Gas exchange of CO$_2$ and O$_2$ in partially ice-covered regions of the Arctic Ocean investigated using in situ sensors

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Sea surface CO$_2$ dynamics are not well characterized in the Arctic Ocean (AO). Most data are from ship-based studies during the low-ice period (May–September) and obtained from near shore areas because of accessibility. More CO$_2$ data are needed to improve models for predicting the future of the carbon cycle in the region and its relationship to ocean acidification. Air-sea gas exchange rates are complicated by the presence of ice. Consequently gas exchange rates have a larger uncertainty in the AO compared to other ocean regions. To provide more information about CO$_2$ dynamics and gas exchange in the AO, in situ time-series data have been collected from the Canada Basin during late summer to autumn of 2012. Partial pressure of CO$_2$ ($p$CO$_2$), dissolved O$_2$ (DO) concentration, temperature, and salinity were measured at ~6-m depth under little ice and multi-year ice on two ice-tethered profilers (ITPs) for 40–50 days. The $p$CO$_2$ levels were always below atmospheric saturation whereas DO was almost always slightly above saturation. Although the two ITPs were on an average only 222 km apart, one was further south and had 14 ± 12% ice cover; whereas the more northern ITP had 63 ± 16% ice cover. Consequently the two data sets differed significantly in external forcings. Modeled variability of CO$_2$ and DO estimate that gas exchange would significantly alter sea surface $p$CO$_2$ in the low ice cover record but minimally in the more extensively ice-covered region. If these conditions extended over the entire AO, the total uptake of atmospheric CO$_2$ would be 28.6 Tg C yr$^{-1}$ and 15.4 Tg C yr$^{-1}$ under low and high ice-covered conditions, respectively.

1. Introduction
The rapid loss of ice covering the Arctic Ocean (AO) is increasing exchange of CO$_2$ and O$_2$ between the atmosphere and AO sea surface. There is evidence that loss of ice has already increased the partial pressure of CO$_2$ ($p$CO$_2$) levels in AO surface waters (Cai et al. 2010; Else et al. 2013). While the additional uptake of atmospheric CO$_2$ may lessen global warming, ocean acidification might be accelerated as ice cover decreases, potentially resulting in a rapid pH decrease (Steinacher et al. 2009). It is uncertain, however, if the AO will absorb significant CO$_2$ under seasonal ice-free conditions. Warming of the shallow isolated surface water and weak biological CO$_2$ drawdown are hypothesized to limit CO$_2$ invasion, keeping the ice-free central AO basins from becoming large atmospheric CO$_2$ sinks (Cai et al. 2010).
The lack of $pCO_2$ and other supporting data has limited our ability to predict how the carbon cycle will respond to diminished ice cover. Sea surface $pCO_2$ data sets from the central AO are scarce with most Arctic studies focused on the AO continental shelves (Anderson et al. 2009; Bates et al. 2006; Murata and Takizawa 2003; Kaltin and Anderson 2005). Those studies that have focused on the central ocean basins have generally found that $pCO_2$ is undersaturated, ranging from 240–350 µatm (Anderson and Kaltin 2001; Bates 2006; Bates et al. 2006; Cai et al. 2010; Else et al. 2013; Robbins et al. 2013). Almost all of these studies were during the low-ice periods in the summer. There continue to be significant gaps in our understanding of CO$_2$ dynamics in the AO, especially under ice. To examine $pCO_2$ and dissolved O$_2$ (DO) variability in the AO, in late August 2012 we deployed $pCO_2$, DO, temperature, salinity and bio-optical sensors on ice-tethered profilers (ITPs) in the Canada Basin. In 2012, the AO reached the lowest seasonal ice extent since satellites began quantifying ice coverage in 1979 (Parkinson et al. 2013; Zhang et al. 2013). The loss of ice is greater in the Canada Basin compared to the other basins in the AO (McLaughlin et al. 2011) and therefore the carbon cycle changes are expected to be the greatest in this region. The two ITPs were deployed in densely and sparsely ice-covered locations, providing a unique opportunity to compare CO$_2$ and DO variability under these different conditions. In this paper we evaluate the gas exchange contribution to these two time series and estimate total air-sea gas flux for the AO.

