Rapid physically driven inversion of the air–sea ice CO₂ flux in the seasonal landfast ice off Barrow, Alaska after onset of surface melt

Daiki Nomura, Hajo Eicken, Rolf Gradinger, Kunio Shirasawa

Abstract

The air–sea ice CO₂ flux was measured over landfast sea ice in the Chukchi Sea, off Barrow, Alaska in late May 2008 with a chamber technique. The ice cover transitioned from a cold early spring to a warm late spring state, with an increase in air temperature and incipient surface melt. During melt, brine salinity and brine dissolved inorganic carbon concentration (DIC) decreased from 67.3 to 18.7 and 3977.6 to 1163.5 µmol kg⁻¹, respectively. In contrast, the salinity and DIC of under-ice water at depths of 3 and 5 m below the ice surface remained almost constant with average values of 32.4 ± 0.3 (standard deviation) and 2163.1 ± 16.8 µmol kg⁻¹, respectively. The air–sea ice CO₂ flux decreased from +0.7 to –1.0 mmol m⁻² day⁻¹ (where a positive value indicates CO₂ being released to the atmosphere from the ice surface). During this early to late spring transition, brought on by surface melt, sea ice shifted from a source to a sink for atmospheric CO₂, with a rapid decrease of brine DIC likely associated with a decrease in the partial pressure of CO₂ of brine from a supersaturated to an undersaturated state compared to the atmosphere. Formation of superimposed ice coincident with melt was not sufficient to shut down ice–air gas exchange.

1. Introduction

Measurements of the partial pressure of CO₂ (pCO₂) in surface waters are an important prerequisite to evaluate the air–sea CO₂ flux in the world’s oceans. Only limited data are available for high latitude regions, particularly during winter, when the oceans are covered by sea ice (e.g., Takahashi et al., 2009). As underlined by Tison et al. (2002), it is often assumed that sea ice effectively caps the surface ocean, greatly restricting gas exchange between the ocean and atmosphere. However, recent observations question this paradigm and suggest that sea ice is a permeable medium for CO₂, at least part of the year (Semiletov et al., 2004; 2007; Delille, 2006; Nomura et al., 2006, in press-a; Zemmelink et al., 2006).

This work is motivated by past studies of CO₂ exchange in the Chukchi Sea, a marginal shelf sea of the Arctic Ocean, with its western limit defined by Wrangel Island and Point Barrow bordering on the eastern margin. Extremely low pCO₂ have been observed in ice-free Chukchi Sea surface waters in late spring through an early autumn, corresponding to high primary productivity and indicating that the waters represent a significant CO₂ sink for the atmosphere (Phipko et al., 2002; Semiletov et al., 2007). In the eastern Chukchi Sea up to Point Barrow, landfast ice occurs in the nearshored region from typically November through June (Mahoney et al., 2007; Druckemiller et al. 2009). During spring melt in June, sea–ice melt ponds and brine channels in the ice cover represent an important sink for atmospheric CO₂ (Semiletov et al., 2004). Earlier in the season during the ice-growth period (February), under-ice water pCO₂ is supersaturated with respect to the atmosphere as detected by moored CO₂ sensors (Semiletov et al., 2004; 2007). Brines also experience pCO₂ supersaturation with decreasing ice temperatures and increasing brine salinities during the first part of the ice-growth season (e.g., Papadimitriou et al., 2003). Thus, CO₂ can be emitted from brine channels to the underlying water and – if the ice permeability is sufficiently high – to the overlying atmosphere (Nomura et al., 2006; Rysgaard et al., 2007; Loose et al., 2009). These processes complicate the net annual balance between the uptake and outgassing through Arctic sea ice (Semiletov et al., 2007), requiring detailed observational data to gain further insight into the timing and physical controls of the cold/warm transition between sea ice as a seasonal source and sink of CO₂. Such data are also necessary to improve assessments and modeling of regional and seasonal carbon budgets in the Arctic.
We studied the air–sea ice CO₂ flux during the ice cover’s transition from a cold early spring to a warm late spring state in the Chukchi Sea, off Barrow, Alaska in late May 2008. The aim of the present study was to examine variability in the air–sea ice CO₂ flux during changing surface states of the ice cover in conjunction with variability in the atmospheric variables, such as air temperature and changes in the properties of surface snow, brine and sea ice.

