Effects of sea-ice and biogeochemical processes and storms on under-ice water fCO$_2$ during the winter-spring transition in the high Arctic Ocean: Implications for sea-air CO$_2$ fluxes

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Abstract We performed measurements of carbon dioxide fugacity (fCO$_2$) in the surface water under Arctic sea ice from January to June 2015 during the Norwegian young sea ICE (N-ICE2015) expedition. Over this period, the ship drifted with four different ice floes and covered the deep Nansen Basin, the slopes north of Svalbard, and the Yermak Plateau. This unique winter-to-spring data set includes the first winter-time under-ice water fCO$_2$ observations in this region. The observed under-ice fCO$_2$ ranged between 315 μatm in winter and 153 μatm in spring, hence was undersaturated relative to the atmospheric fCO$_2$. Although the sea ice partly prevented direct CO$_2$ exchange between ocean and atmosphere, frequently occurring leads and breakup of the ice sheet promoted sea-air CO$_2$ fluxes. The CO$_2$ sink varied between 0.3 and 86 mmol C m$^{-2}$ d$^{-1}$, depending strongly on the open-water fractions (OW) and storm events. The maximum sea-air CO$_2$ fluxes occurred during storm events in February and June. In winter, the main drivers of the change in under-ice water fCO$_2$ were dissolution of CaCO$_3$ (ikaité) and vertical mixing. In June, in addition to these processes, primary production and sea-air CO$_2$ fluxes were important. The cumulative loss due to CaCO$_3$ dissolution of 0.7 mol C m$^{-2}$ in the upper 10 m played a major role in sustaining the undersaturation of fCO$_2$ during the entire study. The relative effects of the total fCO$_2$ change due to CaCO$_3$ dissolution was 38%, primary production 26%, vertical mixing 16%, sea-air CO$_2$ fluxes 16%, and temperature and salinity insignificant.

1. Introduction

The ice cover in the Arctic Ocean has decreased during the last decades, manifested in particular as an extensive transition from multiyear ice (MYI) to first-year ice (FYI) [e.g., Serreze and Stroeve, 2015; Meier et al., 2014; Lindsay and Schweiger, 2015]. As the summer sea-ice cover is decreasing, larger areas have only seasonal sea-ice cover and waters that are exposed to the atmosphere during the Arctic summer, as in the Antarctic Ocean. This open water is favorable for sea-air carbon dioxide (CO$_2$) exchange. The direction and magnitude of the net sea-air CO$_2$ exchange depend on salinity, temperature, wind speed, and the difference in CO$_2$ partial pressure between water and atmosphere. So far, estimates of sea-air CO$_2$ fluxes during the Arctic summer have shown that the Arctic Ocean acts as an atmospheric CO$_2$ sink [e.g., Fransson et al., 2009; Bates and Mathis, 2009; Schuster et al., 2013; Yasunaka et al., 2016].

The surface-water fugacity of CO$_2$ (fCO$_2$) in the Arctic Ocean varies due to physical processes (e.g., temperature, mixing of waters, sea-ice processes, and freshwater addition) and biological processes (e.g., primary production and remineralization of organic carbon) [e.g., Fransson et al., 2009]. In upwelling areas such as the Bering Sea and Arctic polynyas, high CO$_2$ in the surface promotes CO$_2$ release from the ocean to the atmosphere [e.g., Yager et al., 1995; Fransson et al., 2006, 2009; Else et al., 2012]. In parts of the Arctic Ocean, such as the Canadian Arctic Archipelago, the major driver for the surface-water fCO$_2$ change is biological [e.g., Chierici et al., 2011; Fransson et al., 2013]. In addition, several studies have shown the importance of CO$_2$-rich sea-ice brine for mediating vertical transport of CO$_2$ in the water column, often referred as the sea-ice brine CO$_2$ pump [e.g., Omar et al., 2005; Rysgaard et al., 2007, 2009; Miller et al., 2011; Fransson et al.,...
Although the sea-ice cover hampers direct CO₂ flux between air-water interfaces, recent studies have shown that processes within the sea ice indirectly promote sea-air CO₂ [e.g., Rygaard et al., 2007, 2013; Nomura et al., 2010; Fransson et al., 2013; Delille et al., 2014]. While sea ice and brine are forming, salinity and chemical substances such as CO₂ become concentrated. These concentrated components can cause supersaturation in the ice with respect to CO₂ and minerals, such as calcium carbonate (CaCO₃) [Assur, 1960]. Precipitation of CaCO₃ from the brine produces CO₂(aq) and reduces total alkalinity (AT) in the brine (equation (1)).

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O} + \text{CO}_2(aq).
\]  

Ikaite is a form of CaCO₃, which precipitates in both Arctic and Antarctic sea ice [e.g., Dieckmann et al., 2008, 2010; Rygaard et al., 2011]. When solid ikaite dissolves in the surface water, CO₂ is consumed and alkalinity increases (equation (1)). Brine volume depends on ice temperature and salinity, and when brine volume is larger than 5%, the sea-ice layer becomes permeable [Weeks and Ackley, 1986; Golden et al., 1998, 2007] so that brine as well as ikaite can exchange with underlying seawater through gravity drainage [Notz and Worster, 2009]. Consequently, the sea ice can become a source of either CO₂ or alkalinity to the underlying water [Rygaard et al., 2007, 2009, 2012; Nedashkovsky et al., 2009; Geilfus et al., 2012, 2016; Fransson et al., 2013]. Due to the rejection of brine, fCO₂ can become higher than the atmospheric and/or underlying water fCO₂, which can result in CO₂ outgassing from the ice to the atmosphere and/or to the underlying water [e.g., Papadimitriou et al., 2004; Rygaard et al., 2007, 2013; Miller et al., 2011; Geilfus et al., 2012; Fransson et al., 2009, 2013]. On the other hand, brine that contains ikaite can escape from the sea ice to underlying water through brine channels, where ikaite dissolves, consuming CO₂ [e.g., Fransson et al., 2013; Geilfus et al., 2016]. In addition, in spring, primary production decreases fCO₂, and the ice and its meltwater act as a sink of atmospheric CO₂ [e.g., Rygaard et al., 2007, 2013; Fransson et al., 2001, 2013; Nomura et al., 2013]. Moreover, studies in the Canadian Arctic Archipelago showed exchange of CO₂ at openings in the ice cover through leads and cracks in the ice in winter [Else et al., 2013].

Ship-based high-frequency sea-surface fCO₂ measurements, typically based on infrared determination of the CO₂ concentration in an equilibrator headspace, are frequently used to estimate air-sea CO₂ fluxes at regional and global scales [e.g., Takahashi et al., 2009; Le Quéré et al., 2015]. However, such data are scarce in the Arctic Ocean and particularly in ice-covered waters. Fransson et al. [2009] carried out one of the first high-frequency sea-surface fCO₂ measurements in the Arctic Ocean, in the ice-covered Northwest Passage from the Labrador Sea to the Chukchi Sea. They found large variability in surface fCO₂ and sea-air CO₂ fluxes where most of the variability could be explained in terms of freshwater addition (sea-ice melt and river run-off), primary production, and upwelling. Else et al. [2012, 2013] measured fCO₂ continuously under the ice using a ship as a platform during a full sea-ice cycle in a flaw lead in the Canadian Arctic Archipelago, and that is one of few winter-time fCO₂ measurements in the ice-covered part of the Arctic Ocean.