![Figure 1](image.png)

**Figure 1.** Arctic marine regions (left) near the study area (inset) are shown with the ITP drift track overlaid. The study area is magnified on the right. Rectangular boxes labeled with dates highlight measurement start and end points. The $pCO_2$ values at different points over the drift track are shown in color. The most northerly track corresponds to ITP-65 and the southern track to ITP-64. The sensors were deployed ~245 km away from each other. Plotting software is courtesy of Bill Williams (Institute of Ocean Sciences, Canada).

2. Methods

The Canada Basin is the largest sub-basin of the Arctic Ocean, extending approximately 1100 km from the Beaufort Sea shelf to the Canadian Archipelago (figure 1). Our instrumentation was deployed at ~6-m depth on two ITPs (ITP-64 and ITP-65) (Toole et al. 2011; Krishfield et al. 2008) in the Canada Basin from the Canadian Coast Guard Icebreaker *Louis S. St. Laurent*. ITP-65 was deployed on a 1.5-m thick ice floe at 80° 53.4’ N, 137° 25.8’ W and ITP-64 was deployed in open water at 78° 46.5’ N, 136° 39.8’ W. ITP-64 and ITP-65 traveled 513 and 575 km, respectively, during the period when the sensors transmitted data. Our sensors were deployed ~ two weeks before the ice extent reached its minimum on September 16.

The ITPs are described in Krishfield et al. (2008). Autonomous CO$_2$ sensors (SAMI-CO$_2$, Sunburst Sensors, LLC) (DeGrandpre et al. 1995) were connected to the ITP wire at ~6-m depth and recorded $pCO_2$ at 2-hour intervals. The instruments also included DO sensors (Optode 4175, Aanderaa...
Data Instruments) and CTDs (SBE37SI, Sea-Bird Electronics Inc.). The SAMIs transmitted data to the surface controller through an inductive modem interface (SBE UIMM, Sea-Bird Electronics Inc.). SAMI and optode data were quality controlled using shipboard measurements and data collected at the time of deployment. For unknown reasons, the SAMI inductive modem communications failed after 40–50 days. The transmitted data are available at the Woods Hole Oceanographic Institution (WHOI) website (http://www.whoi.edu/page.do?pid=23099) and the Arctic data repository ACADIS.

A variety of other data were obtained from different sources. The wind speed data near ITP locations were downloaded from the Medium range Weather Forecasting (ECMWF) website: http://apps.ecmwf.int/datasets/data/interim-full-daily. Barometric pressure and air temperature data were obtained from the Ice-Mass Balance (IMB) Buoy website: http://imb.erdc.dren.mil/2012L.htm. Atmospheric CO₂ measured at Barrow, Alaska was obtained from the National Snow and Ice Data Center (NSIDC) (Cavalieri et al. 1996) (http://nsidc.org/data).

Alkalinity was derived from a salinity–total alkalinity (Aᵣsaliv) relationship in the AO (Yamamoto-Kawai et al. 2005). Total dissolved inorganic carbon (DIC) was calculated using the measured pCO₂ and Aᵣsaliv using the program CO2SYS (van Heuven et al. 2011). The mixed layer depth (MLD) was calculated from depth-resolved density and temperature, with MLD as the depth where the density difference from the SAMI depth is +0.3 kg m⁻³. We used this density difference because it gives computed MLDs that best match in situ MLDs when observed visually based on the water column density profile. This value is close to the value of 0.26 kg m⁻³ reported by Timmermans et al. (2010) using the same approach for the central Canada Basin. Water was well mixed above 6 m based on ship CTD casts obtained during deployment (not shown).

