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TELLUS

Air–sea flux of CO_2 in arctic coastal waters influenced by glacial melt water and sea ice

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ABSTRACT

Annual air–sea exchange of CO_2 in Young Sound, NE Greenland was estimated using pCO_2 surface-water measurements during summer (2006–2009) and during an ice-covered winter 2008. All surface pCO_2 values were below atmospheric levels indicating an uptake of atmospheric CO_2. During sea ice formation, dissolved inorganic carbon (DIC) content is reduced causing sea ice to be under saturated in CO_2. Approximately 1% of the DIC forced out of growing sea ice was released into the atmosphere while the remaining 99% was exported to the underlying water column. Sea ice covered the fjord 9 months a year and thereby efficiently blocked air–sea CO_2 exchange. During sea ice melt, dissolution of $CaCO_3$ combined with primary production and strong stratification of the water column acted to lower surface-water pCO_2 levels in the fjord. Also, a large input of glacial melt water containing geochemically reactive carbonate minerals may contribute to the low surface-water pCO_2 levels. The average annual uptake of atmospheric CO_2 was estimated at 2.7 mol CO_2 m^{-2} yr^{-1} or 32 g C m^{-2} yr^{-1} for the study area, which is lower than estimates from the Greenland Sea. Variability in duration of sea ice cover caused significant year-to-year variation in annual gas exchange.

1. Introduction

The Arctic Ocean is estimated to contribute 5–14% of the world oceans' total annual uptake of CO_2 (Bates and Mathis, 2009). However, this estimate is based on limited data most of which were collected in open water in spring and summer. One of the major issues concerning air–sea exchange of CO_2 in the Arctic is how the presence of sea ice affects the exchange of CO_2 between the sea surface and the atmosphere. Sea ice strongly reduces gas exchange between the atmosphere and surface water but also influences biogeochemical processes in the surface water. Presence of sea ice is an important regulator of marine production as it blocks the input of light energy for photosynthesis, and thereby new primary production. Therefore, oceanic uptake of CO_2 can be expected to increase if sea ice cover in the Arctic continues to decrease. However, reduced sea ice cover could also increase out-gassing in shallow shelf areas where sub-surface water rich in CO_2 is mixed during fall and winter. pCO_2 values above atmospheric saturation have been found on the Siberian and Beaufort shelves (Semiletov, 1999; Semiletov et al., 2007) and the Chukchi Sea (Fransson et al., 2009). Sea ice formation itself alters the carbonate chemistry in surface waters by concentrating all solutes, including gases, in brine pockets, which form within the ice. In addition to solute rejection, several factors can elevate CO_2 concentrations in the liquid brine during ice formation: (1) as salinity increases, CO_2 solubility decreases and excess CO_2 exist as gas bubbles, (2) bicarbonate dissociates in favour of CO_2 and (3) calcium carbonate can precipitate, decreasing alkalinity and releasing CO_2 in the process (Rysgaard et al., 2007). Brine with a high concentration of CO_2 may vent gas to the atmosphere or convey excess gas (relative to atmospheric equilibrium) to the water column through gravity-driven brine drainage. In addition to these physicochemical processes, biological activity of ice algae and bacterial mineralization of carbon leaked from algae may also influence pCO_2 of the brine system (Delille et al., 2007).

In this study, we present 4 years of surface-water pCO_2 measurements conducted during summer in Young Sound, NE

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Greenland, a site influenced by terrestrial run-off and melting sea ice from the Greenland Sea. We compare data from this coastal site to pCO_2 measurements conducted in the Greenland and Norwegian Seas. Finally, based on winter observations in Young Sound, which is ice-covered for 8–10 months per year, we produce a preliminary estimate of annual CO_2 uptake in the Young Sound area.

2. Methods

2.1. *Greenland sea*

A cruise between Tromsø, Norway, and the coast of East Greenland was carried out from September 30 to October 17, 2003 where oceanic partial pressure of CO_2 (pCO_2) was measured in water sampled continuously from an inlet 2 m below the sea surface. pCO_2 was determined by bringing a volume of air into equilibrium with a continuous stream of sea water and measuring pCO_2 in the air. For this we used an equilibrator system consisting of a 10 l glass cylinder where water is pumped in at the top of the cylinder, in which a series of small glass tubes increases the water–air contact surface in order to quickly achieve equilibrium. Air is sampled continuously from the equilibrator into an infrared CO_2 analyser (LICOR-6262 by LI-COR) and the air flow from the CO_2 monitor is returned to the equilibrator in a circulating flow. The CO_2 monitor, in turn, measured the air sample from the equilibrator system, a calibration gas and the atmospheric air. In this manner, we could use the same instrument for determining pCO_2 in the ocean and the atmosphere. The equilibrator was constructed following Dickson and Goyet (1994) and the ocean–atmosphere difference in pCO_2 was determined as half-hour means during the cruise.