In general, fCO₂ data in the Arctic Ocean are scarce. In this study, we present unique measurements of fCO₂ under ice obtained during a 5 month drift over the deep Arctic basin (Nansen Basin) and the Yermak Plateau north of Svalbard from January (winter) to end of June (spring) [Granskog et al., 2016]. As evaluated from version 4 of the Surface Ocean CO₂ Atlas [Bakker et al., 2016; www.socat.info], no fCO₂ data have previously been obtained in this area. Our data are also unique for the Arctic Ocean since it was collected in the period with the least data, from January to June. R/V Polarstern passed the area and performed underway fCO₂ measurements toward the end of the period covered by the current study, and there may be a few coinciding data points (expocode: 06AQ20150519, 15 May to 27 June 2015). We quantify the major monthly biogeochemical drivers of the observed fCO₂ variability during a 5 month period using ancillary surface-water data. The sea-air CO₂ flux is estimated and related to sea-ice concentration and open-water fraction, and we discuss the effects of storm events on the fCO₂ and the sea-air CO₂ flux.

2. Study Area

The study took place during the Norwegian young sea ICE (N-ICE2015) expedition with R/V Lance, covering the area from the deep Nansen Basin to the slopes north of Svalbard and the Yermak Plateau (80°N–83°N, 8°E–28°E; Figures 1a and 1b) from 15 January 2015 to 22 June 2015 [Granskog et al., 2016]. We drifted with four different ice floes from January (winter) to June (spring) 2015, and fCO₂ was continuously...
measured. In winter, we drifted over the deep Nansen Basin (depth > 3000 m) and over the shallow slope areas toward Svalbard. In spring, the drift was mostly over the slope (Table 1). Table 2 provides an

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Table 1. Start and End Dates for Each Floe, Season, and the Type of Study Area Based on Bathymetry

<table>
<thead>
<tr>
<th>Date (Start, End)</th>
<th>Floe#</th>
<th>Season</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 Jan–21 Feb</td>
<td>1</td>
<td>Winter</td>
<td>Nansen Basin (≥3000 m) and slope (1500–3000 m)</td>
</tr>
<tr>
<td>24 Feb–19 Mar</td>
<td>2</td>
<td>Winter</td>
<td>Nansen Basin (≥3000 m) and slope (1500–3000 m)</td>
</tr>
<tr>
<td>18 Apr–5 Jun</td>
<td>3</td>
<td>Spring</td>
<td>Yermak Plateau (&lt;1500 m) and slope (1500–3000 m)</td>
</tr>
<tr>
<td>7 Jun–22 Jun</td>
<td>4</td>
<td>Spring</td>
<td>Yermak Plateau (&lt;1500 m) and slope (1500–3000 m)</td>
</tr>
</tbody>
</table>
In late spring, the upper 100 m were dominated by a mix of Polar Surface Water and warm Polar Surface Water (PSWw, $\sigma_0 < 27.70$) in the upper 100 m (Figures 3a and 3b), described in detail by Meyer et al. [2017a, 2017b]. In late spring, the upper 100 m were dominated by a mix of Polar Surface Water and warm Polar Surface Water (PSWw, $\sigma_0 < 27.70$ and $\Theta > 0^\circ$C), with occasional intrusions of Atlantic Water (AW, $\Theta > 2^\circ$C and $27.70 < \sigma_0 < 27.97$) close to the surface [Meyer et al., 2017a, 2017b, Figure 7]. The observed sea-surface temperature (SST) corresponded to the freezing point of seawater, approximately $-1.8^\circ$C, between January and May, and increased to above $0.7^\circ$C in June (Table 4 and Figure 4a). In January to mid-May, surface-water salinity was above 34 and in June, vertical mixing of warm Atlantic water caused bottom ice melt, and consequently a decrease of sea-surface salinity of 32.7 [Meyer et al., 2017a, 2017b, Figures 3b and 4b].

The fraction of open water (OW) around R/V Lance varied throughout the study, with a winter maximum of 7% and a spring maximum of 53% in June (Figures 2a and 2b). Increased open-water fractions mostly coincided with storm events defined by Cohen et al. [2017] (Figures 2a and 2b and Table 3).

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**Table 2.** The Meteorological Properties at 10 m Above Sea-Ice Are Shown for Each Floe

<table>
<thead>
<tr>
<th>Floe#</th>
<th>T air (°C)</th>
<th>P air (hPa)</th>
<th>RH (%)</th>
<th>u (m s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27</td>
<td>995</td>
<td>75</td>
<td>7.3</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>997</td>
<td>87</td>
<td>5.7</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>1014</td>
<td>87</td>
<td>6.2</td>
</tr>
<tr>
<td>4</td>
<td>-0.64</td>
<td>1011</td>
<td>94</td>
<td>6.7</td>
</tr>
</tbody>
</table>

The mean, minimum, and maximum (min, max) air temperature (T air, °C), air pressure (P air, hPa), relative humidity (RH, %), and wind speed (u, m s$^{-1}$) are shown [Hudson et al., 2015]. P air is from 22 m height at the same location as the CO$_2$ air intake.

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**Table 3.** Storm Events Summary for All Floes

<table>
<thead>
<tr>
<th>Season/Floe#</th>
<th>Date Start</th>
<th>Date End</th>
<th>Storm Name</th>
<th>Wind Speed</th>
<th>Pressure</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter/Floe1</td>
<td>21 Jan, 21:00</td>
<td>22 Jan, 07:00</td>
<td>M1</td>
<td>10.8</td>
<td>990</td>
<td>-27</td>
</tr>
<tr>
<td>Winter/Floe1</td>
<td>3 Feb, 11:00</td>
<td>8 Feb, 21:00</td>
<td>M2</td>
<td>22</td>
<td>967</td>
<td>-35.5</td>
</tr>
<tr>
<td>Winter/Floe1</td>
<td>13 Feb, 04:00</td>
<td>13 Feb, 09:00</td>
<td>m1</td>
<td>10</td>
<td>989</td>
<td>-36.4</td>
</tr>
<tr>
<td>Winter/Floe1</td>
<td>15 Feb, 12:00</td>
<td>16 Feb, 17:00</td>
<td>M3</td>
<td>23</td>
<td>976</td>
<td>-34.1</td>
</tr>
<tr>
<td>Winter/Floe1</td>
<td>17 Feb, 16:00</td>
<td>21 Feb, 04:00b</td>
<td>M3</td>
<td>11.9</td>
<td>976</td>
<td>-34.1</td>
</tr>
<tr>
<td>Winter/Floe1</td>
<td>22 Feb, 08:00b</td>
<td>23 Feb, 01:00b</td>
<td>m2b</td>
<td>10.3b</td>
<td>980b</td>
<td>-32.3b</td>
</tr>
<tr>
<td>Winter/Floe2</td>
<td>25 Feb, 06:00b</td>
<td>25 Feb, 20:00b</td>
<td>M3b</td>
<td>8.7b</td>
<td>1001b</td>
<td>-29.1b</td>
</tr>
<tr>
<td>Winter/Floe2</td>
<td>2 Mar, 10:00</td>
<td>4 Mar, 01:00</td>
<td>M4</td>
<td>16.8</td>
<td>998</td>
<td>-25.6</td>
</tr>
<tr>
<td>Winter/Floe2</td>
<td>7 Mar, 08:00</td>
<td>8 Mar, 18:00</td>
<td>M5</td>
<td>14.2</td>
<td>966</td>
<td>-19.5</td>
</tr>
<tr>
<td>Winter/Floe2</td>
<td>14 Mar, 21:00</td>
<td>16 Mar, 23:00b</td>
<td>M6</td>
<td>19.2</td>
<td>966</td>
<td>-31.3</td>
</tr>
<tr>
<td>Spring/Floe3</td>
<td>23 Apr, 10:00b</td>
<td>24 Apr, 12:00b</td>
<td>m4b</td>
<td>14.3b</td>
<td>1009b</td>
<td>-22.9b</td>
</tr>
<tr>
<td>Spring/Floe3</td>
<td>25 Apr, 04:00</td>
<td>27 Apr, 23:00</td>
<td>M7</td>
<td>12.6</td>
<td>1021</td>
<td>-20.3</td>
</tr>
<tr>
<td>Spring/Floe3</td>
<td>6 May, 23:00b</td>
<td>8 May, 02:00b</td>
<td>m5b</td>
<td>10</td>
<td>1012</td>
<td>-17.3</td>
</tr>
<tr>
<td>Spring/Floe3</td>
<td>9 May, 16:00b</td>
<td>10 May, 19:00b</td>
<td>m3b</td>
<td>10.4</td>
<td>1012</td>
<td>-17.3</td>
</tr>
<tr>
<td>Spring/Floe3</td>
<td>16 May, 12:00</td>
<td>16 May, 23:00</td>
<td>m6</td>
<td>12.3</td>
<td>1003</td>
<td>-15</td>
</tr>
<tr>
<td>Spring/Floe3</td>
<td>21 May, 10:00</td>
<td>23 May, 01:00</td>
<td>m7</td>
<td>15.4</td>
<td>1004</td>
<td>-13.5</td>
</tr>
<tr>
<td>Spring/Floe4</td>
<td>29 May, 17:00</td>
<td>30 May, 05:00</td>
<td>m8</td>
<td>10.6</td>
<td>1012</td>
<td>-4.2</td>
</tr>
<tr>
<td>Spring/Floe4</td>
<td>2 Jun, 15:00</td>
<td>6 Jun, 13:00b</td>
<td>M8</td>
<td>13.7</td>
<td>1003</td>
<td>-3</td>
</tr>
<tr>
<td>Spring/Floe4</td>
<td>8 Jun, 1:00</td>
<td>8 Jun, 6:00</td>
<td>m9</td>
<td>12</td>
<td>1000</td>
<td>0.2</td>
</tr>
<tr>
<td>Spring/Floe4</td>
<td>11 Jun, 2:00</td>
<td>14 Jun, 5:00</td>
<td>m10</td>
<td>17.3</td>
<td>1002</td>
<td>-2.9</td>
</tr>
</tbody>
</table>

