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# Response of the Arctic Marine Inorganic Carbon System to Ice Algae and Under-Ice Phytoplankton Blooms: A Case Study Along the Fast-Ice Edge of Baffin Bay

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## RESEARCH ARTICLE

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### Key Points:

- An ice algae bloom beneath landfast sea ice did not impact DIC/ $p\text{CO}_2$ , and is not expected to contribute to  $\text{CO}_2$  uptake from the atmosphere
- Under ice phytoplankton blooms did significantly reduce DIC/ $p\text{CO}_2$ , likely making the region a stronger sink for atmospheric  $\text{CO}_2$  at break-up
- Arctic seas do not often experience supersaturation of  $p\text{CO}_2$  during the Arctic winter

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# Response of the Arctic Marine Inorganic Carbon System to Ice Algae and Under-Ice Phytoplankton Blooms: A Case Study Along the Fast-Ice Edge of Baffin Bay

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**Abstract** Past research in seasonally ice-covered Arctic seas has suggested that ice algae play a role in reducing dissolved inorganic carbon (DIC) during spring, preconditioning surface waters to low dissolved  $\text{CO}_2$  ( $p\text{CO}_{2\text{sw}}$ ), and uptake of atmospheric  $\text{CO}_2$  during the ice-free season. The potential role of under-ice phytoplankton blooms on DIC and  $p\text{CO}_{2\text{sw}}$  has not often been considered. In this study we examined the inorganic carbon system beneath landfast sea ice starting midway through a bottom ice algae bloom and concluding in the early stages of an under-ice phytoplankton bloom. During most of the ice algae bloom we observed a slight increase in DIC/ $p\text{CO}_{2\text{sw}}$  in surface waters, as opposed to the expected reduction. Biomass calculations confirm that the role of ice algae on DIC/ $p\text{CO}_{2\text{sw}}$  in the study region were minor and that this null result may be widely applicable. During snow melt, we observed an under-ice phytoplankton bloom (to  $10 \text{ mg/m}^3 \text{ Chl } a$ ) that did reduce DIC and  $p\text{CO}_{2\text{sw}}$ . We conclude that under-ice phytoplankton blooms are an important biological mechanism that may predispose some Arctic seas to act as a  $\text{CO}_2$  sink at the time of ice breakup. We also found that  $p\text{CO}_{2\text{sw}}$  was undersaturated at the study location even at the beginning of our sampling period, consistent with several other studies that have measured under-ice  $p\text{CO}_{2\text{sw}}$  in late winter or early spring. Finally, we present the first measurements of carbonate saturation states for this region, which may be useful for assessing the vulnerability of a local soft-shelled clam fishery to ocean acidification.

## 1. Introduction

The most commonly measured components of the marine carbonate system are dissolved inorganic carbon (DIC), total alkalinity (TA),  $p\text{CO}_{2\text{sw}}$  (partial pressure of carbon dioxide in seawater), and pH (Dickson et al., 2007). In many ocean regions, these parameters follow a typical seasonal pattern (Falkowski et al., 2000), with net autotrophy in the spring and summer leading to DIC uptake, low  $p\text{CO}_{2\text{sw}}$ , and an increase in pH, followed by net heterotrophy in the fall and winter leading to DIC accumulation, increasing  $p\text{CO}_{2\text{sw}}$ , and lower pH. In the Arctic, the inorganic carbon system follows some of these established trends, but with added complications from seasonal sea ice growth and decay and extreme variations in light availability. For example, in the fall and winter during sea ice formation, calcium carbonate crystals (in the form of ikaite) precipitate in sea ice (Dieckmann et al., 2010), partitioning TA in the sea ice matrix and enhancing the DIC concentration of brine that is rejected to the underlying water (Rysgaard et al., 2007). This causes an increase in surface water DIC during the ice formation season, while in the spring and summer, DIC and  $p\text{CO}_{2\text{sw}}$  decrease due to dilution associated with sea ice melt (Rysgaard et al., 2009). Unfortunately, the winter portion of this seasonal pattern is still not well understood, due mostly to a sampling bias arising from the logistical challenge of winter measurements. The lack of carbonate system observations through the fall, winter, and particularly early spring, has led to different interpretations about how biogeochemical processes affect the ability of seasonally ice-covered Arctic seas to act as a  $\text{CO}_2$  sink (Else et al., 2012; Miller et al., 2011; Shadwick et al., 2011; Yager et al., 1995) and uncertainty about their influence on carbonate saturation states (Fransson et al., 2011; Yamamoto-Kawai et al., 2013).

Ice-associated algal communities are a unique biological component of the Arctic marine ecosystem, with the potential to impact inorganic carbon cycles. These communities fall into two main categories: Bottom ice (or interstitial) communities are microalgae accumulations that form shortly after polar sunrise on the

bottom of the ice or in the interstitial spaces of the lowest ice horizons (Horner & Schrader, 1982); sub-ice communities form at ice breakup and are characterized by macroalgae accumulations in the form of films, mats, or filaments that float freely or are attached to the ice (Poulin et al., 2014). Ice algae primarily consist of diatom taxa (Werner et al., 2007) and also contain other autotrophs such as dinoflagellates and cyanobacteria (Poulin et al., 2011). The sea ice matrix also has a diverse range of ice bacteria (Junge et al., 2002) and other grazing organisms like copepods (Conover & Huntley, 1991) that consume ice algae, forming the sympagic food web community. Ice algae may be important in the Arctic marine ecosystem because they are the first photosynthesizing organisms to take advantage of returning spring sunlight after winter darkness (Leu et al., 2015). Primary productivity from ice algae is significant during spring and early summer as it is up to 2 orders of magnitude greater than water column productivity (Gradinger, 2009), and it ultimately accounts for an estimated 3–60% of total Arctic productivity (Gosselin et al., 1997; Legendre et al., 1992).

As described by Miller et al. (2015), the past two decades have seen an acceleration in research to determine the biogeochemical role (Vancoppenolle et al., 2013) that these ice algae play in sea ice, including the potential to impact under-ice seawater. In the winter to spring transition, surface water DIC/ $p\text{CO}_{2\text{sw}}$  levels are generally thought to be at their peak, resulting from net respiration over the dark winter period, and brine rejection due to sea ice growth (Bates, 2006). Ice algae are the first autotrophic organisms that can impact these values. Their first production utilizes materials from brine cavities in the sea ice, consuming nutrients and carbon from inside the sea ice matrix, which can be replenished by exchange with the underlying seawater (Niedrauer & Martin, 1979). If this ultimately results in extraction of DIC and nutrients from the water column, it creates a scenario in which the seasonal increase in DIC/ $p\text{CO}_{2\text{sw}}$  may start to reverse. This may lead to undersaturation of  $p\text{CO}_{2\text{sw}}$  relative to the atmosphere, preconditioning the underlying water column for  $\text{CO}_2$  uptake once the ice cover is removed, or it becomes permeable to gas exchange (Else et al., 2012; Yager et al., 1995). The specific role that ice algae might play in  $p\text{CO}_{2\text{sw}}$  cycles in seasonally ice-covered areas of the Arctic is unclear because relatively few studies have examined the impact of the ice algae community on the carbonate system of the underlying seawater.

The second autotrophic community that may impact surface water DIC/ $p\text{CO}_2$  is the under-ice phytoplankton bloom. Under-ice phytoplankton blooms are triggered later in the spring season when snow melt has advanced far enough (typically to the point of melt pond formation), significantly increasing light transmission to the underlying ocean (Arrigo et al., 2012; Fortier et al., 2002; Mundy et al., 2009, 2014). Stratification of the water column due to ice melt and availability of nutrients that accumulated over the winter also play an important role in triggering the bloom (Mundy et al., 2014). These diatom-dominated blooms are thought to contribute significantly to the overall production of Arctic marine environments, although their distribution and ubiquity is poorly known due to the logistical challenges of observing them. Their role in influencing the marine inorganic carbon system is also poorly known, although a recent study showed strong reduction of DIC during a *Phaeocystis* sp. bloom that was initiated earlier in the season by lead/crack formation in the mobile sea ice cover (Assmy et al., 2017).

Although time series measurements of the carbonate system below Arctic sea ice are rare, a number of studies have published measurements from Antarctic regions. Gibson and Trull (1999) and Roden et al. (2013) both published time series measurements of  $p\text{CO}_{2\text{sw}}$  calculated from DIC/TA in the seasonal ice area of Prydz Bay, East Antarctica. Gibson and Trull (1999) captured a complete annual cycle, while Roden et al. (2013) captured most of the ice-covered season and into spring breakup. Both studies showed a clear drawdown of  $p\text{CO}_{2\text{sw}}$  beneath the ice in the spring period, but neither attempted to determine the relative roles of ice algae and under-ice phytoplankton blooms. Schram et al. (2015) published a similar annual time series ( $p\text{CO}_{2\text{sw}}$  calculated from DIC/TA over an annual cycle) in a seasonal mobile ice zone in the western Antarctic Peninsula but were unable to determine the relative contributions of ice algae and under-ice phytoplankton.