2.2. *Young sound*

During August from 2006 to 2009, sea-surface pCO_2 was measured at individual stations along a gradient from the head to the mouth of the fjord (Fig. 1A) using an infrared CO_2 analyser (EGM-4 by PP Systems). Surface water was pumped through 2 m of Tygon tubing into a membrane equilibrator (Mini Module by Liqui-cel, Charlotte, NC, USA) at a rate of approximately 2 L min^{-1}. See Hales et al. (2004) for a description of the equilibrator. In the equilibrator, the sea water content of dissolved CO_2 equilibrated with a limited volume of atmospheric gas across a gas permeable membrane. The gas was circulated through a drying column (Drierite) before entering the CO_2 analyser. From the CO_2 analyser the gas was passed back into the equilibrator forming a closed circuit containing approximately 200 ml of atmospheric gas at normal atmospheric pressure (monitored by the CO_2 analyser). At daily intervals, the CO_2 analyser was checked against standard gasses with known CO_2 content. The precision was in all cases within ± 2 ppm. Temperature of the inflow and outflow water was checked at regular intervals using a digital thermometer. In all cases, the change in sea water temperature during measurements was <0.1 °C. The atmospheric content of CO_2 was measured 5–10 times during each summer sampling period by pumping atmospheric air through a Tygon tube placed 3 m above sea surface on the boat directly through the drying column and into the CO_2 analyser.

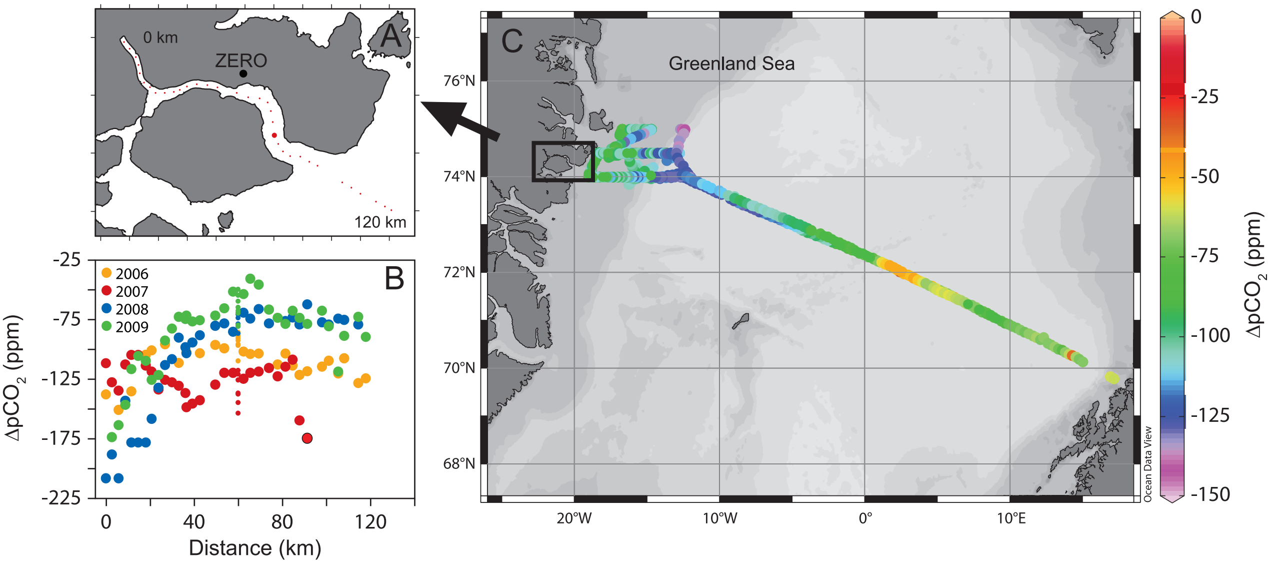

Fig. 1. (A) Map of Young Sound with sampling stations for surface pCO_2. The main sampling station visited repeatedly each summer is indicated by a larger symbol. Wind data was measured at the Zackenberg Research Station (ZERO). (B) ΔpCO_2 values from Young Sound in August 2006–2009. Smaller dots at app. 60 km represent repeated measurements during each summer. (C) ΔpCO_2 values given by colour along the cruise track through the Norwegian and Greenland Seas in October 2003.

