	2.51	1.44	0.010	3.26	0.05	8.87	22%	0.21
	DBO4	55	15.36	0.87	0.149	0.78	0.10	-	150%	-
2015	DBO1	100	4.00	0.20	0.002	2.33	0.01	8.69	32%	0.02
	DBO2	100	27.32	1.96	0.111	1.63	1.32	297.14	8%	0.18
	DBO3W	100	20.15	4.00	0.853	1.00	0.85	-	100%	-
	DBO4	100	7.76	0.66	0.163	1.75	0.40	11.48	40%	1.47
	DBO5	100	7.45	0.31	0.172	0.63	0.09	-	181%	-
2016	DBO1	55	0.27	0.06	0.005	18.51	0.12	6.30	4%	0.76
	DBO2	55	14.91	0.23	0.031	1.99	0.24	101.59	13%	0.10
	DBO3W	55	1.90	14.17	0.072	5.10	0.60	14.01	12%	1.79
	DBO4	55	15.13	1.06	0.045	1.78	0.20	51.58	23%	0.16

Appendix B.

Phytoplankton biomass and productivity on the 2015 Canadian Arctic GEOTRACES

B.1 Objective

To investigate spatial variations in nutrient concentrations, phytoplankton biomass, and rates of carbon (C), nitrate (NO_3^-) and ammonium (NH_4^+) utilization in the euphotic-zone along a transect through the Canadian Arctic Ocean from the Labrador Sea to the Canadian Arctic Archipelago.

B.2 Introduction

The Arctic is a spatially heterogeneous system comprised of a range of ecosystems from the most productive to the most barren. Rapid changes are occurring in the Arctic due to climate-induced changes such as decreased sea-ice thickness and extent, lengthening ice-free periods and changes in the hydrological cycle (Peterson et al., 2002; Rawlins et al., 2010; Stroeve et al., 2011, 2014). These transformations have already been found to have an effect on phytoplankton assemblage composition and productivity (Li et al., 2009; Ardyna et al., 2014; Blais et al., 2017). Polar marine ecosystems are also especially sensitive to changes in phytoplankton assemblage composition and productivity due to their low number of trophic links (e.g. Grebmeier et al., 2006; Kortsch et al., 2015). While research efforts have increased in recent years, the Arctic remains one of the least studied regions of the world's oceans (Wassmann et al., 2011, 2015). In the face of climate-induced changes, the need for methodologically-consistent, pan-arctic studies of nutrient and phytoplankton dynamics is critically important if we are to better understand and predict ecosystem responses to any future changes.

B.3 Methods

B.3.1 Sampling Locations and Seawater Sampling

Water samples were collected at six depths corresponding to light levels of 100%, 50%, 30%, 15%, 1% and 0.2% of the surface incident irradiance (I_0) at the stations described in Chapter 4. At each light level, we measured particulate nitrogen (PN) and carbon (PC) concentrations and ^{13}C , $^{15}\text{NO}_3^-$ and $^{15}\text{NH}_4^+$ utilization rates (ρC , ρNO_3 , and ρNH_4). The precision of these analytical techniques was determined from triplicate subsamples collected at one or more depths at each station sampled. Seawater samples for dissolved nitrate (NO_3^-) and ammonium (NH_4^+) concentrations at the same depths were collected for the GEOTRACES program by Jean-Éric Tremblay (ULaval, Quebec). Samples for total and size-fractionated phytoplankton biomass (as Chl *a*) were also collected at the same depths for the GEOTRACES program by Michel Gosselin (ISMER, Quebec). The concentrations of silicic acid ($\text{Si}(\text{OH})_4$) and particulate silica (as bSiO_2 and lSiO_2), and bSiO_2 production rates using the radioisotope ^{32}Si (ρSi) collected from the same stations and depths are presented in Chapter 4.

B.3.2 Dissolved Nutrients

Water samples for dissolved NO_3^- concentrations were collected and processed on a nutrient autoanalyzer as described for $\text{Si}(\text{OH})_4$ in Chapter 4. Ammonium concentrations were determined by fluorometry following the method of Holmes et al. (1999).