In this paper, we look at the carbonate system in the seawater below Arctic landfast sea ice near Baffin Bay (Nunavut, Canada) to determine what roles ice algae and under-ice phytoplankton blooms play in carbon drawdown from surface waters. Carbonate parameters below the sea ice were measured, along with chlorophyll *a* (Chl *a*), nutrients, and other parameters during a time period where algal biomass was actively accumulating in the bottom layers of the ice and during the beginning of an under-ice phytoplankton bloom. The objective of this paper is therefore to determine if bottom ice algae blooms and under-ice phytoplankton

blooms modify inorganic carbon parameters in the water column to an extent that would significantly impact air-sea exchange of CO<sub>2</sub>. Since this is the first study of its kind in landfast ice near Baffin Bay, we also have secondary objectives to comment on the potential for this region to act as a source or sink of atmospheric CO<sub>2</sub>, and to report on carbonate saturation states.

## 2. Methodology

### 2.1. Study Area

This study was conducted in landfast first-year ice adjacent to Baffin Bay, a deep body of water located between Greenland (Denmark) and Baffin Island (Canada; Figure 1). The general circulation in Baffin Bay is cyclonic (Tang et al., 2004), with Atlantic and Greenland origin waters coming in from the south through the Labrador Sea, and Arctic origin surface waters coming from the north through the Canadian Arctic Archipelago and Nares Strait. Baffin Bay is mostly covered by sea ice from October to July (Tang et al., 2004), but it has a well-known recurrent polynya at its northern extent (the North Water Polynya).

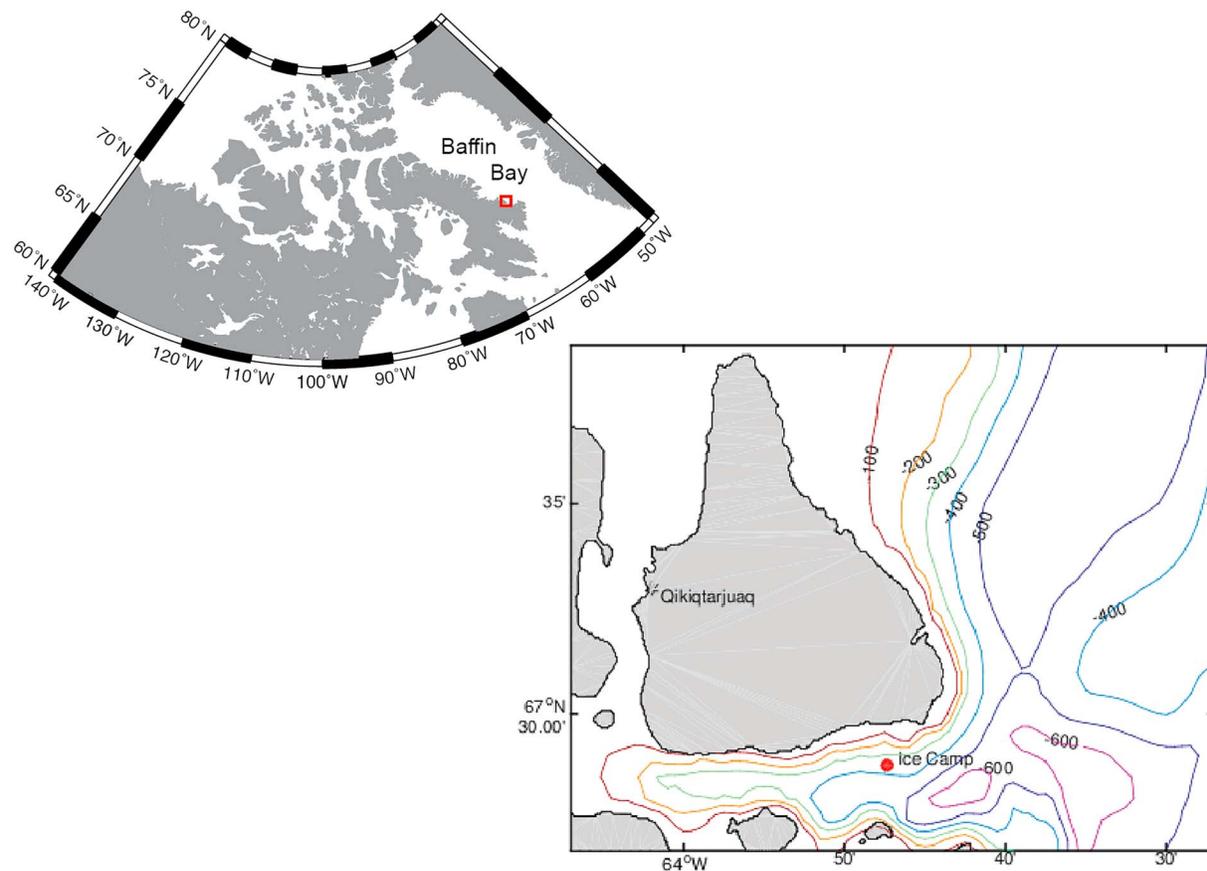
Our study was part of the 2015 GreenEdge project, which was conducted from landfast ice southeast of Broughton Island (67.28774°N, 63.47398°W) and southeast of mainland Baffin Island, approximately 30 km from the town of Qikiqtarjuaq (Figure 1). The field program lasted approximately 17 weeks (28 March to 14 July), but due to logistical constraints, not all sample collection protocols were conducted over the entire period.

The sampling location was not in Baffin Bay itself, but within a fjord at the edge of the Bay where the water depth was 360–370 m. The physical oceanographic setting encountered during the sampling period is detailed in L. Oziel et al. (personal communication, 2019), and briefly reviewed here. The sampling site was covered by thick (>120 cm) first-year landfast ice, with a mobile ice zone to the east, in Baffin Bay. The distance from the ice camp to the mobile ice zone was approximately 300 km near the start of the sampling period, decreasing to ~250 km (as the ice edge began to break up) in early July. Tides were the main driver of local currents, following a semidiurnal pattern that moved water back and forth within the fjord channel. Mean daily current velocities were small (~0.07 m/s) and varied from an out-fjord easterly flow (late-April to mid-May), to northerly, and then westerly (i.e., in-fjord) in mid-June. Estimates using current velocity and the ice edge distance in early July show that water transit time from the mobile zone would have been greater than 40 days. Given that the current direction did not become in-fjord until mid-June, L. Oziel et al. (personal communication, 2019) concluded that any chemical or biological modifications to water masses observed during the study period must have been the result of processes occurring in the fast ice zone. In other words, advection of water masses from the mobile ice zone was not expected or observed during the study.

### 2.2. Sampling and Analysis

Seawater samples were collected approximately every three days from 1 May to 8 July through a 1-m<sup>2</sup> meter hole in the ice, which was covered by a ~35-m<sup>2</sup> tent (“Polar Haven”). DIC and TA samples were collected using Niskin bottles (General Oceanics) deployed at set depths of 1.5, 5, 20, 40, and 60 m. Water was collected at the ice-water interface through an auger hole using a battery operated plastic submersible pump (Waterra WSP-12V-1) secured to the end of an under-ice arm. Seawater was transferred via Tygon tubing into 12-ml vials (LabCo Exetainer). The samples were preserved with 20-μl supersaturated HgCl<sub>2</sub>, stored in a dark cooler, and then refrigerated until analysis.

DIC was analyzed using an Apollo Sci Tech DIC analyzer Model AS-C3 equipped with an infrared CO<sub>2</sub> detector (LiCor Model LI-7000). Instead of operating on a principle of coulometric titration, the AS-C3 uses a nondispersive infrared detector to quantify CO<sub>2</sub> gas. An advantage of this analyzer is the small-volume size required for repeated samples. TA was analyzed by potentiometric titration using a Radiometer Analytical TIM840 titrator. Both instruments used 5% HCl to acidify samples. Seawater reference standards for DIC and TA were used from the Scripps Institution of Oceanography (UCSD), batch #144 to provide high accuracy measurements. TA was determined with a precision of ±3 μmol/kg, and DIC with a precision of ±2 μmol/kg. All sample collection and analysis were based on the standard inorganic carbon procedures (Dickson et al., 2007), with slight modifications for our small-volume sampling protocols. Using the DIC and TA measurements, pH (total scale), pCO<sub>2sw</sub>, and calcium carbonate saturation states (Ω) were calculated using the CO2SYS Excel Program (Pierrot et al., 2006).