2. Measurements and sampling methods

Field observations were carried out 19–26 May 2008 on landfast first-year sea ice in the Chukchi Sea, off Barrow, Alaska (Fig. 1). The air–sea ice CO₂ flux and the physico-chemical properties of brine and under-ice water were examined at a fixed sampling station (71°19’51.5”N, 156°41’17.4”W) located approximately 1 km offshore at a water depth of approximately 6 m. Each observation was carried out from morning (9:00 a.m.) to afternoon (13:00 p.m.). Measurements of air and sea ice temperatures were available from the Barrow sea ice mass balance site near our sampling location for the period February through June 2008 (http://seaice.alaska.edu/gi/data/barrow_massbalance; Druckenmiller et al. 2009). Briefly, the air temperature was measured at a height of 2 m above the ice surface with a shielded Campbell CS500 sensor. Vertical temperature profiles within the sea ice were measured at 10 cm intervals with thermistor strings and recorded with Campbell CS500 logger.

The air–sea ice CO₂ flux was measured with a closed chamber approach, allowing direct determination of the in situ CO₂ flux over sea ice (Nomura et al., in press-a). Replicate measurements for CO₂ flux were carried out on 20, 22 and 23 May 2008 within the same time frame (2–3 h) and area (within 1 m²) as the other measurements. A stainless steel chamber with no fan (50 cm in diameter and 30 cm in height with the serrated bottom edge) was positioned directly over the snow at the sampling site. The chamber was then pushed down firmly into the snow and ice to prevent lateral diffusion of CO₂. The air sampled from within the chamber passed through Teflon tubes connected to a non-dispersive infrared (NDIR) analyzer (carbon dioxide probe, GMP343, Vaisala, Finland) which was connected to a data logger (RVR 52, T & D Corp., Japan). Temperatures in the chamber were measured during each flux measurement, using a temperature data logger (RTR 52, T & D Corp., Japan). The air in the chamber was circulated with a pump at a flow rate of 0.7 L min⁻¹ through a mass flow controller and chemical desiccant column containing Mg(ClO₄)₂. These devices were installed in a portable adiabatic box (40 × 25 × 30 cm³). Electricity was provided by a portable electric generator. The CO₂ concentration in the chamber was measured every 10 s for each experiment’s total duration of 40 min. Four standards (mixing ratio of 324, 341, 363 and 406 ppm) traceable to the World Meteorological Organization (WMO) mole fraction scale (Inoue and Ishii, 2005) were used to calibrate the CO₂ measuring system prior to an in situ observation.

The air–sea ice CO₂ flux was calculated according to

\[ F = p \frac{273.15}{T} \frac{dC}{dt} \frac{dV}{dA} \]