B.3.3 Total and Size-Fractionated Phytoplankton Biomass (Chl *a*)

Seawater (0.1 – 0.5L) for total Chl *a* analysis was filtered onto 0.7 μm pore-size glass fibre filters (GF/F, Whatman). For size-fractionated Chl *a*, separate seawater (0.1 – 0.5L) samples were filtered onto 5 μm and 20 μm pore-size polycarbonate filters. The filtered Chl *a* was processed onboard as described in Chapter 1.

B.3.4 Carbon and Nitrogen Utilization Rates

Carbon and NO_3^- utilization rates were measured using a dual-tracer ^{13}C - $^{15}\text{NO}_3^-$ method as described in Chapter 1. Ammonium utilization rates were measured following the same methods as for the ^{13}C - $^{15}\text{NO}_3^-$ dual-tracer measurements, but using only ^{15}N labelled NH_4Cl (98 atom % ^{15}N , Cambridge Isotope Laboratories) to enrich samples. All samples were collected in 0.5L acid-washed polycarbonate containers and incubated and processed as described in Chapter 1. Ammonium utilization rates were calculated using equations (6) and (3) of Dugdale and Wilkerson (1986). When ambient concentrations of NH_4^+ were below the detection limit ($0.1 \mu\text{mol L}^{-1}$), a value equal to the NH_4^+ detection limit was used to calculate ρNH_4 . Therefore, under those conditions, ρNH_4 represent a potential maximum value of ρNH_4 . We estimated the error associated with our measurements to be $\pm 0.08 \mu\text{mol C L}^{-1} \text{ d}^{-1}$, $\pm 0.01 \mu\text{mol N L}^{-1} \text{ d}^{-1}$, and $\pm 0.004 \mu\text{mol N L}^{-1} \text{ d}^{-1}$, for ρC , ρNO_3 , and ρNH_4 respectively, based on the mean standard deviation of triplicate measurements collected at 100% I_0 at each station ($n = 10$).

B.3.5 Particulate Carbon and Nitrogen

Concentrations of PC and PN were measured from the dual-tracer ^{13}C - $^{15}\text{NO}_3^-$ incubation samples described above. Therefore, these PC and PN represent the particulate concentrations at the end of the 24 h incubation period. Values were corrected to ambient PC and PN concentrations by subtracting the measured utilization rate multiplied by the incubation time from the measured particulate concentration at the end of the incubation period. All values presented are corrected 'ambient' concentrations.

B.3.6 New Production and f-ratios

The ratio of NO_3^- to total N uptake, or f -ratio was calculated as: $f\text{-ratio} = (\rho\text{NO}_3 / \rho\text{NO}_3 + \rho\text{NH}_4)$. New primary production in C-based units (New-Prod) was calculated as $f * \rho\text{C}$.

B.3.7 Data organization and presentation

Data were depth-integrated using trapezoidal integration from the surface to the bottom of the euphotic zone (0.2% of surface irradiance). Figures B1-B2 were created using Ocean Data View version 5.0.0 (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2012). Data were grouped into sub-regions of the Canadian Arctic Archipelago (CAA), Baffin Bay (BB) and Labrador Sea (LS) as described in Chapter 4. Peel Sound, Barrow Strait and Lancaster Sound are all located within the CAA.

B.4 Results

Vertical profiles of NO_3^- show depleted concentrations in the top ~20 m of the euphotic zone, with values increasing to a maximum of up to $10 \mu\text{mol L}^{-1}$ at 0.2% I_0 (Figure B1b). Ammonium concentrations were more spatially variable, though concentrations were generally highest at depths deeper than 20 m (Figure B1d). Profiles of total Chl *a* exhibited subsurface maxima along the most of the transect, and increased northwards to a maximum near the ice-edge station at CAA6 (Figure B1c). The largest relative contributions of phytoplankton $>20 \mu\text{m}$ to Chl *a* (% Chl *a* $>20 \mu\text{m}$) were observed at stations in the CAA (Figure B1e). Rates of ρC and ρNO_3 were highest in the upper 40 m of the water column (Figure B1f-g). The highest rates of ρNH_4 were observed at depths >40 m in the BB and CAA regions, with the exception of Davis Strait. In the Labrador Sea and Davis Strait, ρNH_4 were highest in the upper 40 m.