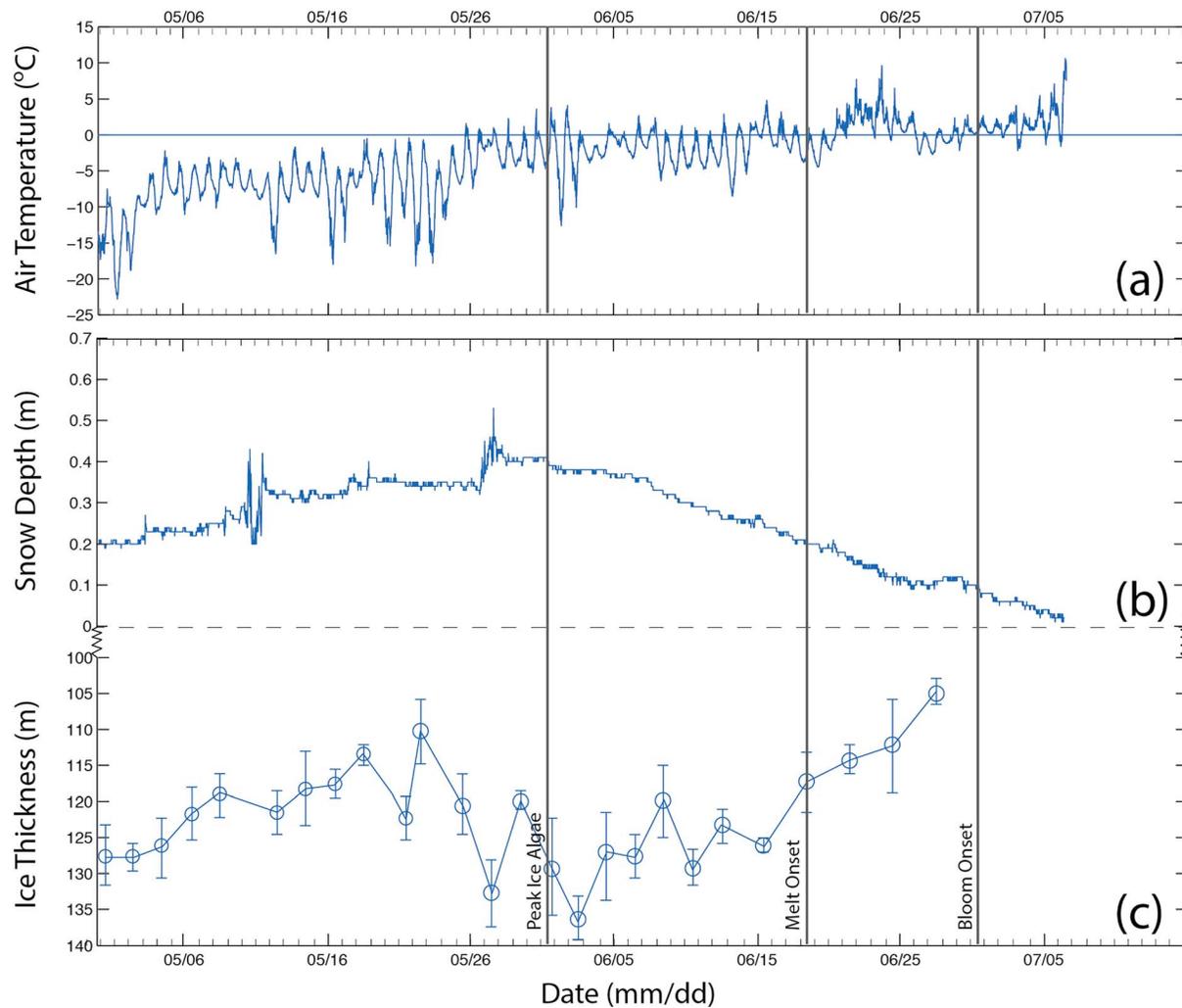
**Figure 1.** Map of the study area. Base of operations were maintained in the Hamlet of Qikiqtarjuaq, while sampling and experiments occurred at the ice camp. Bathymetric data compiled from the International Bathymetric Chart of the Arctic Ocean (IBCAO, V3). Courtesy of E. Rehm.

Samples for nitrogen (nitrate [ $\text{NO}_3^-$ ] and nitrite [ $\text{NO}_2^-$ ]) concentrations were collected from Niskin bottles at the same sampling depths. Samples were filtered through a precombusted (5 hr at 450 °C) Whatman GF/F glass-fiber filter (nominal porosity of 0.7  $\mu\text{m}$ ) inserted in a filter holder, and the filtrate was collected into 20-ml polyethylene flasks. Mercuric chloride (final concentration of 10  $\mu\text{g}/\text{ml}$ ) was added to preserve the samples, which were stored in the dark until analysis. Samples were analyzed using a Bran Luebbe Seal autoanalyzer according to the method of Aminot and K erouel (2007).  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations are precise up to 0.05 and 0.03  $\mu\text{mol}/\text{L}$ , respectively.

General ocean parameters (temperature, salinity, and Chl *a* fluorescence) were collected using a Seabird model SBE9+ V2 conductivity-temperature-depth (CTD) instrument every 3 days (weather permitting) from 28 March to 14 July. CTD casts were made prior to water collection, descending at a rate of 0.3 m/s down to a depth of 350 m. Density at standard atmospheric pressure ( $\sigma_T$ ) was calculated from absolute salinity and conservative temperature using TEOS-10 Oceanographic Toolbox (McDougall & Barker, 2011).

To constrain atmospheric conditions, an automated weather station was operated near the Polar Haven (~500 m to the southwest) from 17 March 17 to 6 July. Air temperature was recorded every 10 min with a shielded probe that ventilated 30 s prior to measurement, while snow depth was measured every 10 min using a Sonic Ranger 50 (Campbell Scientific) located 2 m above the snow-ice interface.

Sea ice sampling was also conducted every three days (approximately) in the vicinity of the main sampling site. Samples were typically collected beneath thick (>25 cm) and thin (15–20 cm less than thick) snow depth using a 14.5-cm internal diameter ice corer (Mark V Coring System, Kovacs Enterprises). The bottom 10- and 3-cm sections of replicate cores were removed and melted with a known volume of fresh filtered seawater in a dark cooler. The melted cores were then analyzed for Chl *a*, total organic carbon (TOC), dissolved organic carbon, and total particulate carbon (TPC). Chl *a* analysis was performed by filtering a known volume of



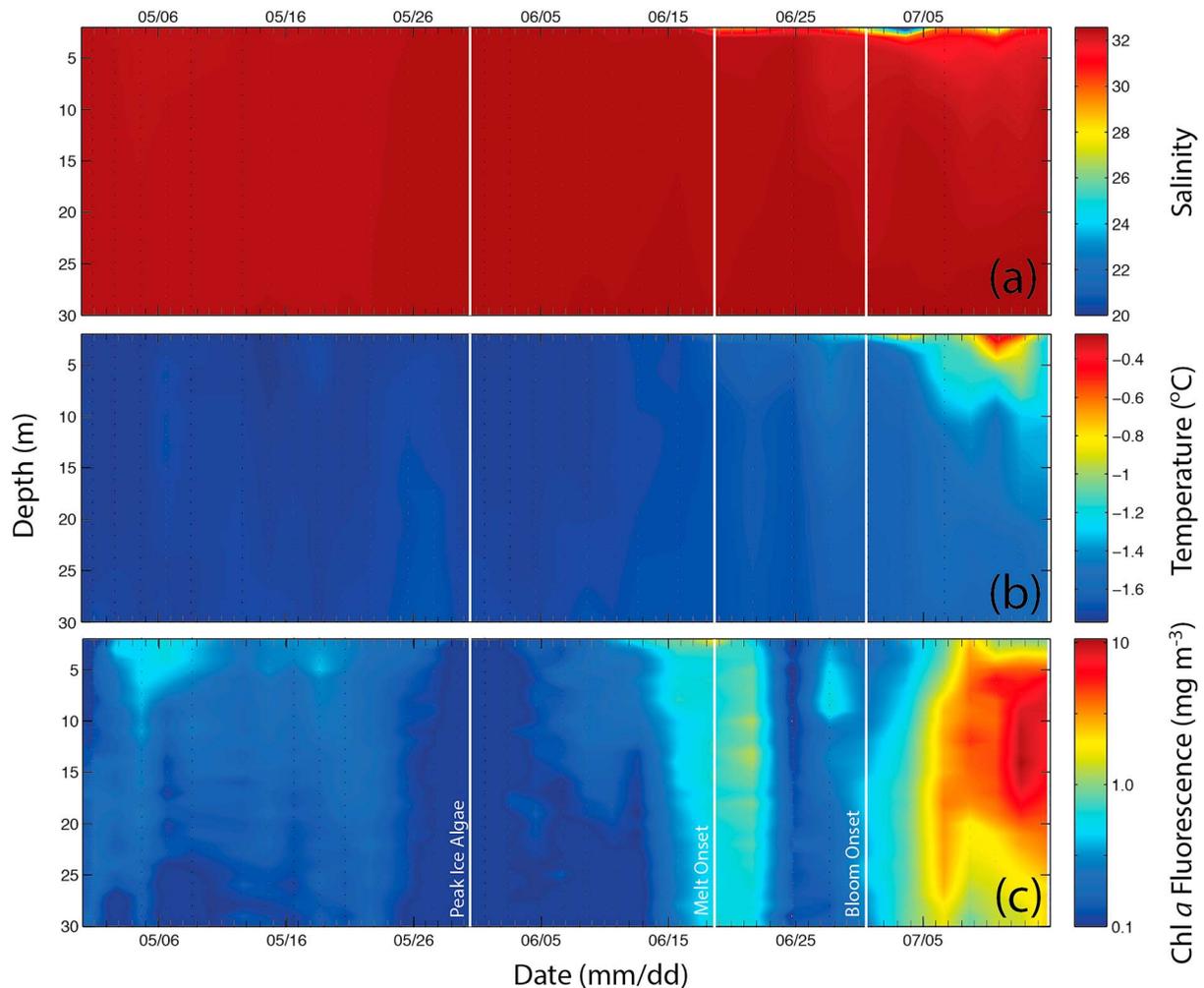
**Figure 2.** Time series of (a) air temperatures, (b) snow depth, and (c) average sea ice thickness. Air temperature and snow depth were recorded at the meteorological station at 10-min intervals. Ice thickness was measured approximately every 3 days until July 26.