Values are from shipboard instruments (meteorological tower data not available).

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However, occasionally in February–March, there was a time lag of 1–3 days between the maximum wind speed and the maximum OW. In April and May, the response time was within 12–24 h. Occasionally, OW decreased due to closing of leads during short pulses of high winds and changes in wind direction, particularly in March.

Figure 2. The ice concentration estimated over a $44 \times 44$ km$^2$ box (blue line, left y axis) and wind speed (u, m s$^{-1}$; orange line, right y axis) along drift of (a) Floe 1 and Floe 2 and (b) Floe 3 and Floe 4. The double arrows indicate the start and end of the study on each floe. The period between Floe 1 and Floe 2 has data gaps caused by the time used to relocate R/V Lance. The areas within the dotted lines and M1–M9 and m10 are storm events (Table 3) defined by Cohen et al., [2017].

However, occasionally in February–March, there was a time lag of 1–3 days between the maximum wind speed and the maximum OW. In April and May, the response time was within 12–24 h. Occasionally, OW decreased due to closing of leads during short pulses of high winds and changes in wind direction, particularly in March.
The ice pack was composed primarily of young ice (YI) with little snow, first-year ice (FYI) and second-year ice (SYI) [Granskog et al., 2017], with thick snow (0.3–0.5 m) [Rösel et al., 2016a]. In the region, modal ice thickness was about 1.3–1.5 m [Rösel et al., 2016b].

3. Data and Methods

The $\text{FCO}_2$ data were obtained by infrared analysis of equilibrator headspace samples. The specific instrument was supplied by General Oceanics® and designed following the principles presented by Pierrot et al. [2009] using two-stage showerhead equilibration and a LICOR® 7000 nondispersive infrared detector. The system was calibrated using three reference gases with approximate values of 250, 350, and 450 ppm, traceable to reference standards provided by NOAA/ESRL (National Oceanic and Atmospheric Administration-Earth System Research and Laboratory; see Pierrot et al. [2009] for a more thorough description of the system). Standards were run every third hour. The zero and span of the LICOR were set approximately once a day. The seawater was supplied from an intake located midships, at approximately 5 m water depth. Temperature was recorded in the equilibrator and the surface-water intake using 1521 temperature probes from Hart Scientific, with an accuracy of 0.01°C. Atmospheric $\text{FCO}_2$ was measured in air samples, pumped from an air intake located in the crow’s nest, approximately 30 m above sea level. Wind speed, air temperature, and air humidity (Tables 2 and 3) were obtained from the ship’s met-station and a weather mast located at the ice camp 300–400 m away from the ship [Hudson et al., 2015]. Air pressure was recorded by a high-precision Druck barometer mounted at the air intake in the crow’s nest.

Sea-ice concentration and open-water fraction were obtained from the AMSR2 microwave radiometer on the JAXA GCOM-W satellite. Sea-ice concentrations were derived from the 89 GHz channels, which allow a daily full global coverage of all sea-ice areas on a $6.25 \times 6.25$ km² grid [Spreen et al., 2008, www.seaice.uni-
bremen.de/amsr2]. The mean ice-sea concentration for a square of 43.75 \times 43.75 \text{ km}^2 (7 \times 7 \text{ grid cells}) with R/V Lance in the center pixel was calculated on an hourly basis. The GPS position of R/V Lance was used to identify the center grid cell in the ice concentration data set. The resulting time series is the sea-ice area fraction of a square of approximately 44 \times 44 \text{ km}^2 along the drift paths of the four N-ICE2015 floes. The open-water fraction is one minus the sea-ice area fraction.

### 3.1. Calculation of Surface-Water fCO2

The fugacity of CO2 (fCO2) is similar to the partial pressure, but takes into account the nonideal nature of the CO2 gas. The General Oceanics® system measures the mole fraction of CO2 (xCO2) in the equilibrator headspace sample, and this is converted to fCO2. This conversion is well described by Wanninkhof and Thoning [1993] and summarized here

\[
fCO2 = xCO2^{eq}(P_T - pH2O) \exp\left(\rho n B_{12} + \frac{2\alpha_{12}}{R \cdot T_{eq}}\right) \exp[0.0423(T - T^0)].
\]  

where fCO2 refers to the value in seawater, xCO2^{eq} refers to the equilibrator, P_T is the total pressure, pH2O is the vapor pressure at the equilibrator temperature T^{eq}, SST is the sea-surface temperature from the seawater intake, and R is the gas constant. The increase in fCO2 from heating over the tubing path length between the water intake and the equilibrator is \((\delta \ln fCO2/\delta T) = (0.0423 \pm 0.0002)\text{C}^{-1}\), as determined by Takahashi et al. [1993]. The terms B_{11} and \(\alpha_{12}\) describe the second virial coefficient of pure CO2 and a correction for air-CO2 mixture [Weiss, 1974], respectively.