Depth-integrated distributions of all nutrients and phytoplankton biomass and productivity were spatially variable, and not all parameters exhibited the same trends (Tables B1-B2; Figure B2). Values for $[\text{NO}_3^-]$ and $[\text{NH}_4^+]$ were highest in Davis Strait and the Labrador Sea, while chlorophyll *a* concentrations were highest value at the ice-edge station at CAA6 (Table B1; Figure B2a-c). Concentrations of PC and PN were

relatively high and invariable all along our sampling transect, with the lowest values being observed in Peel Sound at station CAA7 (Table B1). The highest depth-integrated rates of ρC were found in the Labrador Sea and Davis Strait, and at one station in Lancaster Sound (Table B2; Figure B2d). In contrast, depth-integrated ρNO_3 exhibited the highest rate in Baffin Bay, although rates were generally high all along the sampling transect (Table B2; Figure B2e). Depth-integrated ρNH_4 was the only parameter to exhibit a spatial trend, with rates decreasing along the sampling transect from the Labrador Sea to the ice-edge in the CAA (Table B2; Figure B2f).

Table B.1. Summary of depth-integrated measurements of nitrate (NO_3^-), ammonium (NH_4^+), total chlorophyll *a* (Chl *a*), and particulate C (PC) and N (PN) concentrations. Depth integrations were done from the ocean surface to the 0.2% I_0 depth.

Station	[NO_3^-] (mmol m^{-2})	[NH_4^+] (mmol m^{-2})	Chl <i>a</i> (mg m^{-2})	PC (mmol m^{-2})	PN (mmol m^{-2})
LS2	168.97	29.89	41.82	733.80	83.15
BB1	266.43	11.82	21.49	658.70	86.44
BB3	58.09	3.31	63.47	502.93	82.57
BB2	212.20	2.30	27.46	724.76	75.80
CAA1	53.88	4.99	54.68	716.94	107.40
CAA3	132.64	11.82	16.44	793.01	102.56
CAA5	148.93	9.55	11.70	714.42	83.27
CAA6	109.54	3.19	89.42	887.50	85.97
CAA7	237.14	0.00	19.55	373.33	39.02

Table B.2. Summary of depth-integrated measurements of C utilization (ρC), NO_3^- utilization (ρNO_3), and NH_4^+ utilization (ρNH_4) rates and New Production (New-Prod) and *f*-ratios. Depth integrations were done from the ocean surface to the 0.2% I_0 depth.

Station	ρC (mmol C $m^{-2} d^{-1}$)	ρNO_3 (mmol N $m^{-2} d^{-1}$)	ρNH_4 (mmol N $m^{-2} d^{-1}$)	New-Prod (mmol C $m^{-2} d^{-1}$)	<i>f</i> -ratio
LS2	49.23	3.88	3.23	0.91	0.40
BB1	42.68	1.95	4.40	0.14	0.50
BB3	27.64	2.48	3.57	0.13	0.38
BB2	37.99	5.25	3.24	0.24	0.64
CAA1	48.48	3.27	1.80	0.57	0.60
CAA3	19.10	1.77	2.92	0.14	0.49
CAA5	32.39	3.85	1.55	0.17	0.70
CAA6	27.81	2.93	2.57	0.35	0.67
CAA7	8.17	1.30	0.97	0.44	0.62