seawater through a 25-mm GF/F filter, which was then soaked in 90% acetone and analyzed with a Turner Designs Triology fluorometer that was calibrated prior to the field experiment. TOC was measured on preserved samples, following the wet-oxidation procedure described by Raimbault et al. (1999), and TPC was measured on a PerkinElmer 2400 CHNS/O gas chromatographer using a combustion/reduction method. At each ice core location, ice thickness was measured, and for each day the thick and thin snow ice core thicknesses were averaged to produce a time series through the sampling period.

### 3. Results

#### 3.1. Atmospheric/Sea Ice Conditions

Air temperatures (Figure 2a) remained mostly below freezing for the first 6 weeks of the study, with the first above zero temperatures near the end of May. Late June and early July saw the daytime highs 5–10° above freezing. Snow depth (Figure 2b) remained fairly consistent for the first 10 days of the measurement period, with values in the range of 20–30 cm. Several large snowfall events during the month of May caused snow depth to reach peaks of about 50 cm. Following the final snowfall event, snow depth then declined steadily through the month of June, as a result of compaction and snow melt. Based on snow temperatures from the meteorological tower, snow melt appeared to start at the beginning of June for the upper layers of the snowpack. The first fully formed melt ponds appeared on 24 June. Sea ice thickness measurements mostly varied between 120 and 140 cm, with no distinctive trend through the month of May (Figure 2c). Ice thickness did



**Figure 3.** Near-surface (upper 30 m) water column profiles of (a) salinity, (b) temperature, and (c) chlorophyll fluorescence, as measured by conductivity-temperature-depth casts. The dotted lines indicate when conductivity-temperature-depth casts were made.

decline through the month of June as a result of melt, reaching a minimum thickness of 105 cm at the end of sampling.

### 3.2. Ocean Conditions

Temperature, salinity, and chlorophyll fluorescence as measured by the CTD are shown for the upper water column in Figure 3. For added detail, a time series trace of salinity is shown in Figure 4, while Figure 5 shows profiles of temperature, salinity, and density ( $\sigma_T$ ) near the peak of the ice algae bloom. Prior to ice melt we did not observe any distinct pycnocline, and density increased gradually with depth indicating stratified conditions throughout the water column. Close inspection of the upper water column (Figure 5b) shows that there was a layer of near-neutral stratification in the upper 25 m, through which some tidally driven mixing was likely occurring (L. Oziel et al., personal communication, 2019).

The first noticeable changes in salinity near the sea ice interface occurred on 18 June (Figure 3a), indicating the start of meltwater impacting the surface ocean. At 1.5-m depth, salinity dropped to a minimum of ~18 psu, but at 5-m depth salinity decreased by less than 0.3 psu. Prior to melt onset, salinity measurements varied by less than 0.1 psu (Figure 4), showing limited influence of brine rejection, and no freshwater sources. Water temperatures began to warm around the same date as meltwater was detected (Figure 3b), and melt progressed with further freshening and surface warming impacting the upper levels of the water column. By 8 July (the final day of DIC/TA sample collection), the impacts of ice melt and warming were

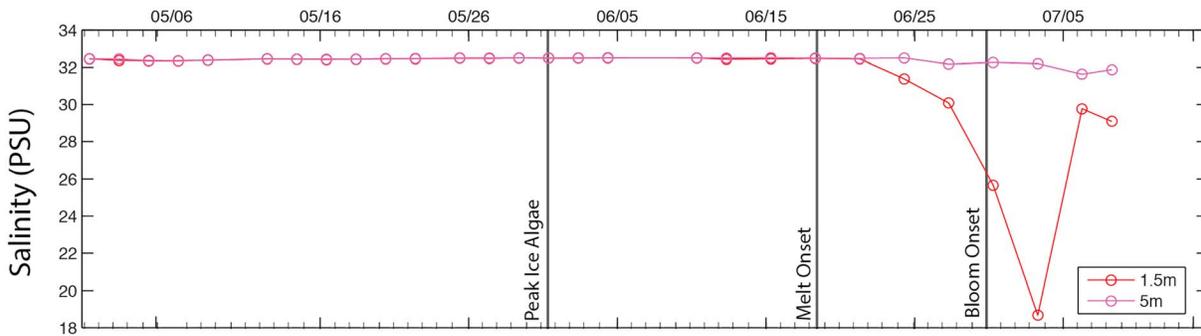


Figure 4. Time series trace of salinity at 1.5 and 5 m.

clear, with freshening and increased temperatures through at least the upper 25 m of the water column. Combined, these changes created a highly stratified surface layer.

### 3.3. Biological Conditions

The most obvious feature of the chlorophyll fluorescence data (Figure 3c) is the strong under-ice phytoplankton bloom that occurred late in the sampling period. Based on current observations and estimated particle sinking rates, L. Oziel et al. (personal communication, 2019) concluded that this bloom was generated in the landfast ice zone and was not advected from the mobile ice zone. Detailed profile plots (Figure 6) show that this bloom reached a maximum of about  $10 \text{ mg/m}^3$  at 15-m depth and extended to a depth of about 30 m. This bloom occurred well after the initial signal of ice melt in the surface water and likely started as a response to increased light transmission through the melting snowpack. A more subtle feature in Figure 3c (and shown in detail in Figure 6) is a smaller peak in chlorophyll fluorescence (to approximately  $1.0 \text{ mg/m}^3$ ) that started around 18 June and peaked on 21 June, shortly after the first observations of meltwater at the surface.

Figure 7a shows sea ice Chl *a* concentrations for the bottom 0–3 cm of ice at thick snow (HS) and thin snow (LS) sampling locations. Sea ice Chl *a* concentrations peaked near 31 May, with values around  $35 \text{ mg/m}^2$  under thick snow, and greater than  $40 \text{ mg/m}^2$  under thin snow. After those dates Chl *a* concentrations fell—with the most drastic drop starting around 12 June—reaching minimum values around 18 June, the