2.3. *Calculation of air–sea exchange*

Air–sea exchange of CO_2 was calculated using the diffusive boundary model: $F = K_{660} S\ \Delta p\mathrm{CO}_2$, where F is the flux of CO_2 (mmol C m^{-2} day^{-1}), K_{660} is the gas-transfer velocity normalized to a temperature of 20 °C and salinity of 35 PSU, S is the CO_2 solubility in sea water, and $\Delta p\mathrm{CO}_2$ is the partial pressure difference between sea surface and atmosphere. Normalization of the transfer velocity, K_{660} was done according to: $K_{660} = K(660/\mathrm{Sc})^{-0.5}$ where the Schmidt number (Sc), was calculated using the algorithm by Wanninkhof (1992). The solubility of CO_2, *S,* was calculated according to Weiss (1974) using data on temperature and salinity from the CTD (see later). The gas transfer velocity, K, is often estimated based on empirically derived relationships with wind speed and we used the formulation by Nightingale et al. (2000): $K = 0.333U + 0.222U^2$, where U is wind speeds (m s^{-1}) at 10 m above sea surface. This formulation was chosen as it was derived for coastal environments. Wind speeds were measured locally at the Zackenberg Research Station at 7.5 m above ground and 1 h average wind speeds were used to estimate K. At each station, measurements of sea surface $p\mathrm{CO}_2$ were supplemented with vertical profiles of temperature, conductivity, oxygen concentration, turbidity, photosynthetic active radiation (PAR) and fluorescence using a CTD (Sea Bird 19 +, Sea Bird Electronics). At a main station in the outer part of Young Sund these measurements were repeated several times during the 3-week summer field campaign. CO_2 fluxes were not calculated from areas in the Greenland Sea with sea ice because the actual surface area for air–sea exchange was unknown and no parameterization of gas transfer velocity corrects for the dampening of waves and surface turbulence due to sea ice.

2.4. *Winter measurements*

During the single winter campaign conducted in late March/early April 2008, all measurements of ice and water characteristics were conducted at the main summer station. In Young Sound land fast sea ice with a thickness of 1.5 to 1.8 m forms every year and covers the entire fjord from October to July. Twice during the sampling period, holes in the sea ice were drilled to allow CTD casts and water sampling using a Niskin type bottle. Measurements of $p\mathrm{CO}_2$ were performed on water samples collected with the Niskin sampler. Water was drained from the Niskin bottle through tygon tubing and into the equilibrator. To estimate $p\mathrm{CO}_2$ content of ice, three ice cores (average length 172 cm) were drilled (Mark II, Kovacs Enterprises, Ø 9 cm) on three different days approximately 50 m from the holes used to collect water samples. Blocks of ice from different sections of each ice core were then melted in 1 l gas tight glass bottles (average 950 g ice per bottle) filled with standard gas containing 450 ppm CO_2 and melted to a temperature of 2–3 °C. When all ice was melted, the bottle was shaken vigorously for 5 min to allow equilibration between melt water and gas. The CO_2 content of the gas phase was then measured using the CO_2 analyser. A glass syringe was used to extract the gas phase and inject it into the CO_2 analyser three times from each bottle to obtain triplicate CO_2 measurements. Temperature, bulk salinity, dissolved inorganic carbon (DIC) and total alkalinity (TA) were also recorded in individual sections of each ice core as described in Rysgaard et al. (2007). To measure air–sea ice flux of CO_2, 4 PVC chambers (internal diameter 23.6 cm, height 40–70 cm, extending 30 cm above the sea ice surface) were placed over (1) existing 1-yr sea ice and (2) holes drilled in the ice allowing new ice to form inside the chambers. Daily or at intervals of a few days, $p\mathrm{CO}_2$ of the air inside the chambers was measured to estimate the flux of CO_2 from ice to air in old as well as in newly formed sea ice. The air was pumped through holes fitted with Tygon tubing in the lid of the chamber through the drying column, into the CO_2 analyser and back again to the chamber in a closed circuit. After 3 days on average 25 cm of ice had formed in each chamber and in each of these blocks of new ice, three cores were drilled and sampled for DIC, TA, temperature and $p\mathrm{CO}_2$ using the same procedure as for established sea ice.