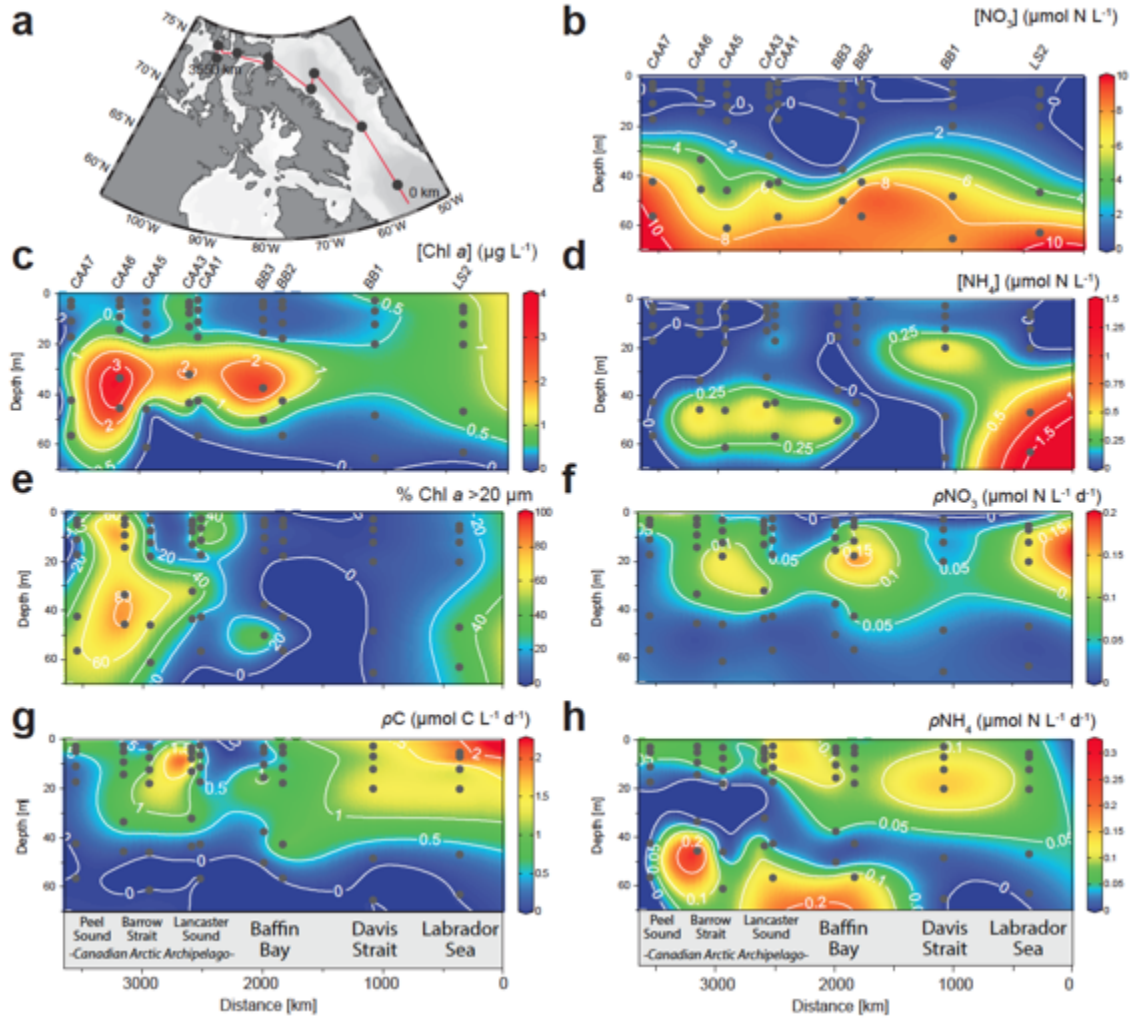


Figure B.1. Vertical profiles of measured euphotic-zone parameters along the 2015 Canadian Arctic GEOTRACES transect. (a) GEOTRACES transect line shown in red, colour and white contour lines for (b) NO_3^- concentration, (c) total Chl a concentration, (d) NH_4^+ concentration, (e) the relative contribution of phytoplankton $>20 \mu\text{m}$ to total Chl a , (f) NO_3^- utilization rate, ρNO_3 , (g) C utilization rate, ρC , and (d) NH_4^+ utilization rate, ρNH_4 . Black dots represent the sampling depths. Regions sampled as described in Chapter 4 are delineated along the bottom of panels (g) and (h). Station names are shown along the top of panels (b) and (c).