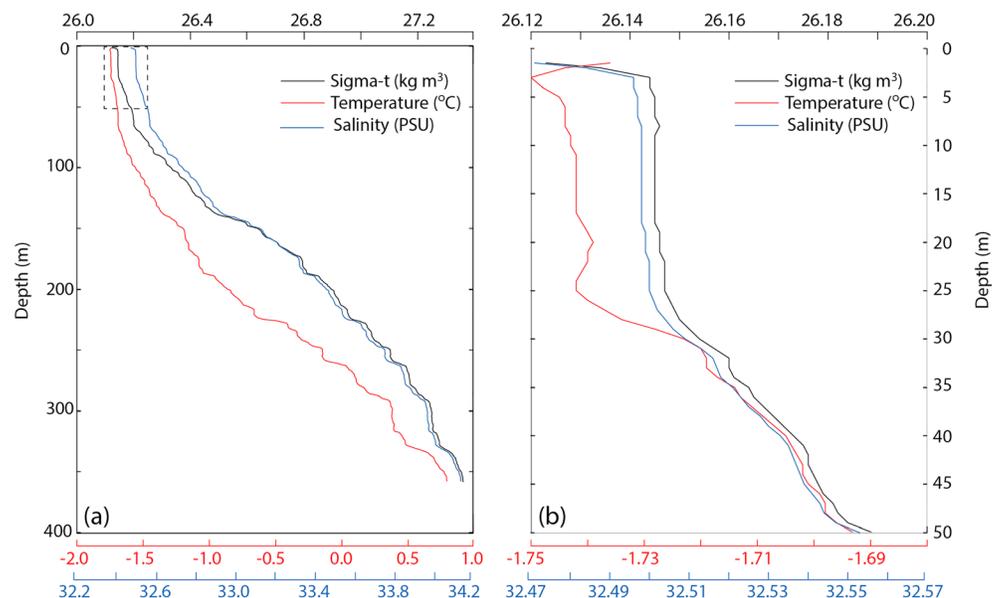
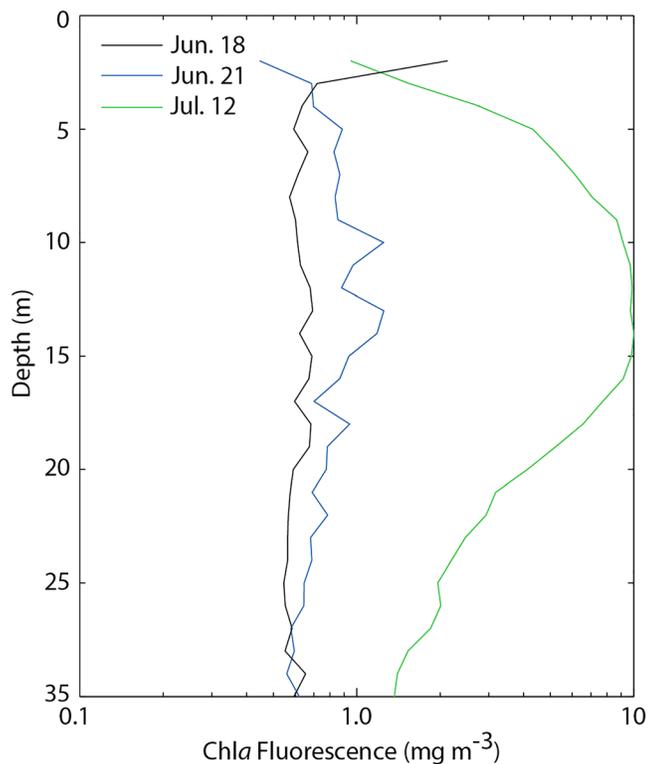


Figure 5. Oceanographic parameters measured via conductivity-temperature-depth casts near the peak of the ice algae bloom (2 June). (a) The entire depth and (b) zoomed in on the upper 50 m of the water column.



**Figure 6.** Profile plots of Chl *a* fluorescence as measured by the conductivity-temperature-depth at three important dates.

first date that ice meltwater was observed (Figure 3a). The timing of decreased sea ice Chl *a* also matches well with the 18 June peak in seawater Chl *a* (Figure 3b).

### 3.4. DIC/TA/Nitrogen Conditions

The time series of carbon system parameters and nitrogen nutrients are shown in Figures 7b–7d. Over our first four observations (30 April to 7 May), we observed a decrease in DIC in the upper water column by 25–40  $\mu\text{mol/kg}$ , with the strongest decrease occurring at the ice interface (Figure 7a). After that period, DIC, TA, and nitrate in the upper 5 m gradually increased through May and early June, before dropping significantly on 18 June; the same date that chlorophyll in the ice reached minimum values, and chlorophyll in the seawater initially increased. This was followed by slight rebounds and fluctuations in all parameters over the course of the next week and then drastic decreases in DIC, TA, and nitrogen after 21 June. The sudden late season decrease in these parameters matches the sudden accumulation of Chl *a* in the water column associated with the under-ice phytoplankton bloom (Figure 3c). The late season decreases also match to some extent the changes in near surface salinity (Figure 3b).

## 4. Discussion

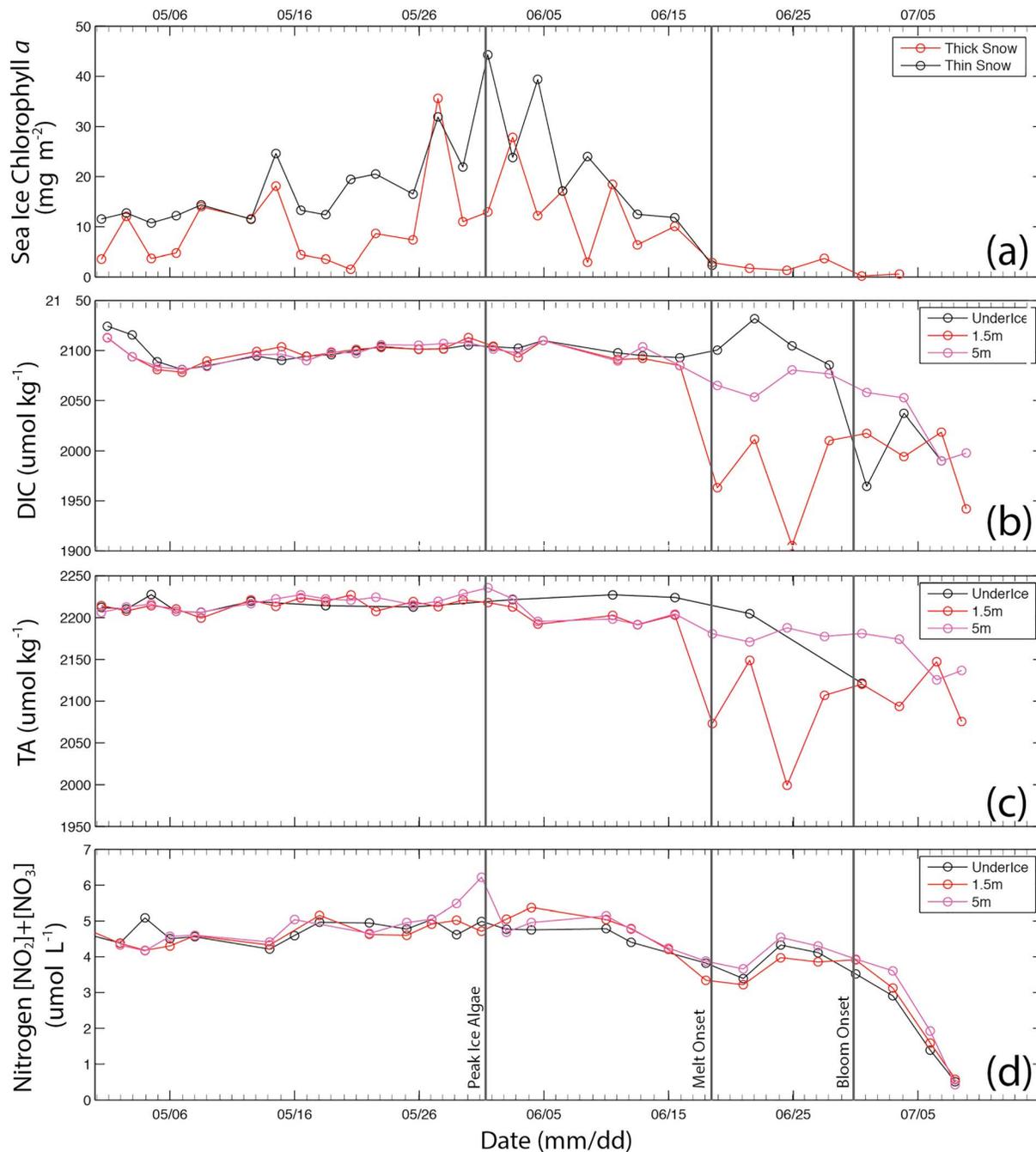
### 4.1. Factors Impacting the Carbonate System

#### 4.1.1. Bottom Ice Algae

As discussed in section 1, the timing of DIC drawdown in the Arctic, and the biological community responsible for it, is subject to considerable uncertainty. Early in our observations (30 April to 6 May) we did see a reduction of DIC, which could be interpreted as drawdown by ice algae (Figure 7b). However, throughout most of the ice algae bloom period (Figure 7a), DIC actually *increased* at a fairly consistent rate. Some insight can be gained from Figure 8, which reports the various observations of carbon content in the bottom 10 cm of sea ice. Although some accumulation of biomass ( $\sim 500 \text{ mg/m}^2$ ) occurred prior to the initiation of our seawater sampling for DIC/TA, substantial accumulation of TPC (from  $\sim 500$  to  $\sim 1,000 \text{ mg/m}^2$ ) did occur over the first week of May (the start of our sampling period) and in the last week of May (from  $\sim 1,000$  to  $\sim 2,000 \text{ mg/m}^2$ ). This long period of biomass accumulation did not result in the persistent DIC drawdown (Figure 7a) that we might have expected from an active ice algae bloom.