3. Results and Discussion

3.1. *Summer $p\mathrm{CO}_2$ measurements*

In summer, all $p\mathrm{CO}_2$ values of the surface water in Young Sound and along the cruise track through the Norwegian and Greenland Seas were below atmospheric (average 382 ppm) levels resulting in negative $\Delta p\mathrm{CO}_2$ values (Fig. 1, Table 1). The sea thus acts as a sink for atmospheric CO_2. Considerable variation in $\Delta p\mathrm{CO}_2$ values was, however, observed in space and time. The most negative values for $\Delta p\mathrm{CO}_2$ were generally found in the inner part of Young Sound, which is influenced by glacial run-off. This was the case especially in 2008 (−209 ppm) and 2009 (−174 ppm). However, in 2007 the lowest values were found in the Greenland Sea (−175 ppm) between melting ice floes. Thus the surface water tended to be most under saturated in CO_2 where temperature and salinity were low due to

Table 1. Average values of salinity (Sal.), temperature (Temp.), pCO_2 and ΔpCO_2 in surface waters measured in late July–early August 2006–2009 in Young Sound (YS) and in October 2003 in the Greenland Sea (GS)

	Sal.	Temp.(°C)	$p\mathrm{CO}_2$(ppm)	$\Delta p\mathrm{CO}_2$(ppm)
YS 2006	22.83	4.91	262	–116
YS 2007	18.47	5.65	247	–133
YS 2008	18.77	8.51	300	–82
YS 2009	22.51	5.76	290	–92
GS 2003	32.03	0.51	271	–111

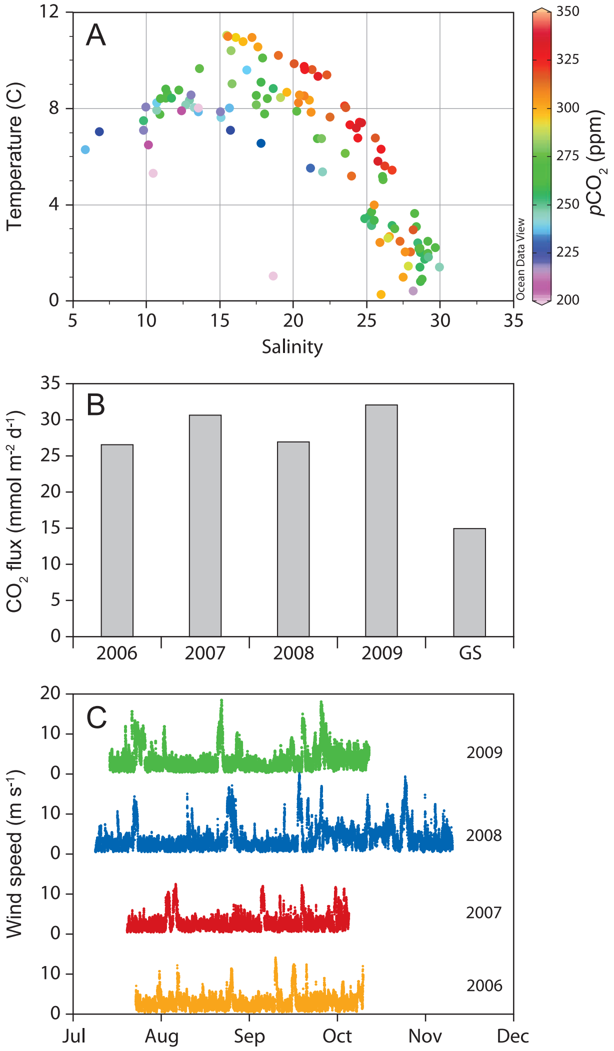

Fig. 2. (A) Salinity-temperature plot with surface pCO_2 values given by colour for all Young Sound samples 2006–2009. (B) Average daily flux rates from the atmosphere to the sea during summer in Young Sound and in the Greenland Sea October 2003. (C) Wind speeds (10 min averages) at the Zackenberg Research Station during the open-water (ice-free) period in Young Sound 2006–2009.

melting ice. In Young Sound, the spatial variation in pCO_2 did not show a simple relationship to temperature and salinity (Fig. 2A). Multiple regression models for each year showed a positive relationship between pCO_2 and salinity and temperature, which generally explained a considerable part of the variability but differed between years (Table 2, Fig. 2A). Primary productivity of phytoplankton was not quantified regularly in the fjord but affect pCO_2 as algae consume CO_2 during photosynthesis. Algal production is influenced by ice cover which limits light availability but also by wind conditions as strong winds can mix nutrient-rich sub-surface layers into the stratified photic zone where nitrate is depleted in August (Rysgaard et al., 1999). On the other hand, mixing may also introduce CO_2 from sub-surface layers and thereby increase surface pCO_2. At the main station sampled repeatedly during three weeks each summer, the average ΔpCO_2 value for each year ranged from -134 ppm in 2007 to -77 ppm in 2008 and 2009 (Fig. 1B, small dots at app. 60 km). The short-term variation (daily) observed each year show no consistent increasing or decreasing trends during August but generally seemed to depend on events of strong winds that mix the stratified surface layer. After periods with high wind speed during summer, surface water often exhibited an increase in salinity, a decrease in temperature and an increase in pCO_2. So, while the difference in pCO_2 between years cannot be related to differences in salinity and temperature it may be due to differences in wind events and sea ice cover affecting primary productivity and mixing of the water column.