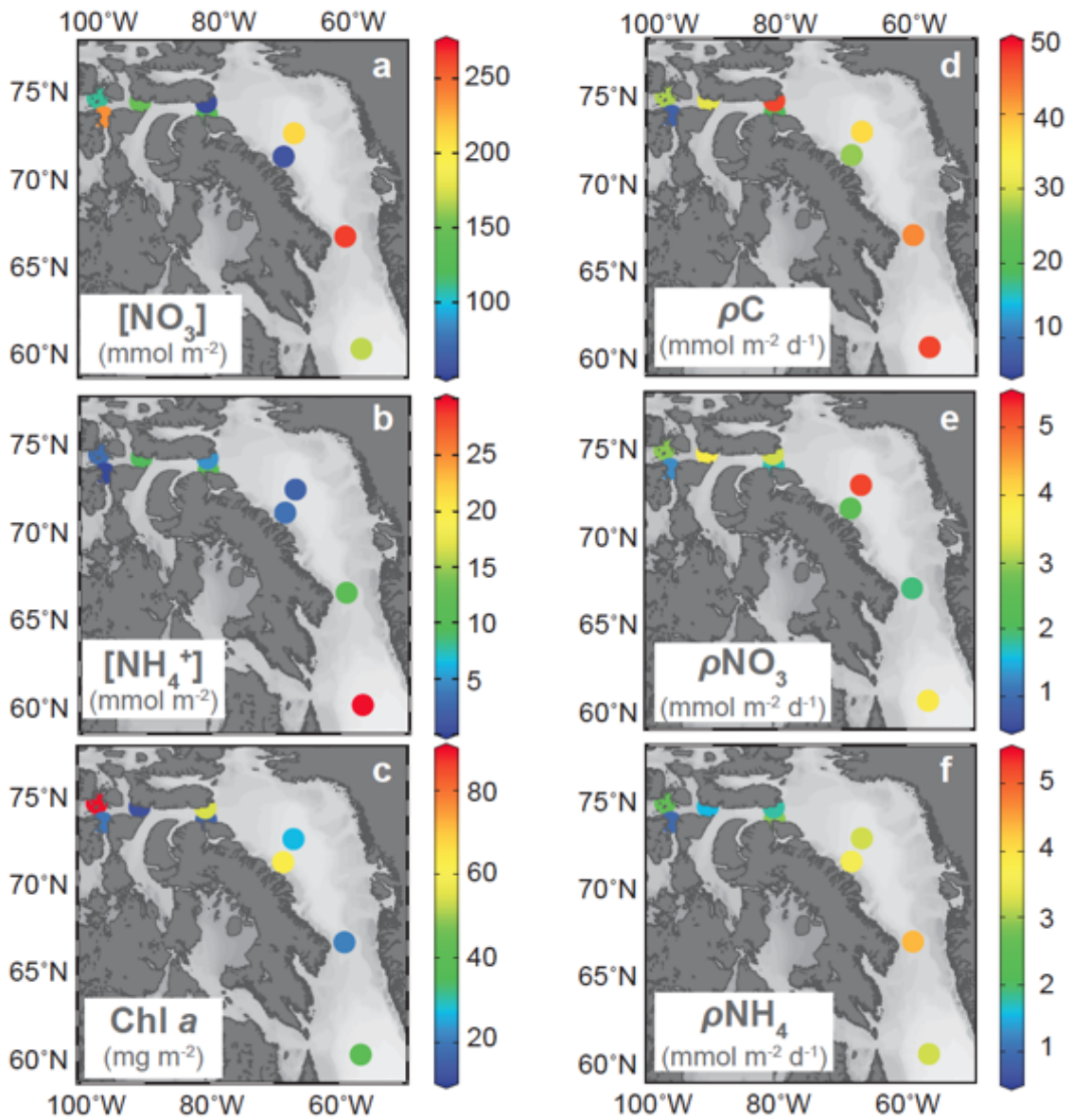


Figure B.2. Horizontal distributions of depth-integrated parameters along the 2015 Canadian Arctic GEOTRACES transect. (a) NO_3^- concentration, (b) NH_4^+ concentration, (c) total Chl *a* concentration, (d) C utilization rate, ρC , (e) NO_3^- utilization rate, ρNO_3 , and (f) NH_4^+ utilization rate, ρNH_4 . Data were depth-integrated from the ocean surface to the bottom on the euphotic zone ($0.2\% I_0$). Each coloured circle represents a sampling station

Appendix C.

A comparison of collection and storage methods for dissolved silica samples

C.1 Objective

Compare $[\text{Si}(\text{OH})_4]$ in seawater samples that were filtered through $0.7\ \mu\text{m}$ glass-fibre filters and stored at -20°C with seawater samples that were filtered through $0.6\ \mu\text{m}$ polycarbonate filters and stored at 4°C .

C.2 Introduction

Filtering samples for $\text{Si}(\text{OH})_4$ analysis through glass fibre filters can lead to an increase of $\sim 0.1\text{--}0.3\ \mu\text{mol L}^{-1}$ (Amniot, 2008) compared to using polycarbonate (PC) filters, while freezing samples for $[\text{Si}(\text{OH})_4]$ analysis can result in an underestimation of $[\text{Si}(\text{OH})_4]$ due to incomplete de-polymerization during thawing (e.g. Burton et al., 1970; Macdonald and McLaughlin, 1986). To evaluate methodological biases in the sampling and storage protocols for $[\text{Si}(\text{OH})_4]$ analysis, samples were collected at all stations sampled in the Pacific Arctic Region from 2014 to 2016 (see Chapter 2 for station locations).