A potential explanation for our inability to see a persistent surface water DIC drawdown by ice algae is that mixing (and hence dilution) may have been occurring over the upper  $\sim 25 \text{ m}$ , where the water column was neutrally stratified (Figure 5b). The relatively small changes in surface water DIC caused by ice algae carbon uptake may not have been detectable when diluted by mixing over a significant depth. There are two interesting cases in the published literature worth comparing to our observations. In a year-long study in the Amundsen Gulf region, Shadwick et al. (2011) and Else et al. (2012) observed a reduction of DIC and  $p\text{CO}_{2\text{sw}}$  in the mixed layer beneath the ice cover in early April, which they attributed to the onset of a bottom ice algae bloom. Peak ice algae Chl *a* concentrations in that study were relatively low ( $\sim 20 \text{ mg/m}^2$ ), but there was a distinct pycnocline at  $\sim 50\text{-m}$  depth, separating the polar mixed layer from underlying Pacific water. Conversely, Brown et al. (2015) saw no impact of ice algae on  $p\text{CO}_{2\text{sw}}$  in the water column through the peak of an intense bottom ice algae bloom near Resolute Bay, Nunavut. Ice algae concentrations in that study were much higher (max  $\sim 80 \text{ mg/m}^2$ ), but the water column in that region is typically mixed to the bottom ( $\sim 150 \text{ m}$ ) due to strong tidally driven currents (Mundy et al., 2014).

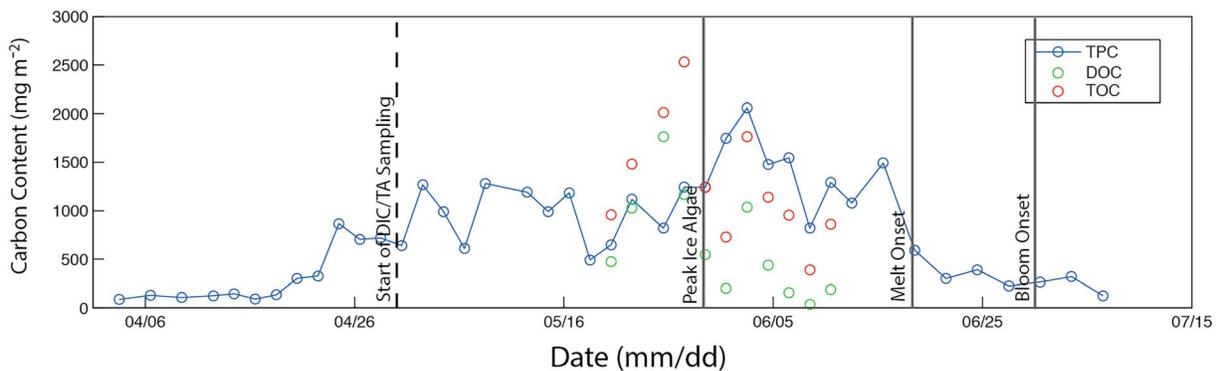
Based on those comparisons, one might be tempted to conclude that the depth of mixing may be important in the detection of ice algae influence on surface water DIC/ $p\text{CO}_{2\text{sw}}$ . A relatively simple calculation illustrates this point. If we take observations of ice algae biomass from the present data set and assume that mixing does occur over a 25-m depth (L. Oziel et al., personal communication, 2019), the change in mixed layer DIC (here denoted  $\Delta\text{DIC}$ ) caused by ice algae biomass accumulation can be estimated by the following:



**Figure 7.** Times series of biogeochemical measurements in the bottom 3 cm of sea ice: (a) chlorophyll *a* concentration; and biogeochemical measurements in near-surface seawater at different depths: (b) dissolved inorganic carbon (DIC) concentrations, (c) total alkalinity (TA), and (c) nitrogen (nitrate [NO<sup>3-</sup>] plus nitrite [NO<sup>2-</sup>]) concentrations.

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

where  $\Delta \text{TOC}$  is the change in TOC in sea ice during the ice algae bloom, MLD is the mixed layer depth, and  $\rho$  is the density of seawater ( $1,026 \text{ kg/m}^3$ ). To take the most extreme estimate of biomass accumulation in the ice, we can set  $\Delta \text{TOC}$  to the peak observed TOC value ( $2,500 \text{ mg/m}^2$ , or  $2.08 \times 10^5 \text{ } \mu\text{mol/m}^2$ ) shown in Figure 8. Even in this maximum case, this calculation yields a total change in DIC of only  $8 \text{ } \mu\text{mol/kg}$  over



**Figure 8.** Time series of the various measures of carbon content in the bottom 10 cm of sea ice: total particulate carbon (TPC), dissolved organic carbon (DOC), and total organic carbon (TOC). Note the different time scale on this figure. The start of DIC/total alkalinity sampling is noted by the vertical dashed line.

the 25-m depth. It is doubtful even in this hypothetical case that we would have been able to detect such a change; the biomass accumulation period apparent in Figure 8 is on the order of 45 days, which would suggest a DIC removal rate of  $<0.2 \mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ . Even modest net respiration in the water column or a small amount of brine drainage enriched in DIC by calcium carbonate formation (e.g., Rysgaard et al., 2007) would overwhelm this signal.

We can also apply this calculation to the Shadwick et al. (2011) study, where a  $20 \mu\text{mol}/\text{kg}$  DIC decrease integrated over a 50-m-deep surface layer was attributed to ice algae production. According to equation (1), this would require an accumulation of approximately  $12,000 \text{ mg}/\text{m}^2$  of organic carbon in the sea ice. Assuming a C:Chl *a* ratio of 60:1 (similar to what we observed, and similar to other observations in the vicinity of Amundsen Gulf; Riedel et al., 2006), this would require bottom-ice Chl *a* values in excess of  $200 \text{ mg}/\text{m}^2$ , an order of magnitude higher than the  $\sim 20 \text{ mg}$  Chl *a* per square meter actually observed (Leu et al., 2015). This is of course a rough estimate since the C:Chl *a* ratio can vary significantly, but Chl *a* greater than  $200 \text{ mg}/\text{m}^2$  would be higher than any values reported in the pan-Arctic summary reported by Leu et al. (2015). It is important to note that the Else et al. (2012) and Shadwick et al. (2011) studies had fairly low temporal resolutions (i.e., monthly) for their measurements and in the heavily fractured Amundsen Gulf region the impact of a rapid-onset under-ice phytoplankton bloom could have been misattributed to an ice algae bloom. Another source of error in this calculation is undersampling of sea ice ridges (recently identified as potential hot spots for biological activity by Fernández-Méndez et al., 2018), since the sea ice Chl *a* measurements in the Amundsen Gulf were primarily made on level sea ice.

Unfortunately, our study cannot completely resolve this ambiguity. It would be a fair criticism to state that by missing DIC/TA observations at the start of the ice algae bloom, we missed important observations that would have allowed us to test the hypothesis that ice algae exert a major control on surface water DIC. Certainly, the observations that we did manage to make at the end of the rapid biomass accumulation point to this as an important time period (i.e., 30 April to 6 May, Figure 7b). However, the calculations based on equation (1) suggest that there is simply not enough biomass in sea ice to impart a significant change in DIC through a large volume of water. The best explanation we can present at this time is that the short-term decrease in DIC that we observed at the start of our measurement period was a transient effect, caused by rapid ice algae accumulation that only persisted until mixing diluted the signal. That explanation is supported by the fact that the decrease was most pronounced in the samples collected at the ice interface and was much less evident at 1.5- and 5-m depths. Figure 5a does show a stable layer near to the ice surface, perhaps allowing for greater ice algae-driven changes in the small water volume directly in contact with the ice. Once biomass accumulation ceased, DIC drawdown from this layer also likely ceased, and mixing negated any significant change in DIC over the upper water column.

A study by Miller et al. (2011) provides support for these conclusions, although the authors did not explicitly discuss the potential role of ice algae on surface water DIC themselves. In that study, weekly measurements of mixed layer DIC were made from December through June aboard a research icebreaker frozen in landfast sea ice in the western Canadian Arctic. Like our study, they observed an increase in surface

water (upper 14 m) DIC through a bottom ice algae bloom of similar magnitude (Riedel et al., 2006). Also, similar to our observations, their time series of mixed layer DIC observations showed a short-lived decrease (by about 10  $\mu\text{mol/kg}$ ) in close coincidence to the initiation of the ice algae bloom (Riedel et al., 2006). These observations lend support to our general conclusions about the short-lived and minor impacts that ice algae appear to have on surface water DIC concentrations.

It is also worth discussing the steady increase in DIC that we observed under the ice, following the initial DIC drawdown period (i.e., between 6 and 31 May). The DIC accumulation rate over this period was approximately  $1.1 \mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$  (Figure 7b), and the attendant increase in nutrients (Figure 6d) indicates that this was driven primarily by heterotrophic activity. This heterotrophic activity must be related to bacteria or grazers, either in the water column or associated with the sea ice algal bloom. Water column community respiration measurements beneath sea ice in winter are rare, but Nguyen et al. (2012) reported a mean value of  $0.90 \mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$  (with a range of  $0.3\text{--}1.8 \mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ ) beneath landfast ice in the western Canadian Arctic. This suggests that much of the increase in DIC we observed can be explained by respiration in the water column. Within the sea ice, net heterotrophy (Søgaard et al., 2013) and remineralization (Fripiat et al., 2017) has been observed at certain times in the year. However, Campbell et al. (2017) showed that Arctic sea ice switches from net heterotrophy to net autotrophy during the period of rapid algal accumulation, which corresponds to the month of May in our study (Figure 8). It therefore seems most likely that the DIC accumulation we observed under the ice was driven by respiration in the water column.