Occasionally, and particularly in January and February, the room housing the seawater inlet was temperature-controlled to prevent freezing and clogging of the intake. Since this affected the temperature of the incoming water, it was decided not to use any of the surface-water intake temperatures as SST. Rather, a combination of ship-CTD (conductivity-temperature-depth) temperature data from 5 m depth [Dodd et al., 2016; Meyer et al., 2017a, 2017b] and measurements of in situ temperature from 1–2 m depth from an on-ice turbulence mast was used in equation (2). The mast was deployed through a hole in the ice, approximately 300–400 m away from the ship. Sensors included high-precision SeaBird temperature and salinity sensors for sampling at 5 m below the ice surface. Data were sampled at 3 Hz, and averaged to 5 min for this study (see Peterson et al. [2017] for a detailed description). The CTD temperatures were point observations and were used to adjust the temperatures from the on-ice turbulent mast. Adjustments were in the range of 0.001–0.015°C. When temperatures from the on-ice turbulent mast were not available (e.g., from January to the first week of March) CTD temperatures from 5 m depth [Dodd et al., 2016] were used, linearly extrapolated between the points, since the seawater temperature was approximately constant at freezing temperatures. Further, due to the heating of the water inlet room, the equilibrator temperature was occasionally substantially larger than the true SST. To limit errors in fCO2 caused by excessive temperature corrections, only fCO2 data with temperature differences (between SST and equilibrator) of less than 3°C are presented here (Integrated Carbon Observing System (ICOS) recommendation for fCO2 measurements class 1 in areas close to the ice edge). The uncertainty due to temperature correction in fCO2 caused by a warming of 3°C was maximum 3.5 \text{µatm}, using Takahashi et al. [1993] and estimates by CO2SYS calculations [Pierrot et al., 2006]. Salinity data were obtained from a combination of the under-ice turbulence mast [Meyer et al., 2016; Peterson et al., 2017] and CTD data [Dodd et al., 2016; Meyer et al., 2017a, 2017b].

The dissolved inorganic carbon (DIC) and total alkalinity (A_t) samples were analyzed at the Institute of Marine
Research (IMR Tromsø, Norway) following the method described in Dickson et al. [2007]. DIC was determined using gas extraction of acidified samples followed by Coulometric titration and photometric detection using a Versatile Instrument for the Determination of Titration Alkalinity (VINDTA 3D, Marianda, Germany). The AT was determined by potentiometric titration with 0.1 N hydrochloric acid using a Versatile Instrument for the Determination of Titration Alkalinity (VINDTA 3S, Marianda, Germany). Routine analyses of Certified Reference Materials (CRM, provided by A. G. Dickson, Scripps Institution of Oceanography, USA) ensured the accuracy of the measurements, which was better than $\pm 1$ and $\pm 2 \mu$mol kg$^{-1}$ for DIC and AT, respectively. We used AT, DIC, and nutrients as input parameters in a CO$_2$-chemical speciation model (CO2SYS program) [Pierrot et al., 2006] to calculate fCO$_2$ based on the carbonate system dissociation.

Figure 4. Spatial variability of surface-water (a) temperature (°C), and (b) salinity, in the upper 5 m for the entire study. Gray-shaded gradients denote bathymetry from dark gray (shallow) to light gray (deep).
constants (K*1 and K*2) estimated by Mehrbach et al. [1973], modified by Dickson and Millero [1987] and the HSO₄⁻ dissociation constant from Dickson [1990]. Measurements of AT and DIC in surface samples (from the seawater intake or CTD casts) were used to calculate $f_{CO_2}$ to compare with the $f_{CO_2}$ measurements of the underway system (Figure 5). We performed a regression analysis between measured $f_{CO_2}$ at SST and calculated $f_{CO_2}$calc (from pairs of AT and DIC). The linear regression resulted in a root mean standard error (rmse) in $f_{CO_2}$ of $67 \mu$atm, a slope of 0.997, and a coefficient of determination ($r^2$) of 0.999 based on 53 data points. The rmse of $67 \mu$atm includes the effect of the location, sampling, warming of the measured $f_{CO_2}$, analytical uncertainties in the determination of AT and DIC, equilibrium constants as well as any error associated with carbonate-chemistry calculations (CO2SYS). However, the sum of all uncertainties includes compensatory effects causing a net error of $67 \mu$atm, which in fact could be larger than the estimated rmse in this method.

Water samples for nutrients were collected in acid-washed 125 mL bottles (Nalgene®, Rochester, NY, USA), fixed with 0.2 mL chloroform and stored refrigerated until analysis [Assmy et al., 2016]. The nutrient samples were analyzed at IMR, Bergen, and the following nutrients: nitrite ([NO$_2^-$]), nitrate ([NO$_3^-$]), phosphate ([PO$_4^{3-}$]) were measured spectrophotometrically at 540, 540, and 810 nm, respectively, on a modified Scalar autoanalyser [Bendschneider and Robinson, 1952] (RFA methodology). The detection limits were 0.06 mmol m$^{-3}$ for [NO$_2^-$], 0.04 mmol m$^{-3}$ for [NO$_3^-$], and 0.06 mmol m$^{-3}$ for [PO$_4^{3-}$].

Chlorophyll-a samples were filtered onto 25 mm GF/F filters (Whatman), extracted on board with 100% methanol for 12 h at 5°C and measured fluorometrically using a Turner Fluorometer 10-AU (Turner Design, Inc.) [Assmy et al., 2016]. Phaeopigments were measured by fluorescence after acidification with 5% HCl [Holm-Hansen and Riemann, 1978].

### 3.2. Calculations of Sea-Air CO₂ Flux

Using the measured $f_{CO_2}$, we calculated the sea-air CO₂ flux, $F$, according to the gas flux formulation (equation (3)),

$$F = K_0 k (f_{CO_2} - f_{CO_2}^{air}) OW,$$  (3)

$$k = 0.251 u^2 \sqrt{\frac{660}{Sc}},$$  (4)

where $K_0$ is the solubility (mol m$^{-3}$ atm$^{-1}$), $k$ is the transfer velocity (cm h$^{-1}$) for sea-air CO₂ exchange, $u$ is the wind speed (m s$^{-1}$), OW is the open-water fraction, and $f_{CO_2}^{air}$ and $f_{CO_2}$ are the atmospheric and sea
surface $fCO_2$, respectively. $K_o$ was calculated according to Weiss [1974] using the measured SST and salinity values. The transfer velocities ($k$) and the Schmidt number (Sc) were calculated according to Wanninkhof [2014] for monthly and daily average observed wind speed (equation (4)) and are based on wind speed ($u$) at 10 m height above sea-ice surface obtained from the weather-mast meteorological data [Hudson et al., 2015]. The transfer velocity can be affected by the sea ice itself, which can generate turbulence, convection, and current shear [McPhee, 2005]. Sea ice related to open water (e.g., leads and cracks) may also attenuate wind-driven turbulence by the reflection and scattering of wind waves [Masson and LeBlond, 1989]. However, in ice-covered oceans and in winter, these interactions on a spatiotemporal range are limited and not accounted for here. The $fCO_2^{atm}$ was set to its average of 406 µatm, based on all our $xCO_2^{atm}$ measurements in this study. We converted the dry atmospheric mole fractions, $xCO_2^{atm}$ to the atmospheric partial pressure of $CO_2$ ($pCO_2^{atm}$) in wet air according to equation (5),

$$pCO_2^{atm} = xCO_2^{atm} (\text{slp} - p_{H_2O}),$$

where slp is the sea-level pressure and $p_{H_2O}$ the vapor pressure at the observed SST and salinity, calculated according to Weiss and Price [1980]. Values of $pCO_2^{atm}$ were converted to $fCO_2^{atm}$ according to Weiss [1974], following the procedure described in Dickson et al. [2007].