C.3 Methods

At each station and at each of the 6 light depths, samples for $[\text{Si}(\text{OH})_4]$ were syringe-filtered through pre-combusted $0.7\ \mu\text{m}$ glass fibre filters, collected in acid-washed 30-mL polypropylene bottles, and immediately frozen at -20°C ($[\text{Si}(\text{OH})_4]_{\text{frozen}}$). Additional replicate samples for $[\text{Si}(\text{OH})_4]$ were syringe-filtered through $0.6\ \mu\text{m}$ PC filters and stored at 4°C ($[\text{Si}(\text{OH})_4]_{\text{cold}}$). All samples were analyzed on shore using an Astoria Nutrient Autoanalyzer and following the protocols of Barwell-Clark and Whitney (1996).

C.4 Results

For all of the samples collected from 2014 to 2016 ($n = 54$), $[\text{Si}(\text{OH})_4]_{\text{cold}}$ had a lower median coefficient of variation (8%) compared to the frozen samples ($[\text{Si}(\text{OH})_4]_{\text{frozen}}$, $\text{CV} = 16\%$). Concentrations agreed well up to $\sim 15 \mu\text{mol L}^{-1}$ (Figure C1). At concentrations higher than $15 \mu\text{mol L}^{-1}$, $[\text{Si}(\text{OH})_4]_{\text{frozen}}$ were approximately $16 \pm 3\%$ (mean $\pm \text{SE}$, $n = 29$) lower than $[\text{Si}(\text{OH})_4]_{\text{cold}}$. A regression through these data gives $[\text{Si}(\text{OH})_4]_{\text{cold}} = 0.73 * [\text{Si}(\text{OH})_4]_{\text{frozen}} + 4.88$.