The Greenland Sea showed a range in ΔpCO_2 from -29 ppm near the Norwegian coast to -145 ppm in dense sea ice off the East Greenland coast. Lowest pCO_2 values were found in areas with visually estimated sea ice cover >75% and surface temperatures < -1.5 °C. Average surface (at approximately 60 cm depth) values of temperature, salinity and $pCO2$ are given in Table 1. Measurements of surface pCO_2 from the central Greenland Sea in October have previously been reported to range from 300 to 350 μatm (Nakaoka et al., 2006; Hood et al., 1999). Our data showed comparable values in the area of approximately 5°W but lower values close to Greenland coast. The decrease in pCO_2 values west of 5°W coincided with a decrease in surface temperature indicating increasing influence of melting sea ice. In the Northeast Water Polynya, summer values of surface pCO_2 have been measured at 218 ppm (ΔpCO_2 of -127 ppm, Yager et al., 1995), which is within the range of values measured in Young Sound.

Assuming that the average ΔpCO_2 value obtained along the sampled transect represented the entire open-water (ice-free) period in Young Sound, we used it in combination with the 1-h average wind speeds and the exchange coefficient of Nightingale et al. (2000) to calculate hourly CO_2 fluxes. Calculations of hourly fluxes of CO_2 were made for the entire ice free season for each year. The observed wind speeds and the duration of the ice free season is shown in Fig. 2C. The average daily CO_2 uptake for 2006–2009 (Fig. 2B) during the ice free period was obtained by dividing the total uptake during the ice free period with the number of days. Average daily uptake was comparable between years, ranging from 27 mmol C m^{-2} d^{-1} in 2006 to 32 mmol C m^{-2} d^{-1} in 2009. It is therefore apparent that the duration of the open-water period (Fig. 2C) is a significant factor influencing the annual rates of air–sea exchange of CO_2. The choice of exchange coefficient and use of wind speeds are also important parameters that influence the estimated CO_2 flux. In Table 3 we have shown calculations for the average daily CO_2 uptake in 2006 using four different exchange coefficients and with different averages for wind speed. We have chosen the formulation of Nightingale et al. (2000) since it was obtained in a coastal environment and

Table 2. Parameter estimates (Est.), levels of significance (p), no. of samples (n) and coefficients of determination (R^2) for multiple linear regression analyses showing the relationship between pCO_2 in surface water of Young Sound and salinity and temperature. The analysis was run for each year separately

	Salinity		Temperature		Intercept			
Year	Est.	p	Est.	p	Est.	p	n	R^2
2006	2.709	< 0.0001	7.079	< 0.0001	165.450	< 0.0001	25	0.702
2007	2.860	0.015	7.827	0.0063	149.944	0.0002	28	0.266
2008	7.769	< 0.0001	9.191	< 0.0001	75.752	0.0016	32	0.840
2009	11.171	< 0.0001	11.837	< 0.0001	–29.133	0.407	33	0.767

Table 3. Average daily uptake of CO_2 (mmol m^{-2} d^{-1}) in Young Sound during the open water (ice free) season in 2006. Calculations made with different estimates of the exchange coefficient, K and different averages (hourly to monthly) for wind speeds (m s^{-1}). K1 from Liss and Merlivat (1986), K2 (Wannikhof, 1992), K3 (Wannikhof and McGillis, 1999) and K4 (Nightingale et al., 2000).

	K1	K2	K3	K4
Hourly	14.3	32.3	39.0	26.6
Daily	10.8	28.2	30.8	23.5
Weekly	6.1	27.4	26.8	22.9
Monthly	5.7	23.3	24.0	19.6

not the open ocean. Hourly wind speeds were used as they give a more accurate estimate of actual conditions compared to daily, weekly or monthly means.

3.2. Winter measurements

The winter campaign revealed that pCO_2 in the surface water just below the ice was 290–310 ppm (Fig. 3A). These observations are comparable to observations made in April 1994 from approximately 150 nautical miles off the coast of Young Sound by Nakaoka et al. (2006). These two observations indicate that the surface water is under saturated throughout the year. This means that polynyas and open leads will be a sink for atmospheric CO_2 during winter. Ice-free conditions often exist 10–20 km outside the Young Sound during late winter and early summer (observed in MODIS satellite images).