### 3.3. Calculations of Drivers Effecting Under-Ice Water $fCO_2$

We estimated the effect of different drivers on the monthly change in the observed surface-water $fCO_2$ ($dCO_2/dt$) and the previous month $fCO_2$ ($fCO_2_{t-1}$) following a similar approach as used elsewhere [e.g., Chierici et al., 2006; Fransson et al., 2006, 2013]. Equations (6–9) below describe the effect of temperature change ($dCO_2/dT$), salinity change ($dCO_2/dS$), biological processes ($dCO_2/dbio$), vertical mixing ($dCO_2/dmix$), the sea-air $CO_2$ flux ($dCO_2/dw$), and the effect of CaCO$_3$ dissolution or precipitation ($dCO_2/dCaCO_3$) in the upper 10 m ($H$) between January and April. In May and June, the surface-mixed layer shoaled to 5 m [Meyer et al., 2017a, 2017b] and is used for calculations during this period. The effect of temperature was estimated using the relationship described by Takahashi et al. [1993] where a 1°C change results in a 4.23% change in $fCO_2$. The monthly mean values of DIC and the Revelle factor for each month (R) were used to convert the change in sea-air $CO_2$ flux to a $fCO_2$ change, and the stoichiometric ratio between carbon and nitrogen (C/N) was used to convert the monthly nitrate change ($dNO_3/dt$) to carbon equivalents, and DIC and R to convert carbon to a $fCO_2$ change. We used the C/N ratio of 5.7 ± 1.3 estimated by Assmy et al. [2017] for our area and time of study. The effect of salinity change was estimated using CO2SYS, where 1 salinity unit change contributed to a change in $dCO_2$ of 4 µatm. In our study, salinity was relatively constant throughout the period except for the freshening between May and June.

$$\frac{dCO_2obs}{dt} = \frac{1}{dt} (dfCO_2 + dfCO_2 + dfCO_{2biomix} + dfCO_{2flux} + dfCO_{2CaCO_3}).$$

$$\frac{dfCO_2}{dt} = fCO_2_{t-1} \cdot e^{0.0423} \cdot \frac{dT}{dt},$$

$$\frac{dfCO_{2biomix}}{dt} = \left( \frac{dfCO_2}{dfNO_3} \cdot \frac{dfNO_3}{dt} \right) \cdot \frac{C}{N} \cdot fCO_2_{t-1},$$

$$\frac{dfCO_{2flux}}{dt} = \frac{R \cdot fCO_2_{t-1} \cdot fCO_2_{flux}}{(DIC \cdot H)}.$$

$dCO_2$ was estimated from the residual between the sum of all other drivers and $dCO_2obs$. The residual is explained by changes in CaCO$_3$ dissolution/formation (see equation (1)), $CO_2$ addition from brine rejection, or $CO_2$ addition from horizontal advection. From this follows an assumption that the contribution of bacterial respiration in the upper 10 m was negligible. A negative change denotes a $fCO_2$ loss larger than the observed decrease. The function $dCO_2/dt$ is equal to $dCO_2/dt$ when $dCO_2/dt > 0$, and equal to 0 when to $dCO_2/dt = 0$. The cumulative error of all uncertainties in the effects of drivers was calculated based on the sum of the quadratic function of the analytical precision in surface-water temperature ($T$), salinity ($S$), nitrate concentrations ($NO_3$), and $fCO_2$ (see section 3), the standard deviation of the monthly mean values, and the variability in C/N ratio ($\pm 1.3$).
4. Results

4.1. Fugacity of Under-Ice Water CO2

From January to June, fCO2 ranged between a maximum fCO2 of 315 μatm (in winter) and a minimum fCO2 of 153 μatm (in spring) (Figures 6 and 7a–7d and Table 4). Consequently, the surface water was undersaturated relative to the atmospheric fCO2 level of approximately 400 μatm. The fCO2 undersaturation ranged between 81 (winter) and 254 μatm (spring) in the deep basin, on the slopes and Yermak Plateau (Table 5). The fCO2 mean values for Floe 1 and Floe 2 were 283 μatm and showed little variation, as shown in the standard deviations (Table 4). By Floe 3, the mean fCO2 had decreased to 272 μatm and had larger variability than previous floes. The decrease continued and reached a fCO2 mean value for Floe 4 of 189 μatm (Table 4). At the end of May, fCO2 decreased rapidly from winter values to 180 μatm and in June reached the minimum fCO2 of 153 μatm (Table 4 and Figure 7d). This decrease coincided with an increase of chlorophyll a (Figure 8a) and a nitrate decrease by 10 mmol m$^{-3}$ (Figure 8b) [Assmy et al., 2017].

4.2. Storm Effect on fCO2 and Response Time

At various occasions, particularly during Floe 1 fCO2 peaked, coinciding with storm events (Table 3 and Figure 7a). On 5–6 February, the wind increased rapidly from 7.3 to 15 m s$^{-1}$ (storm M2; Figures 2 and 9a). After 15 h, fCO2 increased by 42 μatm from 270 to 312 μatm (Figure 9a). However, there was only a 3 h lag between the maximum wind speed and the maximum fCO2 (Figure 9a). After 12 h, fCO2 returned to 270 μatm. However, the timing of the maximum wind speed and the maximum fCO2 differed between storm events. During storm event M3, on 13–14 February, the response time was almost 17 h between the maximum wind speed (10 m s$^{-1}$) and the maximum fCO2 (315 μatm; Figure 9b).

4.3. Sea-Air CO2 Fluxes

From winter to spring, the surface-water fCO2 was undersaturated (ΔfCO2) relative to the atmospheric fCO2 levels and was a potential ocean sink of atmospheric CO2 (Table 5). However, the observed surface-water fCO2 was under sea ice and could only equilibrate with the atmospheric CO2 during short periods of openings in leads and cracks in the ice cover. The ΔfCO2 for each floe was combined with wind speed data and open-water fractions (OW, Table 5) to determine the sea-air CO2 fluxes using...
equations (4) and (5). The average sea-air CO$_2$ fluxes were estimated at average wind speed and average OW, and the maximum (minimum) sea-air CO$_2$ fluxes at maximum (minimum) wind speed (storm event) and maximum OW to evaluate the range of the CO$_2$ fluxes during the study period (Table 5). Storm events contributed to an increase in fCO$_2$, hence, the undersaturation decreased to $(-81 \, \mu\text{atm})$ (less negative $\Delta$fCO$_2$; Table 5). However, the highest wind speeds ($23 \, \text{m s}^{-1}$) caused a sea-air CO$_2$ flux of $-8 \, \text{mmol C m}^{-2} \text{d}^{-1}$ that was more than 20 times larger than at average wind speed and average $\Delta$fCO$_2$ in winter (Floe 1 and 2), and about 3 times larger than during spring average flux (Floe 3 and 4). The largest sea-air CO$_2$ flux of $-80 \, \text{mmol C m}^{-2} \text{d}^{-1}$ occurred at high wind speeds (>15 m s$^{-1}$) combined with the largest undersaturation and largest OW of 53% at Floe 4 (Table 5). At minimum wind speed and maximum undersaturation (most negative $\Delta$fCO$_2$), the CO$_2$ fluxes were insignificant (Table 5). The average sea-air CO$_2$ fluxes using mean wind speed varied between $-1.2$ and $-14 \, \text{mmol C m}^{-2} \text{d}^{-1}$ and were used for comparison with other studies for each floe. Table 6 summarizes the rapid and short-term sea-air CO$_2$ fluxes during major storm events. During storms with wind speed higher than $19 \, \text{m s}^{-1}$, CO$_2$ sink was larger than $10 \, \text{mmol m}^{-2} \text{d}^{-1}$, lasting from 12 h to 2 days. Lower wind speed in April caused 50% less CO$_2$ sink.