The flux of DIC and DO originates primarily from four different processes in the AO, as shown in equation 1.

\[ \text{MLD} \times \frac{dC}{dt} = F_{\text{gasex}} + F_{\text{NCP}} + F_{\text{mix}} + F_{\text{brine}} \]  

(1)

where \( dC \) is the difference in DIC or DO values between two measurements over time (dt), and \( F_{\text{gasex}}, F_{\text{NCP}}, F_{\text{mix}}, \) and \( F_{\text{brine}} \) are the fluxes due to gas transfer across the air-water interface, net community production (NCP), vertical mixing and advection, and brine rejection during ice formation, respectively. We assume CaCO₃ dissolution and formation are not significant. In this evaluation, we focus on calculation of \( F_{\text{gasex}} \).

The \( F_{\text{gasex}} \) of CO₂ and DO across the air-water interface was calculated using the diffusive boundary layer model:

\[ F_{\text{gasex}} = k \Delta C f \]  

(2)

where \( k \) is the gas transfer velocity, \( \Delta C \) is the concentration gradient across the air-sea interface, and \( f \) is the fraction of open water. \( k \) was estimated using the wind speed relationship in Wanninkhof (2014) and adjusted for different temperatures and gases (i.e., CO₂, DO). The bubble flux equation in Stanley et al. (2009) was included for the DO fluxes to account for O₂ supersaturation due to complete bubble injection. We have not used relationships that account for other processes such as ice-sea surface turbulence in partially ice-covered oceans (Loose et al. 2014) but rather explore the range of air-sea CO₂ and DO fluxes by comparing models with the recorded sea ice extent and without ice, as discussed below.

The mass balance (equation 1) was used in a spreadsheet model for carbonate system calculations (DeGrandpre et al. 2004). The model takes the initial DIC, a constant Aᵣ, and the in situ temperature and salinity in the surface seawater as the initial input. The DIC was incremented at each time step for contributions from air-sea gas exchange using the calculated pCO₂. The new pCO₂ was then calculated...
from the constant $A_T$, \textit{in situ} temperature and salinity, and the new DIC. This calculation gives the modeled variability of $pCO_2$ from gas exchange and temperature. A similar approach was used in the DO model. Both $pCO_2$ and DO gas exchange models were calculated assuming ice-free conditions as well, with the goal to show to what extent AO ice-coverage controls $pCO_2$ and DO variability.

3. Results

The 49-day time-series data for ITP-64 and 41-day time-series data for ITP-65 are shown in figure 2. Gaps in the data correspond to instrument data communication dropouts between the SAMI and inductive modem. The average ice cover at ITP-64 and ITP-65 was 14 ± 12% and 63.2 ± 15.8%, respectively (figure 2). The average $pCO_2$ at ITP-64 and ITP-65 was 334 ± 9 µatm and 304 ± 16 µatm, respectively. DO showed very little variability at both locations with a mean of 392 ± 2 µmol kg$^{-1}$ at ITP-64 and 385 ± 2 µmol kg$^{-1}$ at ITP-65 (figure 2). Note that the diurnal cycles are distinct early in ITP-64 DO data but are not apparent in the ITP-65 DO data. Diurnal cycles in DIC at ITP-64 are also evident once the long-term trend is removed with a bandpass filter (Islam et al. 2016).

4. Discussion

4.1. ITP-64

The modeled $pCO_2$ trend due to gas exchange initially closely follows the measured $pCO_2$, but undershoots after 9/9/12 (figure 3). The modeled gas exchange with no ice is very similar because there is very little ice coverage at this location (figure 2). Gas exchange without bubble injection drives modeled DO quickly to saturation and underpredicts the observed DO levels (figure 3). Bubble fluxes account for part of the supersaturation (red curve). The $pCO_2$ and DO model deviations from the \textit{in situ} data indicate that there are other processes altering the $pCO_2$ and DO levels. These other sources of variability are evaluated in Islam et al. (2016).
4.2. ITP-65

The contribution from gas exchange to the ITP-65 $p$CO$_2$ variability is relatively small (figure 4) and would be significantly larger if no ice was present (dashed blue curve). The modeled gas exchange departs significantly from the observations. Much of this variability is likely due to spatial $p$CO$_2$ gradients as mentioned above. In contrast, gas exchange explains almost all of the DO variability (figure 4). Bubble fluxes add a slight supersaturation. The underestimate of $p$CO$_2$ and overestimate of DO can be attributed, in part, to biological processes, in this case, net respiration (Islam et al. 2016).