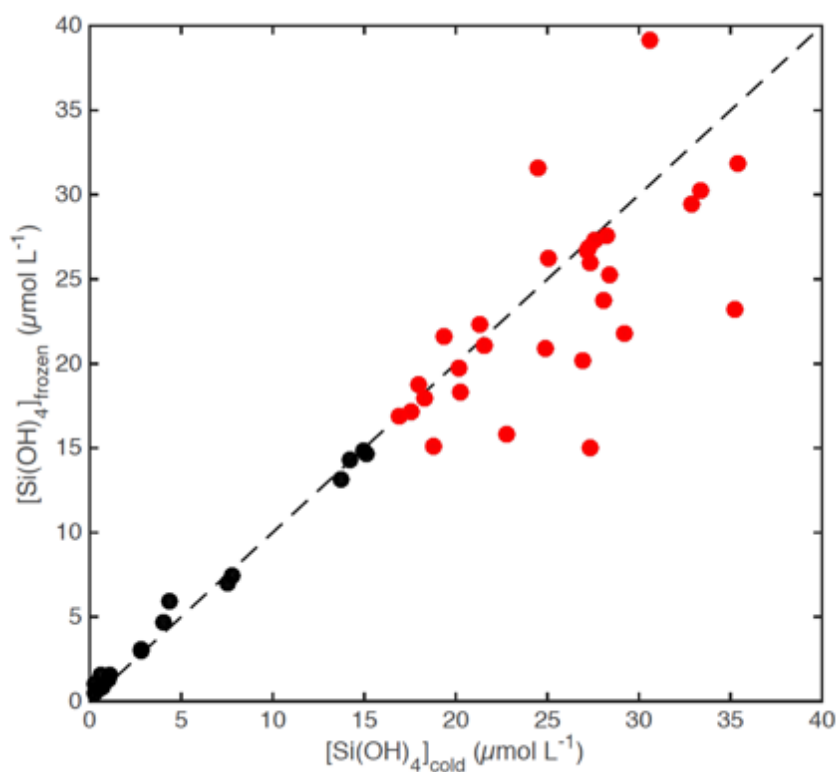


Figure C.1. Comparison of $[\text{Si}(\text{OH})_4]$ in seawater where samples were either pre-filtered through a glass-fibre filter and frozen at -20°C prior to analysis ($[\text{Si}(\text{OH})_4]_{\text{frozen}}$), or pre-filtered through a $0.6 \mu\text{m}$ polycarbonate filter and stored cold at 4°C prior to analysis ($[\text{Si}(\text{OH})_4]_{\text{cold}}$). Black dots represent samples where $[\text{Si}(\text{OH})_4]_{\text{cold}} < 15 \mu\text{mol L}^{-1}$. Red dots represent samples where $[\text{Si}(\text{OH})_4]_{\text{cold}} > 15 \mu\text{mol L}^{-1}$. The black dashed line represents a 1:1 relationship between $[\text{Si}(\text{OH})_4]_{\text{cold}}$ and $[\text{Si}(\text{OH})_4]_{\text{frozen}}$.

Appendix D.

Recycling of biogenic silica in the Canadian Arctic Ocean during the 2015 Canadian Arctic GEOTRACES

D.1 Objective

To investigate spatial variations in the net accumulation of biogenic silica (bSiO_2), bSiO_2 dissolution rates ($\rho_{\text{Si}_{\text{diss}}}$), and the ratio of bSiO_2 production to dissolution ($\int \text{D} : \int \text{P}$) in the euphotic zone along a transect through the Canadian Arctic Ocean from the Labrador Sea to the Canadian Arctic Archipelago.

D.2 Introduction

The balance between euphotic-zone integrated bSiO_2 production (P) and dissolution (D) controls the marine Si cycle in surface waters (Tréguer and De La Rocha, 2013), while the ratio of these two parameters ($\int \text{D} : \int \text{P}$) can be used as a measure of the efficiency of the ‘silica pump’, or the ability of the system to export bSiO_2 (Dugdale et al., 1995; Brzezinski et al., 2003). This ratio, compared to the relative rate at which organic matter is recycled in the euphotic zone, can determine if a system will be driven to Si or nitrogen (N) limitation (Brzezinski et al., 2003).

D.3 Methods

D.3.1 Sampling Locations and Seawater Sampling

Water samples were collected at six depths corresponding to light levels of 100%, 50%, 30%, 15%, 1% and 0.2% of the surface incident irradiance (I_0) at the stations described in Chapter 4. At each light level, we measured net bSiO_2 accumulation rates (ΔbSiO_2). The precision of all analytical techniques was determined from triplicate subsamples collected at one or more depths at each station sampled every year. Seawater samples for the concentrations of silicic acid ($\text{Si}(\text{OH})_4$) and particulate silica (as bSiO_2

and lSiO_2), and for bSiO_2 production rates using the radioisotope ^{32}Si (ρSi) collected from the same stations and depths are presented in Chapter 4.

D.3.2 Rates of net accumulation and dissolution of biogenic silica

Water samples for the net accumulation rate of bSiO_2 (ΔbSiO_2) were collected, incubated, and processed as described in Chapter 3. Silica dissolution rates ($\rho\text{Si}_{\text{diss}}$) were calculated as in Chapter 3.

D.3.3 Temperature effects on biogenic silica production and dissolution rates

Rates of bSiO_2 production (ρSi) from Chapter 4, and rates of ΔbSiO_2 and $\rho\text{Si}_{\text{diss}}$ at each light depth were corrected the effect of incubation at non-ambient temperatures (i.e. surface seawater) as in Chapter 3. All rates presented here are temperature-corrected.

D.3.4 Biogenic silica dissolution (D) to production (P) ratios

The proportion of bSiO_2 production sustained by Si(OH)_4 regenerated in the euphotic zone ($[\text{D}]:[\text{P}]$) was calculated at the ratio of depth-integrated $\rho\text{Si}_{\text{diss}}$ to depth-integrated ρSi .

D.3.5 Data organization and presentation

Data were depth-integrated using trapezoidal integration from the surface to the bottom of the euphotic zone (0.2% of surface irradiance). Figures B1-B2 were created using Ocean Data View version 5.0.0 (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2012). Data were grouped into sub-regions of the Canadian Arctic Archipelago (CAA), Baffin Bay (BB) and Labrador Sea (LS) as described in Chapter 4.