![Figure 7. Continuous high-frequency under-ice fCO$_2$ measurements (fCO$_2$, µatm; black, filled circles, left y axis) and surface-water temperature (SST, C$^\circ$; gray, filled circles, right y axis) from January to June for the different floes, where the dotted areas show the major storm events, defined by Cohen et al., [2017], affecting fCO$_2$; (a) Floe 1, (b) Floe 2, (c) Floe 3, and (d) Floe 4. M1, M2, m1 and M3 are storm events during Floe 1; M4, M5 and M6 are storm events during Floe 2; M7 and M8 during Floe 3; and m10 during Floe 4 (Table 3).]
Table 5. Sea-Air CO₂ Fluxes (F) at Average Observed fCO₂ (µatm) and at Different fCO₂ and Wind Speed Scenarios (u, m s⁻¹) for Each Floe, “Max” and “Min” Denote Scenarios at Maximum and Minimum Wind Speed (u), Respectively

<table>
<thead>
<tr>
<th>Floe</th>
<th>fCO₂ (µatm)</th>
<th>ΔfCO₂ (µatm)</th>
<th>u (m s⁻¹)</th>
<th>OW (%)</th>
<th>F (mmol C m⁻² d⁻¹) Potential</th>
<th>F (mmol C m⁻² d⁻¹)</th>
<th>F (mg C m⁻² d⁻¹)</th>
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<td>−37</td>
</tr>
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</tr>
</tbody>
</table>

*At minimum wind speed, the estimate is based on maximum ΔfCO₂ and the maximum wind speed at the minimum ΔfCO₂ since fCO₂ generally increased during storm events. Negative ΔfCO₂ means potential for CO₂ flux from atmosphere to water. OW refers to the maximum and average percentage (%) of open water for each floe used in the estimates of the flux. We assumed 100% open water to estimate the potential CO₂ fluxes if no sea ice is present. C in the unit denotes carbon. Negative flux (F) means ocean uptake (or influx) of atmospheric CO₂.
4.4. Drivers Affecting Under-Ice Water $fCO_2$

4.4.1. Monthly Changes in $fCO_2$ Drivers

Figure 10a summarizes the monthly change in the observed $fCO_2$ change ($dfCO_2obs$) from the different biogeochemical drivers. A positive change denotes that the driver has resulted in a $fCO_2$ gain and a negative change refers to a loss of $fCO_2$ in the surface waters. Also, included are the uncertainties of the calculations for each driver shown as error bars. The uncertainty was largest in the estimates of $dfCO_2CaCO_3$ since that calculation includes all uncertainties from all drivers.

In February, May, and June had the largest observed $fCO_2$ change (Figure 10a). In February, a net gain in $fCO_2$ was observed, whereas in May and June the observed $fCO_2$ showed a net loss (negative). It is evident that biological processes ($dfCO_2bio$) played a major role in June, with a $fCO_2$ loss of 71 µatm, explained by CO$_2$ consumption during primary production (Figures 10a and 10b). The effect of vertical mixing ($dfCO_2mix$) was important in February in May, resulting in a $fCO_2$ gain of 19 and 17 µatm, respectively. This was likely a contribution of CO$_2$ from subsurface waters to the upper 10 m. Part of this gain was balanced out by the loss in CaCO$_3$ dissolution, particularly in May (~34 µatm). In March and April, the observed $fCO_2$ changed.

Figure 8. The daily averages of observed fugacity of carbon dioxide ($fCO_2$, µatm; black, filled circles, left y axis), and the (a) chlorophyll a concentration (Chl a, mg m$^{-3}$; open circles, right axis,) and (b) nitrate concentration (NO$_3$, mmol m$^{-3}$; open circles, right axis) from January to June 2015 [Assmy et al., 2016]. M2, M3, and M6 in Figure 6b denote storm events (Table 3) defined by Cohen et al., [2017].
insignificantly, and the gain from mixing and the CO2 flux (\( \frac{df\ CO2}{dt} \)) was balanced by the loss due to CaCO3 dissolution (\( \frac{df\ CO2}{dt} \)). During winter, salinity and temperature were relatively constant (Table 4 and Figures 7a and 7b) and the effects on \( fCO2 \) (\( \frac{df\ CO2}{S\ dt} \), \( \frac{df\ CO2}{T\ dt} \)) were insignificant (Figure 10a). However, toward the end of the study in spring (in May–June), the salinity effect decreased \( fCO2 \) by approximately 4 \( \mu \)atm. The loss by freshening in June was nearly canceled out by the \( fCO2 \) gain of 6 \( \mu \)atm from warming. The gain in \( fCO2 \) from uptake of CO2 by sea-air CO2 flux (\( \frac{df\ CO2}{\text{flux}} \)) was 31 \( \mu \)atm (Figure 10a). During the other months, the CO2 flux contributed to the change in \( fCO2 \) of a small gain of between 2 and 7 \( \mu \)atm (Figure 10a). From this study, we also found that the other major driver explaining the \( fCO2 \) change was the loss of \( fCO2 \) from CaCO3 dissolution, which consumed CO2 throughout the whole 5 month period (Figure 10a). Between January and April, the effect of \( \frac{df\ CO2}{\text{diss}} \) was the only driver resulting in a loss of \( fCO2 \), varying between 2 \( \mu \)atm (January), 12 \( \mu \)atm (February) and 10 \( \mu \)atm (March). In May and June, this effect resulted in a net loss of 34 and 41 \( \mu \)atm, respectively.

Figure 10b shows the relative contribution of each effect on the total \( fCO2 \) change (absolute sum) during the 5 month period. Biological processes and CaCO3 dissolution were the two major drivers for the total \( fCO2 \) change, contributing 26 and 38\%, respectively (Figure 10b). The gain through vertical mixing was large
in winter and contributed 16% of the total fCO2 change, and sea-air CO2 flux contributed 16% of the total fCO2 change, mainly in June. The salinity and temperature played minor roles in the total change; 2% due to freshening by meltwater and 3% due to warming (Figure 10b).

### 4.4.2. Effect of Drivers on fCO2 During Storm Events

We used the same approach to estimate the monthly fCO2 change described in equations (6–9) to derive the major drivers during one major storm event M2 on 5–6 February (Table 3). Consequently, the increase of 42 μatm in under-ice water fCO2 was largely caused by the addition of 72 μatm of fCO2 by mixing of subsurface water. In addition, CaCO3 dissolution resulted in a fCO2 loss of 31 μatm. The temperature, salinity, and sea-air CO2 flux had negligible effects.

### 5. Discussion

#### 5.1. Drivers of Observed fCO2 and Sea-Air CO2 Flux Variability

From the study of monthly drivers of the observed fCO2 change we discovered that biological effects (spring), CaCO3 dissolution (winter and spring), and vertical mixing (winter) had the major impacts on the fCO2 changes. Here we further investigate these processes to confirm our findings. We found that calculated fCO2 was >300 μatm at 100 m in the water column based on AR and DIC values [Fransson et al., 2016], which partly supports our results of increased fCO2 as a result of vertical mixing of CO2 with the surface water. It was clear that mixing of subsurface water occurred during winter from observations on salinity and temperature in the upper 10 m. This was particularly active during storm events. For example, Peterson et al. [2017] explained a temperature increase at 10 m depth to be caused by vertical mixing of the surface layer. Moreover, Meyer et al. [2017a, 2017b] observed deepening of the mixed layer explained by vertical mixing of subsurface water during the storm event on 5–7 February (Figure 2a). In addition, Koenig et al. [2016] observed increased salinity in the surface water under the ice during storm events in winter based on IAOOS buoy data. This increase was suggested to be a result of vertical mixing and brine rejection. Fer et al.
[2017] investigated the proportions of vertical mixing and brine contribution to salinity in winter to be 90 and 10%, respectively.