The sampled sea ice in Young Sound was 190 cm thick on average and temperatures in the upper 25 cm of all cores was < -20 °C. Measurement in this first year ice revealed that bulk pCO_2 in the ice averaged 165 ± 23 (SD) ppm ($n = 12$) compared to 193 ± 19 ppm in the newly formed ice. We measured no significant efflux of CO_2 across the ice–atmosphere interface of the established first year ice (chamber measurements, Fig. 3B and C). However, during formation of new ice, we measured marked increases in pCO_2 in the air above the ice (130 ± 31 (SD) ppm d^{-1}; average of 4 chambers, Fig. 3B), equivalent to a flux of 1.1 mmol CO_2 m^{-2} d^{-1}.

A simple DIC budget (Fig. 3C) showed DIC concentration of (1) sea water below the sea ice (2) DIC concentration in newly formed ice (in chambers) and (3) DIC in 1-year ice. Based on the CO_2 flux into the gas phase of the chambers, we further estimated that approximately 99% of the reduction in bulk DIC of new ice compared to sea water was lost through brine rejection to the water below. These findings match experimental studies in small ice tanks (Nomura et al., 2006; Rysgaard et al., 2007).

3.3. Annual CO_2 uptake in Young Sound

A preliminary estimate of the annual uptake of CO_2 in Young Sound of 2.7 mol m^{-2} yr^{-1} or 32 g C m^{-2} yr^{-1} was calculated based on a summer uptake of 29.1 mmol m^{-2} d^{-1} (average for 2006–2009) during an ice-free period of 94 days (average), an estimated ice formation period of 10 days with an efflux 1.1 mmol m^{-2} d^{-1} and the remaining 261 days with thick ice cover preventing exchange of CO_2. With the observed variation in sea ice cover and summer air–sea flux rates the estimate of CO_2 uptake in the fjord ranged from 25 g C m^{-2} yr^{-1} (2006) to 42 g C m^{-2} yr^{-1} (2008). This estimate is lower than those from the central Greenland Sea; 55 g C m^{-2} yr^{-1} (Hood et al., 1999), 71 g C m^{-2} yr^{-1} (Skjelvan et al., 1999), 53 g C m^{-2} yr^{-1} (Anderson et al., 2000) and 52 g C m^{-2} yr^{-1} (Nakaoka et al., 2006). The lower flux in Young Sound is a result of the short open-water period in summer, which allows air–sea exchange for only 3 months a year on average. As the choice of transfer velocity parameterization influences the calculated CO_2 uptake, we have shown how different transfer velocities and wind speed averages influence the average daily CO_2 uptakes based on the observed average value for ΔpCO_2 in 2006 (Table 3). Our choice of Nightingale et al.'s (2000) transfer velocity combined with hourly averaged wind speed resulted in relatively high flux rates compared to the total range but lower than based on the commonly used transfer velocity formulation of Wanninkhof (1992).