where \( F \) is the flux (mmol C m⁻² day⁻¹), \( p \) is the CO₂ density at standard temperature and pressure (= 44.5 mol m⁻³ × (12/44)), \( T \) is the temperature in the chamber (°K), \( dC/dt \) is the rate of time variation (ppm day⁻¹) of CO₂ concentration in chamber, \( V \) is the volume (m³) of the chamber headspace adjusted for the volume occupied by the solid phase of snow and \( A \) the sea ice surface area (m²) sampled by the chamber. The values of 12 and 44 indicate the atomic mass of carbon and molecular mass of CO₂, respectively. The ratio of 273.15/T corrects for the temperature effect relative to the standard state. The stability of our NDIR has been verified during CO₂ concentration measurements. Hence, \( r^2 \) for the model from which fluxes have been derived scaled with the magnitude of \( dC/dt \) in Eq. (1) (Mariko et al., 1994). The precision of the air–sea ice CO₂ flux examined by duplicate measurements \((n=14)\) was within ±0.2 mmol m⁻² day⁻¹ (Nomura et al., in press-a). The detection limit of the CO₂ flux was <0.1 mmol m⁻² day⁻¹, which was estimated from the precision of the NDIR. The accuracy of the air–sea ice CO₂ flux is difficult to establish, because the true value of CO₂ flux between sea ice and the atmosphere could not be quantified. The CO₂ flux estimated by chamber methods can be affected by many factors which are not easy to evaluate. For example, the CO₂ flux is influenced by wind-driven variations in atmospheric pressure (Winston et al., 1995; Luo and Zhou, 2006; Takagi et al., 2005). Additionally, air in the chamber has to be mixed without generating localized pressure gradients (Luo and Zhou, 2006). Furthermore, the buffering effect of the snow can allow CO₂ to build up in the snowpack in the case of outgassing (Takagi et al., 2005; Zemmelink et al. 2006). When the flux chamber is placed over the snow, this excess CO₂ may be released into the chamber, particularly if a fan is used. In order to overcome these restrictions, we adjusted the gas flow with a pump (rather than a fan) to homogenize the sample air within the chamber. The mass flow controller that regulates pressure was carefully adjusted to minimize the pressure differential between the inside and outside of the chamber. Also, during the measurement period, the wind speeds were low with a mean of 3.4 m s⁻¹, suggesting that the wind-driven turbulent flux was small, reducing impacts on derived CO₂ fluxes. Other factors influencing the CO₂ flux are that the changes of CO₂ concentration in the chamber can suppress the real CO₂ flux with respect to the ambient CO₂ concentration (Winston et al., 1995). We used a chamber with a large volume to minimize the impact of temporal variations in the CO₂ concentration (Nomura et al., in press-b). Therefore, the data collected with our chamber system should be close to the true flux values during the observation period.

Our chamber system was very similar to other systems generally employed for measurements over sea ice (Debille, 2006), snow (Winston et al., 1995; Schindlbacher et al., 2007) and the ocean (Frankignouille, 1998). Therefore, we argue that our results can be directly compared against other chamber measurements. For example, as shown in Nomura et al. (in press-a), we were able to compare our data with those of Debille (2006). Briefly, when the brine pH₂O was of the same order of magnitude, the range of CO₂

Fig. 1. Location map of the sampling site on first-year landfast sea ice in the Chukchi Sea, off Barrow, Alaska.
flux values obtained from the chamber method was identical between our measurements and Delille’s study.

Sea ice was collected using an ice corer with an inner diameter of 9 cm (Mark II coring system, Kovacs Enterprises, Inc., USA). Ice temperatures were measured by inserting a needle-type temperature sensor (Fisher-Scientific Traceable Datalog Digital Thermometer, Thermo Fisher Scientific Inc., USA) in the holes drilled into the core immediately after the sample was collected. Then, the ice core was cut with a stainless steel saw and ice sections were placed into new polyethylene zip-lock bags. Thereafter, the ice samples were transported to the Ukpeagvik Ilulissat Corporation (UIC)-Naval Arctic Research Laboratory (NARL) (Fig. 1).

Brine samples from sea ice were obtained using the sack hole method (e.g., Gletz et al., 1995). A 0.5 m depth hole was drilled below the ice surface using an ice corer, and then covered with a 5 cm-thick urethane lid to reduce heat and gas transfer across the brine/ atmosphere interface. After the brine accumulated at the bottom of the hole over a period of approximately 10–15 min, the brine was sampled with a polypropylene syringe. The collected brine sample was split between two vials: a 10-mL plastic vial for measuring salinity and a 120-mL glass vial for measuring the dissolved inorganic carbon (DIC) of the brine. An amount of 50 mL saturated-mercuric chloride (HgCl2) was added to the DIC sample to terminate biological activity. The total alkalinity (TA) of the brine was not measured, since the volume of the collected brine was insufficient. Temperatures of the brine were measured by inserting a needle-type temperature sensor into the volume of brine filling up the hole.