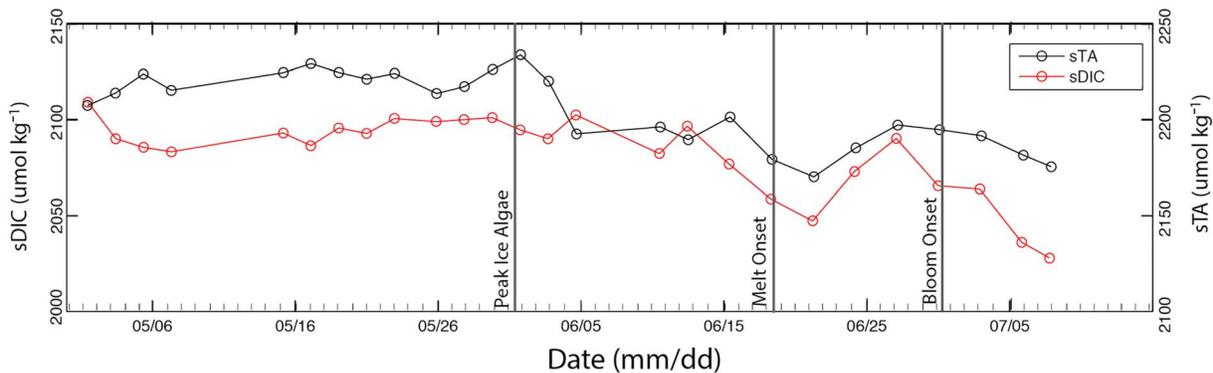
#### 4.1.2. Under-Ice Phytoplankton

Although the role of ice algae on the surface water carbonate system appears to be minor, our observations do point to a clear and important role for under-ice phytoplankton blooms. The major under-ice bloom (Figures 3c and 6) was first observed on 30 June, and from the previous sampling date (27 June) to the final sampling date (8 July) it was associated with a DIC drawdown of  $\sim 80 \mu\text{mol/kg}$  at 5-m depth, with greater drawdown at 1.5 m (Figure 7b). One other potential cause of the DIC drop could be dilution from sea ice melt; however, the salinity at 5 m decreased by less than 0.5 psu during that time (Figure 4). We can test the dilution effect on DIC by applying a simple two-component end-member mixing analysis with an assumed ice melt salinity of 5 psu (L. Oziel et al., personal communication, 2019) and DIC of  $330 \mu\text{mol/kg}$  (Miller et al., 2011; Rysgaard et al., 2007) and assumed seawater salinity of 32.4 psu and DIC of  $2100 \mu\text{mol/kg}$  (i.e., the premelt conditions as per Figures 4 and 7b). Using those end-members, a 0.5-psu decrease is only expected to decrease DIC by  $30 \mu\text{mol/kg}$ , whereas the observed decrease was on the order of  $100 \mu\text{mol/kg}$ . Further evidence is shown in the salinity normalized DIC at 5 m (Figure 9), which still showed a decline of  $64 \mu\text{mol/kg}$  over that time period.

If this drawdown of DIC was caused completely by biological production, we would expect the nitrate + nitrite concentrations to also decrease at a rate similar to the Redfield ratio (14 mol: 117-mol DIC, or a ratio of 0.11; Almon & Martin, 2014; Redfield, 1958), and TA should increase at a similar ratio (Zeebe & Wolf-Gladrow, 2001). Over the observed bloom period (30 June to 8 July) the ratio of N decrease (also normalized by salinity) to nDIC was 0.09, which is within the expected variation from the standard Redfield Ratio (DeVries & Deutsch, 2014). This result suggests that biological drawdown was the main cause of DIC decline during the under-ice bloom period.

It should be noted, however, that TA did not follow the expected ratio. During the under-ice bloom period, TA decreased at a nTA:nDIC ratio of  $\sim 0.5$ , when it should have been increasing slightly if biological production was the only factor affecting TA. Indeed, the TA results for much of the observation period are difficult to understand. The first interesting deviation in TA happened just after the ice algae peak (Figure 7a), where TA dropped by  $\sim 30 \mu\text{mol/kg}$ . At the same time, Chl *a* was decreasing significantly in the sea ice (Figure 7c). It is possible that during this time period the ice was warming, brine drainage was increasing, and ice algae were being sloughed out of the ice as a result (e.g., Lavoie et al., 2005). As discussed by Rysgaard et al. (2011), precipitation of calcium carbonate crystals in sea ice lowers brine TA. What we may have been seeing during this time period was the release of low-TA brine. Similar processes may also be influencing the DIC:TA ratios during the under-ice bloom period.

Another period of time worth considering is the  $\sim 1$ -week period following the onset of ice melt. This decrease corresponds to the subtle seawater chlorophyll peak discussed in section 3.3 (see Figures 3c and 6). Since this event also coincides with the appearance of freshwater in the surface ocean (Figure 3a),



**Figure 9.** Normalized dissolved inorganic carbon (sDIC) and total alkalinity (sTA) at 5 m in the water column to a salinity of 32.46. Meltwater did not intrude into 5 m until the end of sampling.

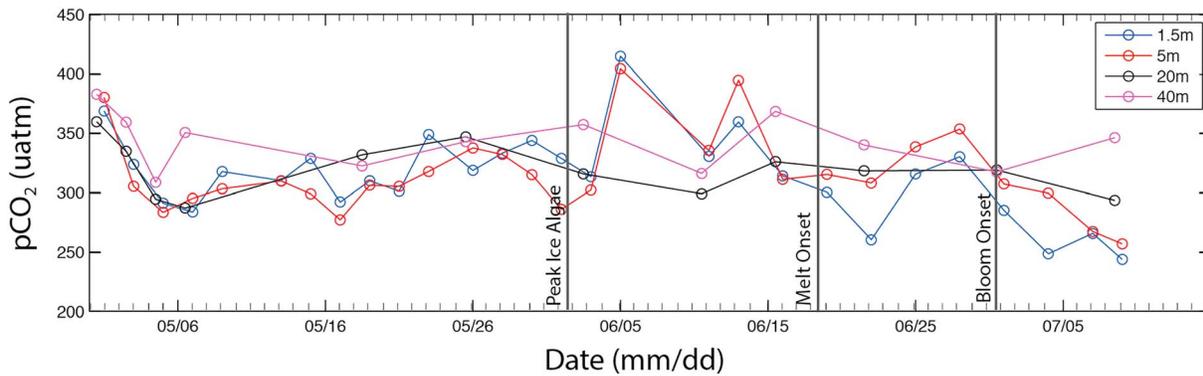
and the removal of Chl *a* from the ice (Figure 7a), a likely explanation is that the event was caused by ice algae flushing out of the sea ice as meltwater percolated through the ice. Standardized DIC (Figure 9) and nitrate + nitrite (Figure 6d) also declined following the ice algae flushing event (Figure 9), from which one might be tempted to conclude that the ice algae immediately begin photosynthesizing once they entered their new seawater habitat. However, the N to DIC ratio during this event was 0.03, which is quite far from the expected Redfield ratio. A more reasonable explanation might be that the ice flushing event brought melt water with nutrient, TA, and DIC concentrations that were heavily modified by processes occurring within the ice matrix. Another complicating factor is that gas exchange could have been affecting the biogeochemistry of the sea ice at this time, as past studies have shown the potential for gas exchange between the sea ice and the atmosphere once the ice has warmed and permeability has increased (Delille et al., 2014). Future studies should perhaps focus not only on high-resolution time series of the biogeochemistry beneath the ice but also on the biogeochemistry of the sea ice itself (and particularly the brine). Such an approach would make it possible to disentangle the many complicated processes occurring during this time period.

#### 4.2. $p\text{CO}_2$ and Atmospheric $\text{CO}_2$ Uptake Potential

Arctic marine systems generally absorb  $\text{CO}_2$  from the atmosphere, but considerable variability has been observed between different regions (Bates & Mathis, 2009; Manizza et al., 2013; Parmentier et al., 2017). Although most  $\text{CO}_2$  exchange is thought to occur in open water during summer and fall, it is still useful to examine  $p\text{CO}_{2\text{sw}}$  in the ice-covered season during spring. As first postulated by Yager et al. (1995) and later developed by Else et al. (2012), biogeochemical processes during the ice-covered season precondition  $p\text{CO}_{2\text{sw}}$  prior to ice breakup and to a large extent determine the direction and magnitude of annual  $\text{CO}_2$  flux budgets.