D.4 Results:

Net accumulation rates of bSiO_2 in Lancaster Sound exhibited the highest and lowest values of the whole sampling transect, with the highest values at CAA3 and lowest values at CAA1 (Table D1). No consistent spatial trends in ΔbSiO_2 were observed. Biogenic silica dissolution rates were highest at station CAA5 and more than twice as high at this

station than any of the other stations sampled (Table D1). Like ΔbSiO_2 , no consistent spatial trends were observed. The ratio of bSiO_2 dissolution to production ranged from 0.02 to 0.96, with an average value of 0.51 for our entire sampling transect, indicating that approximately 50% of the bSiO_2 produced in the euphotic zone is recycled (Table D1).

Table D.1. Summary of temperature-corrected and depth-integrated measurements of the rate of bSiO_2 production (ρSi), net accumulation (ΔbSiO_2), and dissolution ($\rho\text{Si}_{\text{diss}}$), and the ratio of depth-integrated bSiO_2 production to dissolution ($[\text{D}]:[\text{P}]$). Depth integrations were done from the ocean surface to the 0.2% I_0 depth.

Station	ρSi (mmol m ⁻² d ⁻¹)	ΔbSiO_2 (mmol m ⁻² d ⁻¹)	$\rho\text{Si}_{\text{diss}}$ (mmol m ⁻² d ⁻¹)	$[\text{D}]:[\text{P}]$
LS2	1.70	1.67	0.03	0.02
BB1	1.10	0.42	0.68	0.62
BB3	2.53	1.21	1.33	0.52
BB2	3.66	1.13	2.53	0.69
CAA1	1.94	0.20	1.74	0.90
CAA3	2.28	2.09	0.18	0.08
CAA5	8.68	0.32	8.35	0.96
CAA6	1.69	1.17	0.52	0.31
CAA7	1.70	1.67	0.03	0.02

Appendix E.

Estimating the biogenic ^{30}Si fractionation factor in surface waters from the Canada Basin to Baffin Bay using water mass composition data from a preliminary Optimum Multiparameter Analysis

E.1 Objective

To estimate the biogenic ^{30}Si fractionation factor in surface waters from the Canada Basin to Baffin Bay using data from a preliminary Optimum Multiparameter Analysis (OMP).

E.2 Methods

Using the preliminary OMP water mass analysis and following Varela et al. (2016), we calculated the source water $[\text{Si}(\text{OH})_4]$ based on the relative contributions of each water mass and their associated $[\text{Si}(\text{OH})_4]$ values:

$$[\text{Si}(\text{OH})_4]_{\text{source}} = \sum R_{\text{water mass}} \times [\text{Si}(\text{OH})_4]_{\text{water mass}} \quad (1)$$

where R is the relative fraction (%) for each water mass. Seven distinct source water masses were identified: the Polar Mixed Layer (PML), Meteoric Water (MW) from the Mackenzie River, Sea-ice melt water (SIM), Pacific-origin Upper Halocline Water (UHL), Atlantic waters originating from Fram Strait (N-ATW) and the Labrador Sea (S-ATW), and Baffin Bay Arctic Water (BBAW). For the $[\text{Si}(\text{OH})_4]$ source values, we used 48 μM for $[\text{Si}(\text{OH})_4]_{\text{MW}}$ (Simpson et al., 2008) and 3.2 μM for $[\text{Si}(\text{OH})_4]_{\text{SIM}}$ (Fripiat et al., 2013). For $[\text{Si}(\text{OH})_4]_{\text{PML}}$ and $[\text{Si}(\text{OH})_4]_{\text{UHL}}$ we used the same values as those described in Chapter 5 (i.e. 20 μM and 30 μM). We assume $[\text{Si}(\text{OH})_4]_{\text{BBAW}}$ is equal to the source water $[\text{Si}(\text{OH})_4]$ of 12.4 μM that we estimated for the BB domain in Chapter 5. We derived $[\text{Si}(\text{OH})_4]_{\text{source}}$ values of 14.5 μM and 17.5 μM for N-ATW and S-ATW, respectively, based on an average of our measured $[\text{Si}(\text{OH})_4]$ for samples where the

relative contribution of these water masses is >90%. We then used linear regressions based on equations (5) and (6) to estimate $^{30}\epsilon$ for all domains where preliminary OMP water mass data was available (BS-CB, CAA and BB domains).

E.3 Results

For surface waters, we calculated a mean ($\pm 1\text{SE}$) $^{30}\epsilon$ of $-0.47 \pm 0.04\text{‰}$ using the closed system model (equation 5) and $-1.08 \pm 0.15\text{‰}$ using the open system model (equation 6).