Under-ice water was collected approximately 15 min after drilling a hole in order to avoid any disturbances caused by drilling (Nomura et al., 2009). A Kemmerer water sampler was used to collect under-ice water through the hole in sea ice at depths of 3 and 5 m below the sea–ice surface. Temperatures of the under-ice water were measured by inserting a needle-type temperature sensor into the outlet of the sampling tube connected to the water sampler. The water samples were treated in the same manner as the brine samples for further analysis. The amount of water was large enough to measure both DIC and TA.

3. Sample analysis

The salinity of the melted ice was measured with an YSI Oxygen, Conductivity, Salinity and Temperature reader (YSI 85, YSI Inc., USA) at NARL, while the salinity of the brine and the under-ice water samples were measured, using a salt analyzer (SAT-210, Toa Electronics Ltd., Japan) at Hokkaido University, Sapporo (Nomura et al., 2009). A Kemmerer water sampler was used to collect under-ice water through the hole in sea ice at depths of 3 and 5 m below the sea–ice surface. Temperatures of the under-ice water were measured by inserting a needle-type temperature sensor into the outlet of the sampling tube connected to the water sampler. The water samples were treated in the same manner as the brine samples for further analysis. The amount of water was large enough to measure both DIC and TA.

The pCO2 of under-ice water was computed from DIC and TA

4. Results

4.1. Air and sea ice temperature at the Barrow sea ice mass balance site

A sharp increase in air temperature was observed from 13 to 16 May, just prior to the sampling period; the air temperature began to exceed 0.0 °C on 20 May (Fig. 2a). Ice temperatures varied though delayed by thermal conduction – with air temperature and increased rapidly to –1.0 °C at the surface of sea ice at the end of our sampling period on 26 May (Fig. 2b). Rapid surface warming was also promoted by rain events that lasted a few hours, starting on 24 May. Rain and snow meltwater...
percolated down to the ice–snow interface and resulted in the formation of superimposed ice, typically several centimeters in thickness.

4.2. Sea ice thickness and snow depth

Sea ice thickness was almost constant in the range 144–157 cm with an average of 149 ± 5 cm (standard deviation) during the sampling period (Fig. 3a). There was a considerable decrease in the snow depth from 16 cm on 20 May to only 2 cm on 26 May, due to snow melting caused by the increase in air temperature, rain events and high fluxes of solar radiation (Figs. 2 and 3b). Superimposed ice of roughly 3 cm thickness was observed at the base of the snowpack (visible in the core stratigraphy photograph shown in Fig. 4b), but no presence of a slush layer could be detected.

4.3. Sea ice bulk salinity, temperature, brine volume, chlorophyll a concentration and δ18O

Salinity profiles exhibit a weakly defined C-shape, decreasing from approximately 7–3 across 15 and 140 cm depth, then increasing to between 8 and 14 at the ice base (Fig. 5a). Values ranged 1–7 at the surface. As observed at the sea ice mass balance site (in Fig. 2b), the increase in ice temperature was prominent in the upper ice layer compared to the middle and bottom (Fig. 5b). The brine volume was higher than 5% throughout the ice core (Fig. 5c), indicating that dissolved constituents like CO2 in the brine were capable of diffusing through the brine channel network, due to higher permeability of sea ice (Golden et al., 1998). Chlorophyll a concentrations ranged 152–322 μg l−1 in the bottom layer of the ice, while they were negligible everywhere else (Fig. 5d).

As shown in Fig. 4, a 3 cm-thick layer of relatively clear, low-salinity ice with δ18O of −11.8‰ was found above the whitish granular and darker columnar ice in the uppermost ice layers. With δ18O for snow ranging between −19.8 and −23.2‰, this layer was composed to more than half of the meteoric water, indicative of superimposed ice forming as a result of snow melt and rain refreezing on top of the cold sea ice in the early melt season.

