Distributions of surface water CO$_2$ and air-sea flux of CO$_2$ in coastal regions of the Canadian Beaufort Sea in late summer

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Abstract

To quantify the air-sea flux of CO$_2$ in a high-latitude coastal region, we conducted shipboard observations of atmospheric and surface water partial pressures of CO$_2$ ($p_{CO_2}$) and total dissolved inorganic carbon (TCO$_2$) in the Canadian Beaufort Sea (150° W–127° W; 69° N–73° N) in late summer 2000 and 2002. Surface water $p_{CO_2}$ was lower than atmospheric $p_{CO_2}$ (2000, 361.0 μatm; 2002, 364.7 μatm), and ranged from 250 to 344 μatm. Accordingly, Δ$p_{CO_2}$, which is the driving force of the air-sea exchange of CO$_2$ and is calculated from differences in $p_{CO_2}$ between the sea surface and the overlying air, was generally negative (potential sink for atmospheric CO$_2$), although positive Δ$p_{CO_2}$ values (source) were also found locally. Distributions of surface water $p_{CO_2}$, as well as those of Δ$p_{CO_2}$ and CO$_2$ flux, were controlled mainly by water mixing related to river discharge. The air-sea fluxes of CO$_2$ were $-15.0$ and $-16.8$ mmol m$^{-2}$ d$^{-1}$ on average in 2000 and 2002, respectively, implying that the area acted as a moderate sink for atmospheric CO$_2$. The air-to-sea net CO$_2$ flux in an extended area of the western Arctic Ocean (411 000 km$^2$) during the ice-free season (=100 days) was calculated as $10.2 \pm 7.7$ mmol m$^{-2}$ d$^{-1}$, equivalent to a regional CO$_2$ sink of $5.0 \pm 3.8$ Tg C. The estimated buffer factor was 1.5, indicating that the area is a high-capacity CO$_2$ sink. These CO$_2$ flux estimates will need to be revised because they probably include a bias due to the vertical gradients of physical and chemical properties characteristic in the region, which have not yet been adequately considered.

1 Introduction

Atmospheric CO$_2$ is now increasing at the rate of 1.9 ppmv yr$^{-1}$ (Solomon et al., 2007) by emissions of CO$_2$ resulting from human activities such as consumption of fossil fuels, deforestation, and cement production. CO$_2$ that originates from human activities is called anthropogenic CO$_2$. Accurate estimation of the uptake of anthropogenic CO$_2$ by the ocean is an urgent task for the scientific community, which has undertaken the task
of forecasting global warming and relevant climate changes in the near future. For this reason, anthropogenic CO$_2$ uptake by the ocean has been evaluated by using several approaches: model calculations (Le Quéré et al., 2000; Obata and Kitamura, 2003; Wetzel et al., 2005), global integration of air-sea fluxes of CO$_2$ calculated from field observations (Takahashi et al., 2002), and water column inventory of anthropogenic CO$_2$ (Sabine et al., 2004). Currently, it is estimated that the ocean and the terrestrial biosphere absorb about 50% of anthropogenic CO$_2$, with each absorbing a similar amount (Solomon et al., 2007).

The Arctic Ocean has not been taken into account sufficiently in the global estimation of the CO$_2$ budget in the ocean, because, in addition to sparse data coverage, it has been plausibly inferred that the air-sea exchange of CO$_2$ in the Arctic Ocean is negligible owing to the presence of sea-ice during a long period of each year. However, we should nevertheless evaluate CO$_2$ uptake in the Arctic Ocean because (1) CO$_2$ is expected to have high solubility because of the low water temperature, and (2) seas adjacent to the Arctic Ocean lie above continental shelves, where biological production is high. These factors operate to reduce the surface water $p$CO$_2$ to a level much lower than the atmospheric CO$_2$ level. Accordingly, it is likely that the Arctic Ocean acts as a substantial sink for atmospheric CO$_2$ in spite of its brief ice-free period. Furthermore, the area covered by sea ice is reducing rapidly (Rothrock et al., 1999; Stroeve et al., 2005), which implies that the area for air-sea exchange of CO$_2$ is increasing. In fact, it has been reported that uptake of CO$_2$ by the Arctic Ocean has tripled over the last three decades as a result of sea-ice retreat (Bates et al., 2006).