Interestingly, the effect on the $f_{\text{CO}_2}$ change due to CaCO$_3$ dissolution was prominent throughout the study and larger than the biological effect (Figures 10a and 10b). In our calculations, this effect was derived from the residual of the sum of all other drivers and the observed $f_{\text{CO}_2}$. Consequently, this term has the largest uncertainty and it is useful to consider another independent calculation method to investigate the magnitude to this effect.

Fransson et al. [2013] used AT and salinity ratio (AT/S) in under-ice water to estimate CaCO$_3$ (ikaite) dissolution. In our study, the AT/S in seawater was 66 from the water below 50 m.
[Fransson et al., 2016] and 69 from under-ice water (upper 5 m). This enhanced AT/S under the ice supported CaCO₃ dissolution in the under-ice water [Fransson et al., 2016]. The maximum AT/S increase was converted to a dissolution of CaCO₃ of 74 mmol kg⁻¹, corresponding to a DIC change of 37 μmol kg⁻¹ (74/2; equation (1)). From the driver estimates in this study, CaCO₃ dissolution decreased fCO₂ by 34 μatm in May and a maximum of 41 μatm in June (Figure 10a). This corresponds to a DIC change of 19 and 36 mmol kg⁻¹, respectively. This comparison of the two methods supports the finding that CaCO₃ dissolution was an important driver for the fCO₂ loss during our study. The total loss of fCO₂ due to CaCO₃ dissolution corresponds to 0.7 mol m⁻² in the upper 10 m. Our findings are also supported by the results from a study in Arctic sea ice by Rysgaard et al. [2013], where they estimated higher ikaite concentrations (100–200 mmol kg⁻²) than our results using another method on nonmelted sea ice at the ice-water interface. These values are considered comparable to our results of 64 mmol kg⁻¹ as the sum of ikaite dissolution for the entire study. Geilfus et al. [2016] estimated the effect of ikaite dissolution of 64–66 mmol kg⁻¹ in an experimental mesocosm in an outdoor pool in Greenland.

Our study supports previous findings that dissolution of CaCO₃ contributes to sustaining the relatively low surface-water fCO₂ values and undersaturation (with regard to atmospheric CO₂ levels) in the surface water in winter in polar oceans, as also suggested by Rysgaard et al. [2012] and Geilfus et al. [2016].

The pronounced loss of fCO₂ due to biological processes at the end of May and June coincided with an extensive under-ice phytoplankton bloom dominated by the haptophyte algae Phaeocystis pouchetii observed by Assmy et al. [2017] at the same location. This supports our finding that a large part of the fCO₂ decrease was explained by biological CO₂ drawdown. Recalculating our results of biological effect in the upper 50 m, we obtain values of approximately 1.6 mol m⁻², which is similar to a study by Assmy et al. [2017] of 1.3 mol m⁻² using another method in the same area, and lower than the result of 2.6 mol m⁻² in a study by Fransson et al. [2001], in the Barents Sea. However, the Arctic Ocean has large regional differences in shelf areas and deep ocean entailing river runoff and variable conditions for primary production [e.g., Carmack et al., 2006].

Except for June, the surface ocean was more than 90% ice-covered. This implies that surface-water fCO₂ could only equilibrate with the atmospheric CO₂ during short periods of openings in leads and cracks in the ice cover. The relatively large surface-water fCO₂ undersaturation due to primary production increased the potential for CO₂ uptake from the atmosphere, in combination with more open water. In spring, Floe 4 had the largest ΔfCO₂, which resulted in the largest sea-air CO₂ flux at average and maximum wind speed. However, scenarios with the lowest wind speed resulted in insignificant CO₂ flux, suggesting that strong wind, even in winter, with more ice cover, was as important as large ΔfCO₂ for driving the sea-ice CO₂ fluxes. This result is supported by a previous sea-air CO₂-flux study by Fransson et al. [2004] which found that the fluctuations in wind speed showed a larger impact on the variability of the fluxes than the fluctuations in ΔfCO₂.

In spring, surface-water temperature increased and salinity decreased due to bottom ice melt [Meyer et al., 2017a, 2017b]. Studies by Rysgaard et al. [2012] and Fransson et al. [2013] showed that CaCO₃ dissolution increased the potential for atmospheric CO₂ uptake by the surface ocean during ice melt by 10.5 mmol m⁻² ice d⁻¹ and 50 mmol m⁻² d⁻¹, respectively. This process, in combination with primary production and open water, contributes to the large fCO₂ undersaturation and sea-air CO₂ flux in spring.

### 5.2. Sea-Air CO₂ Fluxes Comparison in the Arctic Ocean

The sea-air CO₂ fluxes using average wind speed and average OW for each floe were compared to a scenario of an ice-free ocean (100% OW), referred as the potential CO₂ flux (Table 5). The potential sea-air CO₂ fluxes using average wind speed were between −10 and −26 mmol C m⁻² d⁻¹ (Table 5) and 8–48 times higher than average sea-air CO₂ fluxes (−0.3 to −3.1 mmol m⁻² d⁻¹). However, during storm events with maximum wind speed varying between 15 and 23 m s⁻¹, and with the estimated potential sea-air CO₂ fluxes at 100% OW, the fluxes largely increased (Table 5).

The first high-frequency fCO₂ measurements under the sea ice, and estimates of sea-air CO₂ fluxes, were carried out in the Canadian Arctic Archipelago (CAA) by Fransson et al. [2009]. They estimated that sea-air CO₂ fluxes varied between −50 mmol C m⁻² d⁻¹ (CO₂ sink) and 18 mmol C m⁻² d⁻¹ (CO₂ source) in open water (OW) in summer 2005. In the ice-covered part of the CAA, the surface water was a CO₂ sink of about −6 mmol m⁻² d⁻¹ [Fransson et al., 2009]. They found that CO₂ fluxes were affected by freshwater from river runoff and sea-ice melt as well as upwelling and primary production. Else et al. [2012] did seasonal studies.
in the CAA and in the upwelling region off Cape Bathurst and estimated CO2 fluxes between −10 and 6.5 mmol C m\(^{-2}\) d\(^{-1}\). These values are similar to our study for the average total CO2 fluxes (100% OW) of between −10 and −26 mmol C m\(^{-2}\) d\(^{-1}\).

Studies using calculated \(fCO_2\) from \(A_T\) and DIC, such as Bates et al. [2006], estimated winter-time average CO2 fluxes of −1 to −3 mmol C m\(^{-2}\) d\(^{-1}\) (i.e., influx of <3 mmol C m\(^{-2}\) d\(^{-1}\)) in the Central Arctic basin, based on 1% OW. These estimates are slightly larger than our winter-time CO2 fluxes in February (Floe 1), which was less than −0.3 mmol m\(^{-2}\) d\(^{-1}\) at average wind speed and OW (as determined for Floe 1 and 2 using average fraction of OW). However, during storm events at peak wind speed, the average sea-air CO2 flux at maximum wind speed was −10 mmol m\(^{-2}\) d\(^{-1}\) (Floe 1) and −17 mmol m\(^{-2}\) d\(^{-1}\) (Floe 2). Extrapolated flux estimates reported by Yasunaka et al. [2016] for the Barents Sea, the Chukchi Sea, and an average for the whole Arctic Ocean found the strongest sea-air CO2 flux (i.e., ocean CO2 influx) of approximately −12 mmol m\(^{-2}\) d\(^{-1}\) occurred in winter in the ice-free regions of the Barents Sea (due to storm events). The summer CO2 influxes were highest in the Chukchi Sea in summer of −10 mmol m\(^{-2}\) d\(^{-1}\). The average for the whole Arctic Ocean was −4 mmol m\(^{-2}\) d\(^{-1}\). Our estimates at 100% OW, but recalculated using the transfer formulation of Wanninkhof [1992] to be consistent with Yasunaka et al. [2016], resulted in a potential winter-time (100% OW) sea-air CO2 flux of between −12 and −20 mmol m\(^{-2}\) d\(^{-1}\). This is similar to the magnitude determined for the ice-free waters in the Barents Sea in winter by Yasunaka et al. [2016]. In spring and summer our total CO2 flux at 100% OW and mean wind speed ranged between −17 and −32 mmol C m\(^{-2}\) d\(^{-1}\) (Floe 3 and Floe 4). These estimates are larger than the CO2 flux of −10 mmol C m\(^{-2}\) d\(^{-1}\) estimated by Yasunaka et al. [2016] in summer.