![Fig. 4](image-url) (a) δ18O profile through snow and upper sea ice layers at the ice sampling site on 26 May 2008 and (b) shown at right at the same scale as the depth axis, is the core stratigraphy from a photograph taken at the sampling site.

4.4. Physico-chemical properties of brine and under-ice water

Brine temperatures increased from −3.7 °C on 19 May to −2.3 °C on 26 May, while temperatures of under-ice water were constant at −1.7 ± 0.0 °C during the sampling period (Fig. 6a). Brine salinity decreased drastically from 67.3 on 19 May to 18.7 on 26 May, while the salinity of under-ice water was constant at 32.4 ± 0.3 (Fig. 6b).

In accordance with the temporal variations of brine and under-ice water in salinity (Fig. 6b), the DIC of brine decreased from 3977.6 μmol kg−1 on 19 May to 1163.5 μmol kg−1 on 26 May, while the DIC of under-ice water remained constant at 2163.1 ± 16.8 μmol kg−1 (Fig. 6c).

In order to assess the effects of dilution and/or concentration processes on the DIC in the brine, as opposed to the carbon uptake and/or release by biological activity, data were normalized to a salinity of 32.4, the mean value of under-ice water salinity during the sampling period (Fig. 6b, c and d). The normalized-brine DIC was constant throughout the sampling period (Fig. 6d). In addition, the salinity and DIC of brine and under-ice water are highly correlated (r2 = 0.99, p < 0.0001; not shown). These results indicate that the decrease of brine DIC was mainly caused by dilution, due to melting of snow and ice rather than biological uptake by photosynthesis. TA of under-ice water was constant at 2247.3 ± 8.0 μmol kg−1 during the sampling period. Chlorophyll a concentration of under-ice water ranged 0.1–2.3 μg l−1 with a mean of 1.0 μg l−1 during the sampling period.

The pCO2 for under-ice water was almost constant at 424.8 ± 18.8 μatm and was slightly higher than that for the atmosphere (395.5 ± 3.5 μatm) throughout the sampling period.

4.5. Temporal variations of the air–sea ice CO2 flux

The air–sea ice CO2 flux was positive in the range between +0.1 and +0.7 mmol m−2 day−1 from 19 to 23 May, while it was negative at −1.0 mmol m−2 day−1 on 26 May (Fig. 7). This illustrates that the sea ice cover switched from a CO2 source to a CO2 sink during the observation period.
5. Discussion

The air–sea ice CO₂ flux underwent a change from positive (+0.7 mmol m⁻² day⁻¹) to negative (−1.0 mmol m⁻² day⁻¹) during the sampling period, tracking the variations of brine salinity and brine DIC (Fig. 6). The constant normalized-brine DIC throughout the sampling period (Fig. 6d) indicates that brine DIC was mainly controlled by the influx meltwater almost devoid of DIC, at least in the ice interior, where ice temperatures and incipient salinity reductions were evident in bulk salinity and brine salinity (Figs. 5 and 6).