The Arctic Ocean, especially its surface layer, is subject to physical and biogeochemical processes such as cooling, stratification, water mixing, primary production, and respiration. These processes jointly affect carbon dynamics in the Arctic Ocean, although the relative importance of the different processes differs from region to region. Thus, it is important to elucidate the dominant process controlling CO$_2$ dynamics in the Arctic Ocean to estimate more accurately its uptake of CO$_2$.

The present study aimed to examine air-sea exchange of CO$_2$ in coastal regions of
the Canadian Beaufort Sea. As part of this examination, we clarified the influence of river discharge, mostly from the Mackenzie River, on the CO$_2$ dynamics in the region. Spatial variations in oceanic CO$_2$ in western Arctic Ocean seas, west of 150°W, have been previously reported (Murata and Takizawa, 2003). The present study focused on the area east of 150°W using data obtained during cruises in 2000 (Murata and Takizawa, 2003) and 2002. We also point out that it is likely that the vertical oceanic structural characteristics in the region cause a bias in the estimated air-sea CO$_2$ flux.

2 Data and methods

2.1 Data

Data used in the present study were obtained by shipboard observations in the western Arctic Ocean during the MR00-K06 (13–22 September 2000) and MR02-K05 (15–30 September 2002) cruises (Fig. 1) of the R/V Mirai of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). For details of the cruises, please refer to the cruise reports (http://www.jamstec.go.jp/cruisedata/mirai/e/index.html).

Atmospheric and surface water mole fractions of CO$_2$ (xCO$_2$ in ppmv) were measured continuously by a nondispersive infrared gas analyzer system installed in the research vessel. The CO$_2$ standard gases used to calibrate the system on board the Mirai were calibrated against gases from the Scripps Institution of Oceanography (SIO). The precision of the atmospheric and surface water xCO$_2$ measurements was estimated to be 0.2 and 1.7 ppmv, respectively, for 2000, and 0.2 and 1.0 ppmv, respectively, for 2002. The xCO$_2$ values were converted to partial pressures of CO$_2$ (pCO$_2$ in µatm) under saturated water vapor pressure at sea surface temperature (SST) by using an air pressure of 1.0 atm and the SST. The saturated water vapor pressure was computed according to Weiss and Price (1980). The xCO$_2$ and pCO$_2$ data used in the present study will be made available to the public through the Surface Ocean CO$_2$ Atlas (SOCAT) project of the International Ocean Carbon Coordination Project.
Surface water total dissolved inorganic carbon (TCO$_2$) was also measured continuously by the system with a coulometer installed on the R/V Mirai. The precision was estimated to be 1.6 and 2.0 µmol kg$^{-1}$ for the 2000 and 2002 cruises, respectively. The TCO$_2$ data were recalibrated by using a certified reference material (CRM) provided by A. G. Dickson of SIO.

For details of the analytical methods, please refer to Murata and Takizawa (2003).

Both onboard systems for $p$CO$_2$ and TCO$_2$ independently recorded SST and sea surface salinity (SSS) at the sampling time of each property. In addition to the underway observations, chemical properties such as TCO$_2$ and total alkalinity (TAlk) in the water column were measured at conductivity-temperature-depth (CTD) stations during both cruises (Fig. 1).