![Figure 3](image1.png)

**Figure 3.** ITP-64 $p$CO$_2$ and DO data (black) and modeled gas exchange using the ice cover (blue solid) and without ice cover (blue dashed). Modeled DO gas exchange including complete bubble injection is shown in red. The green line corresponds to the equilibrium concentration of O$_2$ at in situ temperature, salinity and atmospheric pressure. The $p$CO$_2$ data were calculated using in situ temperature and salinity, constant $A_T$, and with DIC incremented due to gas exchange (see text for more details).

![Figure 4](image2.png)

**Figure 4.** ITP-65 $p$CO$_2$ and DO data (black) and modeled gas exchange using the ice cover (blue solid) shown in figure 2 and without ice cover (blue dashed). Modeled DO gas exchange including complete bubble injection is shown in red. The green line corresponds to the equilibrium concentration of O$_2$ at in situ temperature, salinity and atmospheric pressure. The $p$CO$_2$ data were calculated using in situ temperature and salinity, a constant $A_T$, and with DIC incremented due to gas exchange (see text for more details). The x-axis scale is selected to match the other time-series figures.
4.3. Air-sea CO₂ fluxes
The CO₂ fluxes from our data fall within the range found by others for the Canada Basin and
nearby regions. The CO₂ flux at ITP-64 was $-4.8 \pm 3.8$ mmol m⁻² d⁻¹ and $-2.5 \pm 2.6$ mmol m⁻² d⁻¹ for
ITP-65 (negative values indicate uptake of CO₂). Murata and Takizawa (2003) report that the CO₂
flux during the summers of 1998–2000 was $-12$ mmol m⁻² d⁻¹ in the western Beaufort Sea. Bates et
al. (2006) estimated that during summertime the fluxes in the Canada Basin averaged $-55$ mmol m⁻² d⁻¹.
Assuming $p$CO₂ and ice coverage characteristic of the means found at the ITPs extended over a 90-
day period and extrapolating over the entire Canada Basin (4,489,000 km²) (Macdonald et al. 2009),
the CO₂ flux is estimated to be $-12.5$ Tg C yr⁻¹ under ITP-64 conditions (14 ± 12% ice cover) and $-6.5$
Tg C yr⁻¹ under ITP-65 conditions (63 ± 16% ice cover). Bates et al. (2006) estimate the annual CO₂
flux in the Canada Basin to be in the range of $-6$ to $-19$ Tg C yr⁻¹. Our annual fluxes at ITP-64 are also
similar to those estimated by Evans et al. (2015) for the western Arctic coastal ocean. When the entire
AO area of 10,700,000 km² (Macdonald et al. 2009) is considered, our flux estimates are $-28.6$ Tg C
yr⁻¹ and $-15.4$ Tg C yr⁻¹ under ITP-64 and ITP-65 conditions, respectively. The ITP-65 values are on
the high end of the flux estimates reported by Bates et al. (2011) for the central Arctic basins likely
because of the low ice cover during 2012.

5. Conclusions
This study documented the $p$CO₂ levels in marginally and partially ice-covered regions in the Canada
Basin. The $p$CO₂ and DO were significantly undersaturated and slightly supersaturated, respectively.
In low ice cover, gas exchange had a significant influence on $p$CO₂ but was a minor contributor in the
more highly ice-covered region. If ice cover continues to diminish in the AO, we expect the CO₂
accumulation will outpace the sinks of CO₂ in the AO sea surface because of the low NCP (export
production), isolation of the surface layer because of strong stratification and the long residence time
of the surface water. Therefore, $p$CO₂ levels may continue to rise towards saturation from year to year
and the net air-sea flux observed in this study will diminish. Continued monitoring of $p$CO₂ in the AO
is required to document these predicted trends.

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