Using our DIC/TA measurements to calculate  $p\text{CO}_{2\text{sw}}$ , we found that seawater at all sampling depths was essentially undersaturated (below the atmospheric value of  $\sim 400 \mu\text{atm}$ ) throughout the entire sampling period (Figure 10). Concentrations ranged between 300 and 350  $\mu\text{atm}$  throughout the month of May, and with few exceptions our June measurements also stayed between 300 and 350  $\mu\text{atm}$ . In July, when ice melt was well under way and the under-ice phytoplankton bloom had been initiated, concentrations fell below 300  $\mu\text{atm}$ .

Table 1 shows reported  $p\text{CO}_{2\text{sw}}$  measurements in various sea ice-covered regions during similar seasons (late winter, prior to sea ice melt). This summary, in conjunction with the present results, shows a convergence toward the observation that Arctic seas are typically undersaturated at ice breakup, confirming a basic tenant of the Yager et al. (1995) seasonal rectification hypothesis. For our specific study area, we do not have observations into the open water summer season, when significant air-sea  $\text{CO}_2$  exchange might occur. However, since nutrients were still available at the end of the study period (Figure 7d), the phytoplankton growing season should have continued to reduce  $p\text{CO}_{2\text{sw}}$  further into the summer. Sea ice melt and dilution would also have continued, making this region a significant sink for atmospheric  $\text{CO}_2$  once open water had



**Figure 10.** Time series of  $p\text{CO}_2$  concentrations ( $\mu\text{atm}$ ) for the upper 40 m of the water column calculated with  $\text{CO}_2\text{SYS}$ .

been achieved. Furthermore, our observations show that significant under saturation prevailed until at least 40-m depth (Figure 10), indicating that a considerable volume of surface water would need to reach saturation before atmospheric  $\text{CO}_2$  uptake ceased.

### 4.3. Carbonate Saturation Calculations

Qikiqtarjuaq is home to a small-scale commercial clam fishery, which a review of Nunavut fisheries identified as having potential for economic development (Brubacher Development Strategies Inc., 2004). The soft-shell clams (*Mya* spp.) are harvested by scuba divers, at depths of 10–20 m (Misiuk et al., 2015). The vulnerability of these clams (along with other calcifying organisms) to ocean acidification is subject to considerable debate. Although experimental studies have shown soft calms to be susceptible to aragonite dissolution from acidification (Gazeau et al., 2013; Ries et al., 2016), it is difficult to say how those experiments relate to the natural environment that the clams actually live in. Other lines of research have shown that vulnerability to acidification also depends on food supply (Ramajo et al., 2016) and the ability for the surrounding habitat to regulate pH (e.g., Krause-Jensen et al., 2016). Nevertheless, since our sampling coincides with the clam harvesting depth and was conducted during the season with expected minimum pH values, we felt it would be useful to report the calcium carbonate saturation states based on our measured carbon system parameters (Table 2).

During our sampling period, calcium carbonate saturation states for both aragonite and calcite in the water column were  $\Omega > 1$ , indicating that seawater was supersaturated with respect to calcium carbonate (Rossum

**Table 1**  
 *$p\text{CO}_{2\text{sw}}$  From Previous Studies During the Spring (April, May, and Early June)*

Study	Time period	Region	$p\text{CO}_{2\text{sw}}$ ( $\mu\text{atm}$ )	$\Delta p\text{CO}_2$ ( $\mu\text{atm}$ )
Miller et al. (2011)	January–June 2004	Franklin Bay (Canadian Arctic Archipelago)	below saturation (exact values not reported)	
Else et al. (2012)	April–June 2008	Amundsen Gulf (Canadian Arctic Archipelago)	April: 363 May: 305	–29 <sup>a</sup> –87 <sup>a</sup>
Else et al. (2012)	May 2008	Banks Island (Beaufort Sea)	May: 301	–91 <sup>a</sup>
Papakyriakou and Miller (2011)	April–June 2002	McDougall Sound (Canadian Arctic Archipelago)	May: 440 to 380 June: 370 to 350	2–62 <sup>a</sup>
Omar et al. (2007)	April–June 1990–1999	Barents Sea	April: 340 May: 330 June: 300	–30 –40 –70
Rysgaard et al. (2012, 2013)	March–June	Greenland Sea	March: 335 June: 163 to 210	–60 <sup>a</sup> –231 to –184 <sup>a</sup>
Bates (2006)	Springtime 2002	Central Chukchi Sea shelf, (Perennial sea ice)	300 to 350 (200 to 250)	–100 to –50 <sup>a</sup> –200 to –150 <sup>a</sup>

Note. Measurements were made under sea ice but prior to sea ice melt decay and the phytoplankton blooms.

<sup>a</sup> $\Delta p\text{CO}_2$  ( $\mu\text{atm}$ ) values estimated using flask atmospheric measurements of  $\text{CO}_2$  recorded at Alert, Nunavut, Canada ([ftp://afpt.cmdl.noaa.gov/data/trace\\_gases/](ftp://afpt.cmdl.noaa.gov/data/trace_gases/)).

**Table 2**  
Average Calcium Carbonate Saturation States of Calcite ( $\Omega_C$ ) and Aragonite ( $\Omega_A$ ) ( $\pm SD$ ) Calculated From  $CO_2SYS$

Depth	Average $\Omega_C$	Average $\Omega_A$
1.5 m	2.15 ( $\pm 0.17$ )	1.34 ( $\pm 0.11$ )
5 m	2.20 ( $\pm 0.19$ )	1.37 ( $\pm 0.12$ )
20 m	2.20 ( $\pm 0.13$ )	1.37 ( $\pm 0.08$ )
40 m	2.07 ( $\pm 0.12$ )	1.29 ( $\pm 0.08$ )

& Merrill, 1983). Saturation levels were lower for 1.5 and 5 m than 20 m because of the higher  $pCO_{2sw}$  values. Saturation levels for 40 m were lowest because of colder temperatures and constant  $pCO_{2sw}$  values. Aragonite was close to saturated levels at the surface, although both calcite and aragonite's  $\Omega$  value increased as further production lowered  $pCO_{2sw}$  values.

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

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

It is well known that increased  $CO_2$  and enhanced sea ice melt results in lower, even unsaturated conditions in certain Arctic regions (Robbins et al., 2013; Yamamoto-Kawai et al., 2012). The Earth system model presented by Steinacher et al. (2008) predicts that the entire Arctic Ocean water column will have undersaturation (except between 1,000 and 2,000 m) by 2100. There will be undersaturation of at least 10% of Arctic surface waters within a decade, with over 50% of the Arctic surface waters undersaturated by year 2050 in the A2 emissions scenario. For the Baffin Bay region, in particular, Steiner et al. (2015) predict that the saturation depth of aragonite will rise about 60 m per decade. Building from the observation that our site near Qikiqtarjuaq is fairly typical for the Arctic, these projections suggest aragonite undersaturation at the depth of the clam shelves within three to four decades.

## 5. Conclusions

The first main conclusion of this study is that bottom ice algae production does not appear to affect mixed layer DIC/ $pCO_{2sw}$  concentrations to an extent that would significantly impact air-sea exchange of  $CO_2$  in the ice-free season. One caveat to this conclusion is that we did not manage to capture DIC/ $pCO_{2sw}$  measurements of the initial ice algae biomass accumulation. Observations from the beginning of our time series suggest that a minor impact on DIC may occur during periods of rapid biomass accumulation, although the effect may be transient and limited to the water layers in closest contact with the sea ice. In general, our calculations show that there is not enough biomass in bottom ice algae to impart a significant and persistent reduction in surface layer DIC/ $pCO_{2sw}$ . It remains an open question, however, if sub-ice algae blooms (e.g., the dramatic *Melosira arctica* aggregations described by Poulin et al., 2014, and other researchers) might have a significant effect on the carbonate system.

The second major conclusion of this study is that while the role of bottom ice algae may be minor, the role of under-ice phytoplankton is clearly not. In our study, an under-ice phytoplankton bloom had an immediate and significant impact on DIC and  $pCO_{2sw}$ . One possible reason that under-ice phytoplankton blooms have been overlooked in past discussions about the “seasonal rectification hypothesis” is that their significance has only come to light in recent years. Although observed at least two decades ago (Fortier et al., 2002), their importance—particularly in the changing Arctic icescape—has only been identified recently (Arrigo et al., 2012; Mundy et al., 2009).

Another conclusion of our study is that  $pCO_{2sw}$  was undersaturated (with respect to the atmosphere) as the region emerged from polar night into its spring awakening. This validates a key point of the “seasonal rectification hypothesis” (Yager et al., 1995), and as we illustrated in Table 1 this observation seems to be widespread. What is noteworthy is that if bottom ice algae are indeed unimportant to the seawater carbonate system, then  $pCO_{2sw}$  in these studies was undersaturated *before* any significant photosynthetic impact on DIC/ $pCO_{2sw}$  occurs (i.e., under-ice or open-water phytoplankton blooms). It is not immediately clear why this widespread undersaturation beneath the ice cover exists, but further studies into the fall and winter time periods are likely necessary to fully understand the phenomenon.

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

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