2.2 Calculation of TAlk

Surface water TAlk was calculated from surface water $p$CO$_2$ and TCO$_2$, which were measured continuously on board the Mirai. Since sampling times of the measured properties were different, data adjustment for the calculation was necessary; first, data for $p$CO$_2$, TCO$_2$, SST and SSS measured within ±30 min of hours were averaged. Then, TAlk (µmol kg$^{-1}$) on hours was calculated from the averaged $p$CO$_2$, TCO$_2$, SST, and SSS values by using Eq. (1):

$$\text{TAlk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}],$$

(1)

where the square brackets [ ] indicate the concentration (µmol kg$^{-1}$ in seawater) of each respective species. Dissociation constants necessary for the calculation were taken from Weiss (1974) for the solubility coefficient of CO$_2$ in seawater, Goyet and Poisson (1989) for the first and second dissociation constants, Dickson (1990a) for boric acid, Millero (1995) for water, Dickson (1990b) for bisulfate ion and Dickson and Riley (1979) for hydrogen fluoride.
The actual calculations were done using an MS Excel® version of the software program of Lewis and Wallace (1998) created by Dr. D. Pierrot. The calculated TAlk adequately represents the temporal and spatial variations during the cruises because the averaged $p\text{CO}_2$ could be used to reconstruct variations of nonaveraged surface water $p\text{CO}_2$ without any loss of major variation patterns.

The data set for $p\text{CO}_2$, TCO$_2$, and TAlk was used examine the spatial variability of surface water $p\text{CO}_2$ from the viewpoint of the oceanic carbonate system (Sect. 4.2).

2.3 Calculation of the air-sea flux of CO$_2$

The net air-sea flux of CO$_2$, $F$ (mmol m$^{-2}$ d$^{-1}$), was computed with Eq. (2):

$$F = k \cdot s(\Delta p\text{CO}_2),$$

where $k$ (cm h$^{-1}$) indicates the transfer velocity, $s$ (mol kg$^{-1}$ atm$^{-1}$) is the solubility of CO$_2$ (Weiss, 1974), and $\Delta p\text{CO}_2$ is calculated by subtracting atmospheric $p\text{CO}_2$ values from surface water $p\text{CO}_2$ values. For atmospheric $p\text{CO}_2$, we used averages of measured values in the study area: 361.0 and 364.7 µatm for 2000 and 2002, respectively (Table 1).

How to reliably parameterize $k$ is still debated (Ho et al., 2006), and several formulas have been used in actual calculations of CO$_2$ fluxes. However, the most frequently used formulas may be those of Liss and Merlivat (1986) and Wanninkhof (1992) (hereafter abbreviated as W92). In the present study, we used the formula of W92 for the following analysis.

According to W92, there is a quadratic relationship between wind speed $w$ (m s$^{-1}$) and transfer velocity $k$:

$$k = 0.31(w_{10})^2(Sc/660)^{-0.5},$$

where $w_{10}$ is wind speed at 10 m elevation and $Sc$ is the Schmidt number, which we calculated using the equation given by Wanninkhof (1992). The wind speeds used for
the calculation of the CO$_2$ fluxes were measured on board the *Mirai* during the cruises. For comparison with the CO$_2$ fluxes reported in previous studies, we also show the results calculated using the parameterization of Liss and Mertlivat (1986), Wanninkhof and McGillis (1999), Nightingale et al. (2000), and Ho et al. (2006).

### 3 Results

#### 3.1 Distributions of surface water \( pCO_2 \) and related properties

The basic statistics for atmospheric CO$_2$ are summarized in Table 1. Mean atmospheric \( xCO_2 \) was 363.2 ± 1.8 in 2000 and 367.0 ± 1.4 ppmv in 2002, values which are close to the monthly mean (September) obtained at Point Barrow (Alaska, USA). Surface water \( pCO_2 \) (Table 2) shows variations about 10-fold those of atmospheric \( pCO_2 \). Mean surface water \( pCO_2 \) was calculated as 292.1± 22.1 and 306.5±27.6 µatm for 2000 and 2002, respectively. Although the means, standard deviations, and minima differed little between the years, the surface water \( pCO_2 \) maxima differed markedly between 2000 (395.4 µatm) and 2002 (490.0 µatm).