Brine pCO₂ is an important factor controlling the air–sea ice CO₂ flux (e.g., Nomura et al., 2006). Although we did not estimate brine pCO₂, the variations of brine DIC and brine salinity can help to understand pCO₂ dynamics. Previous studies indicated that brine pCO₂ changes dramatically from the season of sea ice formation to melting conditions (Papadimitriou et al., 2003; Delille, 2006; Nomura et al., 2006, in press-a). During sea ice formation, brine pCO₂ increases with increases in brine DIC, and with changes in CO₂ solubility and the dissociation constants of carbonic acid as a function of brine salinity, which increases as a result of the progressive rejection of dissolved impurities from growing ice (Nomura et al., 2006). Therefore, brine pCO₂ is supersaturated with respect to the air during periods of ice growth. On the other hand, during ice melt, the same process occurs for brine pCO₂ due to the dilution effect, but in the opposite direction (decrease in brine pCO₂ with decreases in brine DIC). This explains the observed transition of the air–sea ice CO₂ flux from positive to negative as a consequence of reducing pCO₂ during the period of ice melt. The biological productivity in sea ice also reduces the brine pCO₂ in addition to the dilution effect (e.g., Gleitz et al., 1995). However in the coastal landfast ice near Barrow, high algal biomass and high productivity are concentrated into a very thin bottom layer (own data, Manes and Gradinger, 2009), while our brine sack hole sampling reflects mostly the conditions in the ice interior. The large spatial
Much higher magnitudes in the downward-directed CO₂ flux, ranging between $-38.6$ and $-19.5$ mmol m$^{-2}$ day$^{-1}$ were observed over melt ponds and highly permeable ice with open brine channels in the landfast ice near Point Barrow, Alaska almost one month later in the season (4–26 June) at a time when daily mean temperatures were above 0°C (Semiletov et al., 2004). Under these conditions, melt ponds and open brine channels can effectively exchange CO₂ because they are exposed directly to the atmosphere, similar to the free ocean surface. However, CO₂ flux results over sea ice from open-path eddy covariance systems, like that used by Semiletov et al. (2004) should be interpreted with caution, given that the fluxes may be prone biases, not fully yet understood by the flux community (Burba et al., 2008; Amiro et al., 2010).

6. Conclusions

During the rapid transition of sea ice from a “cold” early spring to a “warm” late spring state, the air–sea ice CO₂ flux decreased from $+0.7$ to $-1.0$ mmol m$^{-2}$ day$^{-1}$ with a corresponding rapid and highly correlated decrease in brine salinity and brine DIC. These results suggested that the sea ice shifted from a source to a sink for atmospheric CO₂, with rapid decrease of brine DIC likely associated with a decrease in brine pCO₂ from a supersaturated to an undersaturated state compared to the atmosphere. While snow deposited over sea ice and formation of superimposed ice did not completely seal off the ice interior from the atmosphere, it remains to be investigated to what extent snow and superimposed ice are impeding gas exchange, relative to higher fluxes measured over much warmer sea ice in an advanced state of melt.

This study provides valuable information on the brine biogeochemistry and gas exchange processes between the atmosphere and sea ice during the rapid cold/warm transition in landfast sea ice in the seasonally ice-covered Chukchi Sea. However, this is only a first step towards regional carbon cycle assessments in seasonally ice-covered waters, since the effect of parameters, such as snow depth, snow properties, surface state of the sea ice, its porosity and permeability need to be investigated in more depth as well.

To our knowledge, this is the first time that such a rapid and substantial change in the air–sea ice CO₂ flux has been reported for Arctic ice-covered regions. While the onset of melt in this case was triggered by a rain event, such rapid transitions in the thermal state of the sea ice are not unusual for the Arctic (Perovich et al., 2003) and may well be typical of the marginal seas, where interaction with land surface processes impacts melt patterns.

Acknowledgements

Prof. J. L. Tison and two anonymous referees are thanked for their constructive comments that improved the paper. This study was supported by the Research Fellowship of the Japan Society for the Promotion of Science (#195968) and funds from University of Alaska Fairbanks and International Antarctic Institute (IAI) of Hokkaido University. Support by the National Science Foundation (OPP-0632398 and 0805703) is gratefully acknowledged. We express heartfelt thanks to all the members of the GEOS/MSL 695 field techniques in the interdisciplinary sea-ice research, jointly with University of Alaska Fairbanks and Hokkaido University for sampling assistance and for analyzing samples. Thanks also to Prof. H. Y. Inoue, Prof. M. Fukuchi, Prof. T. Odate, Dr. T. Toyota and Dr. S. Aoki for providing measurement devices and for their useful comments.