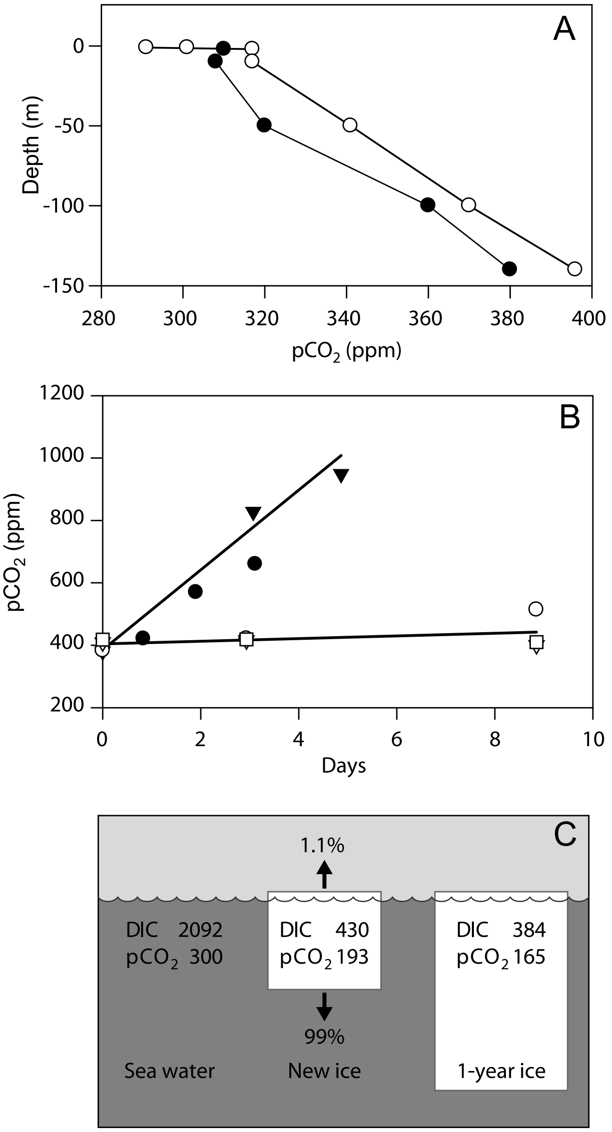

Fig. 3. (A) Water column profiles of $p\mathrm{CO_2}$ during the ice-covered winter period in Young Sound. (B) $\mathrm{CO_2}$ concentrations in the gas phase of chambers above 1-year ice (open symbols) and above forming ice (black symbols). Different symbols (triangles, squares, circles) represent different chambers. (C) Preliminary DIC budget during ice formation in winter in Young Sound. DIC (μmol kg^{-1}) and $p\mathrm{CO_2}$ (ppm) values in water just below sea ice, in newly formed ice and in 1-year ice. During the formation of new ice in chambers, the increase in the gas phase $\mathrm{CO_2}$ and estimated relative flux of carbon (%) to the atmosphere and the under laying water are given.

Primary production is an important driver of oceanic uptake of $\mathrm{CO_2}$. In Young Sound, the annual pelagic primary production was estimated at only 10 g C m^{-2} yr^{-1} (Rysgaard et al. 1999) and the vertical carbon flux at 65 m at 17 g C m^{-2} yr^{-1} (90% of the annual flux occurs in July and August, with an estimated 50% of the particulate organic matter being of terrestrial origin (Rysgaard and Sejr, 2007). Thus, primary production in Young Sound was lower than the 34 g C m^{-2} yr^{-1} estimated for the Greenland Sea (Anderson et al., 2000), indicating that factors other than primary production contributed to the relatively low surface-water $p\mathrm{CO_2}$ levels of the fjord.

Brine rejection during ice formation is thought to transport carbon from the sea ice to deeper waters (Anderson et al., 2004; Rysgaard et al., 2007; Rysgaard et al., 2009). We also observed low $p\mathrm{CO_2}$ levels in melted sea ice in this study. Melting of sea ice in summer is thus expected to contribute to the low $p\mathrm{CO_2}$ levels observed in the surface. The amount of ice varied greatly between years, from very few scattered ice floes to very dense pack ice outside the fjord approaching 90% cover (such as in 2007 which prevented sampling at outer stations along the transect). Overall, periods of intense ice-melts were not well represented in the data and this could imply some underestimation of the annual $p\mathrm{CO_2}$ exchange rates. Photos of Young Sound obtained daily since 2003 by the Greenland Ecosystem Monitoring Program (www.G-E-M.dk) reveal that melt water ponds begin to form in early June or about 5–6 weeks prior to break-up of land fast ice in the fjord and cover $>$50% of the surface area 2–4 weeks prior to ice break-up. Melt water ponds can take up significant amounts of atmospheric $\mathrm{CO_2}$ (Semiletov et al., 2004) but at present we do not know the $p\mathrm{CO_2}$ levels of these ponds and have not included their potential contribution in the annual budget, possibly leading to underestimation of the annual $\mathrm{CO_2}$ uptake.