Our average sea-air CO2 fluxes (average OW and wind speed) in spring (Floe 3 and 4) were similar to the estimated fluxes in ice-covered areas in Arctic summer [Bates et al., 2006; Fransson et al., 2009]. In winter (Floe 1 and 2), the average fluxes were less than previously reported values due to extensive sea-ice cover. However, at storm events in ice-covered winter conditions, the maximum sea-air CO2 flux was in the same order of magnitude or larger than the CO2 fluxes in ice-free regions as the Barents Sea and Chukchi Sea [Fransson et al., 2009; Yasunaka et al., 2016]. This result means that the openings in the ice cover due to storm events were highly efficient as promotor for CO2 exchange, even in winter.

### 5.3. Sea-Air CO2 Fluxes Comparison in the Antarctic Ocean

In contradiction to the mixture of FYI and FYI ice in the Arctic Ocean, the Antarctic Ocean (or Southern Ocean) consists mostly of seasonal FYI, which forms and melts every year. With climate change, less ice cover, thinning of ice, and more FYI in the Arctic Ocean, a comparison between the two oceans is highly relevant.

Mu et al. [2014] used measured \(fCO_2\) to estimate sea-air CO2 fluxes in the Amundsen Sea (Antarctica) and found a large net sink for atmospheric CO2 (with a spatially averaged flux density) of −18 ± 14 mmol C m\(^{-2}\) d\(^{-1}\). This high flux suggested a large influence on the uptake of CO2 by the Antarctic Ocean. Our average CO2-flux estimates varying between −1.2 and −14 mmol m\(^{-2}\) d\(^{-1}\) (Table 5) are within the range of flux estimates by Mu et al. [2014]. The Amundsen Sea region has experienced a significant increase in open-water duration (1979–2013), and Mu et al. [2014] discuss whether this CO2 sink will increase with future climate-driven change. The central region revealed a high CO2 flux of −36 ± 8.4 mmol C m\(^{-2}\) d\(^{-1}\), which was approximately 50% larger than that reported for the peak of the bloom in the Ross Sea (Antarctica), comparable to high rates reported for the Chukchi Sea (Arctic Ocean) [Mu et al., 2014]. Chierici et al. [2012] projected a potential for CO2 uptake in the open-water area north of the Amundsen Sea and in the Ross Sea in austral summer due to the large \(fCO_2\) undersaturation of about −150 μatm in the Ross Sea. This undersaturation was similar to the estimates by Bates et al. [1998] in the Ross Sea polynya where they used calculated \(fCO_2\) from \(A_T\) and DIC to estimate sea-air CO2 fluxes of −10 mmol CO2 m\(^{-2}\) d\(^{-1}\). By calculating \(fCO_2\) from \(A_T\) and DIC, Metzl et al. [2006] estimated sea-air CO2 fluxes of −1 to −4 mmol C m\(^{-2}\) d\(^{-1}\) in the seasonal ice zone (SIZ) south of 58°S in the Antarctic Ocean during the open season in austral summer. Chierici et al. [2004] estimated sea-air CO2 fluxes which ranged between −20 (CO2 sink) and 1.3 (CO2 source) mmol m\(^{-2}\) d\(^{-1}\) with an average of −3 mmol m\(^{-2}\) d\(^{-1}\) from the polar front to the continent in the Atlantic sector of the Antarctic Ocean. In that region, the largest ocean CO2 uptake (sink) was estimated at the polar front [Chierici et al., 2004].

There are few previous estimates of sea-air CO2 fluxes in winter in Antarctica. Our wintertime average CO2-fluxes (average wind speed and OW) were lower compared to the estimates in the SIZ (seasonal ice zone) of the Antarctic Ocean [Metzl et al., 2006]. However, at storm events in winter, our fluxes were within the
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range of CO2 fluxes estimated by other studies in the open parts of the Antarctic Ocean [Bates et al., 1998; Chierici et al., 2004; Metzl et al., 2006; Mu et al., 2014]. Our results indicate that openings and lead in the ice cover in winter during storm events were as important for the ocean CO2 uptake as in the seasonally ice-free summers in summer in Antarctica. This result implies an increased potential of ocean CO2 uptake in the Arctic Ocean in a future climate, similar to the open water in the Antarctic Ocean.

6. Conclusion

During the N-ICE2015 expedition north of Svalbard [Granskog et al., 2016], we explored an area in the Arctic Ocean where no winter-time surface-water fCO2 under the ice has previously been measured. From this unique data set obtained from January to June, we followed the changes in the underlying water (upper 10 m) fCO2 drivers and sea-air CO2 fluxes. The effect of dissolution of CaCO3 (e.g., ikaite) decreased under-ice water fCO2 during the entire study, and biological CO2 uptake was the main cause of fCO2 drawdown in spring. We found substantial peaks in fCO2 coinciding with storm events, which induced more ocean mixing of CO2. Storm events caused rapid warming in air and water [Peterson et al., 2017; Cohen et al., 2017], and opening of leads, that resulted in substantial and short-term increase in the underlying fCO2, facilitating ocean CO2 uptake. Increased air temperature has been shown to increase the sea-ice brine volume and permeability of the ice [e.g., Cox and Weeks, 1983], creating pulses of CO2-rich brine or CaCO3 rejected from the ice to underlying water. Consumption of CO2 based on CaCO3 dissolution sustained undersaturation of fCO2, which is supported by previous findings [Rygaard et al., 2013; Geifus et al., 2016]. By June, the CO2 loss due to primary production confirmed by Assmy et al. [2017] further enhanced the fCO2 undersaturation relative to the atmospheric CO2 level. At that time, we estimated the largest oceanic CO2 sink (influx) of atmospheric CO2. This was a result of the combined conditions of the largest ΔfCO2 (largest undersaturation due to the bloom), relatively high wind speeds and open water of up to 53%. In a scenario of a change from a perennial MYI to seasonal and warmer FYI in combination with more openings in the Arctic sea-ice pack, such as leads and cracks, will facilitate additional gas exchange between the atmosphere and the Arctic Ocean. Increased storm activity would also increase addition of CO2 from subsurface waters due to vertical mixing, hence decreasing the fCO2 undersaturation. In addition, it is likely that the combination of more open water and high wind speeds will result in increased CO2 flux (ocean uptake). Perhaps also occasionally, net outgassing of CO2 would occur, as has been observed in the wind-induced upwelling areas of the southern Bering Sea [Fransson et al., 2006] and the Canadian Arctic Archipelago [e.g., Fransson et al., 2009; Else et al., 2012]. The Arctic Ocean might perhaps become more similar to the Antarctic Ocean, so-called “Antarcticification,” with more seasonal FYI and less MYI over the deep basins, and increased open-water exposure to sea-air CO2 exchange in summer. However, the direction of the net CO2 flux in the Arctic Ocean water-ice-air system needs further investigation.

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