Freshwater run-off from land most likely also exerts a strong influence on the air–sea exchange of $\mathrm{CO_2}$ in the fjord by stratifying the surface water. However, glacial melt water can also influence carbonate chemistry. An experimental study (Brown, 2002) showed that solutions of bed rock particles from glacial melt water containing carbonate minerals were geochemically reactive. During 3 h trials, the dissolution of particles increased pH and $\mathrm{Ca^{2+}}$ concentrations of glacial melt water and also reduced its $p\mathrm{CO_2}$ (Brown, 2002). Such weathering processes would result in glacial melt water low in $p\mathrm{CO_2}$ but high in alkalinity. There are some indications that glacial run-off could influence surface-water carbonate chemistry in the fjord. We measured DIC (432 μmol kg^{-1}) and TA (440 μmol kg^{-1}) in the glacial river at ‘Lerbugt’ situated at app. 40 km in Fig. 1B and in the glacial river of Tyrolerdal situated at 0 km in Fig. 1B (265 and 269 μmol kg^{-1} of DIC and TA, respectively), indicating transport of water with excess alkalinity (relative to DIC) and consequently low $p\mathrm{CO_2}$ (57.6 and 39.1 ppm, respectively). Surface DIC and TA were also measured along the fjord transect in 2006 concomitantly with direct $p\mathrm{CO_2}$ measurements. When DIC and TA concentrations were used to calculate $p\mathrm{CO_2}$, the calculated $p\mathrm{CO_2}$ was in all cases lower than the measured $p\mathrm{CO_2}$. The average difference was 121 ppm, which is orders of magnitude higher than the uncertainties related to either method. The difference in $p\mathrm{CO_2}$ obtained with the two methods is correlated to surface-water turbidity ($R^2 = 0.77$, $p < 0.01$), the largest difference between methods being found near glaciers with high sediment load. A possible explanation could be carbonate particles in the water samples collected for alkalinity and DIC measurements reacting chemically either during storage or during the analytical acid addition, resulting in dissolution of the carbonates and, hence, calculated $p\mathrm{CO}_2$ values that are lower than those observed directly in the field. An approximate increase in alkalinity of 7–10% due to reactive particles would explain the observed discrepancy between $p\mathrm{CO}_2$ measurements. From these observations, we hypothesize that glacial melt water low in $p\mathrm{CO}_2$ containing chemically reactive particles which 'consume' CO_2 could contribute to lowering the $p\mathrm{CO}_2$ of the fjord. The total catchment area for Young Sound is estimated to discharge 630 000–1.570 million $\mathrm{m}^3\ \mathrm{yr}^{-1}$ fresh water from June to September containing up to 670 000 tons of suspended sediments (Mernild et al., 2007). The entire fjord has high concentrations of suspended particulate material, the outer part displaying a vertical flux of inorganic particles of 1.4 kg of dry weight $\mathrm{m}^{-2}\ \mathrm{yr}^{-1}$ (Rysgaard and Sejr, 2007). Furthermore, a study from a Svalbard glacier showed that chemical weathering leads to significant uptake of atmospheric CO_2 by glacial melt water (Krawczyk and Bartoszewski 2008) supporting the hypothesis that glacial melt water could influence carbonate chemistry of the surface water in Young Sound.

In addition to inflow of glacial melt water with low levels of $p\mathrm{CO}_2$, freshwater also creates a strong stratification of the surface layer. In the inner part of Young Sound, surface salinity is below 10 and the mixed layer depth, estimated as the depth having the largest density gradient, is between 4 and 8 m (Bendtsen et al., 2007). Stratification effectively de-couples primary production (which consumes CO_2) in the surface from mineralization of organic matter sinking out of the surface water. Stratification also prevents mixing of nutrients from deeper water into the photic zone, thereby limiting annual primary production.

4. Conclusions

The observation that the surface water is under-saturated in $p\mathrm{CO}_2$ in both summer and winter implies that Young Sound is a sink for atmospheric CO_2 on an annual scale. However, large uncertainties are associated with the actual flux estimate, most notably related to the choice of gas exchange formulation, and neglection of gas exchange of CO_2 from melt water ponds and polynya areas outside the fjord may potentially underestimate the size of the CO_2 sink. We encourage further studies to evaluate the relative importance of the different processes causing low surface-water $p\mathrm{CO}_2$ levels in the Arctic coastal zone and how they might change in response to global warming. Phytoplankton production is certainly important for the low $p\mathrm{CO}_2$, as observed by the vertical flux of carbon and chlorophyll following the break-up of sea ice, and is expected to increase as a function of longer open-water periods (Rysgaard et al., 1999). Formation and melting of sea ice also play a role, the size of which depends on the water masses affected by this annual carbon pump. Moreover, glacial melt-water has been shown to act as a sink of atmospheric CO_2 (Brown, 2002) but whether this process is of importance only locally near glaciers or contributes to lowering $p\mathrm{CO}_2$ more widely in Young Sound or along the East Greenland coast is unknown. In any case, a warmer future climate is expected to increase the amounts of melt water, which would act to lower surface-water $p\mathrm{CO}_2$ levels. As these main factors identified to cause low surface-water $p\mathrm{CO}_2$ levels all respond to warming, it is highly likely that annual air–sea CO_2 exchange in Young Sound, and potentially the East Greenland coastal region, will change in response to global warming, which is expected to increase the open-water period from the present 3 months to 5 months by the end of the century (Rysgaard and Glud, 2007).

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