Distributions of surface water \( pCO_2 \), surface water TCO$_2$, calculated surface water TAlk, SST, and SSS in 2000 are shown in Fig. 2a–e, respectively, as a function of sequential day. We use sequential day to display variations in the properties to eliminate overlap, which would occur if we plotted the properties by longitude and latitude.

Surface water \( pCO_2 \) was mostly lower than atmospheric \( pCO_2 \) (361.0 µatm) except around day 260 (Fig. 2a). The highest surface seawater \( pCO_2 \) was measured near the mouth of the Mackenzie River. Surface water TCO$_2$ and SST (Fig. 2b and d) were positively correlated with surface water \( pCO_2 \) from the initial day to around day 263, whereas SSS variations (Fig. 2e) were negatively correlated during the same period. TAlk (Fig. 2c) also varied positively with surface water \( pCO_2 \), although its variations were less pronounced, probably at least in part because the smaller number of the calculated TAlk values led to a lower time and space resolution. Around day 263,
pCO₂ decreased abruptly by approximately 50 µatm, whereas on about the same day, the other properties increased.

Distributions of surface water pCO₂, surface water TCO₂, calculated surface water TAlk, SST, and SSS in 2002 are shown in Fig. 3a–e, respectively, as a function of sequential day. As in 2000, surface water pCO₂ (Fig. 3a) was usually lower than atmospheric pCO₂ (364.7 µatm), although supersaturation of surface water pCO₂ was observed locally. In 2002, shipboard observations were made near the mouth of the Mackenzie River on two different legs of the cruise: legs 3 and 5 (Fig. 1b’). Around day 263 on leg 3, surface water pCO₂ decreased by about 50 µatm concurrently with decreases in TCO₂, TAlk, and SSS (Fig. 3b, c, and e) and with an increase in SST (Fig. 3d). On leg 5, however, a similar distinct relationship among the properties cannot be discerned. Instead, the properties all showed relatively higher variability during leg 5 than during the other legs. On leg 4, TCO₂, TAlk, and SSS distributions exhibit V-shaped valleys, but SST exhibits a peak (an inverted V). In spite of these changes, surface water pCO₂ was approximately constant at 320 µatm during leg 4.

In summary, surface water pCO₂ was mostly undersaturated with respect to atmospheric pCO₂, as 97% of the observations (n=2561) in the two years were between 250 and 344 µatm.

3.2 Air-sea exchanges of CO₂

ΔpCO₂, the driving force of air-sea exchange of CO₂ calculated as the difference of pCO₂ between the sea surface and the overlying air (the latter is subtracted from the former), was mostly negative in both years except in areas close to the mouth of the Mackenzie River, where it became positive, reaching +125 µatm at maximum (2002). The averaged ΔpCO₂ was −68.8±22.2 and −58.2±27.6 µatm in 2000 and 2002, respectively (Table 3). The ΔpCO₂ distribution displayed the same patterns as the relationship between atmospheric and surface water pCO₂ each year (Figs. 2a and 3a).

CO₂ flux distributions in 2000 calculated using the W92 formulation are shown as a function of sequential day in Fig. 4a. The CO₂ fluxes were generally negative except
around day 260, when observations were made near the mouth of the Mackenzie River (Fig. 1a'). The averaged CO$_2$ flux in 2000 was $-15.0 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 3).

CO$_2$ flux distributions in 2002 are displayed in Fig. 4b. During the first three legs in 2002, the CO$_2$ fluxes were consistently negative but close to zero, whereas in the during legs 4, 5, and 6, large negative fluxes with high variability were observed. The averaged CO$_2$ flux in 2002 was $-16.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Table 3), nearly the same as that in 2000. Nevertheless, the temporal and spatial variability of the CO$_2$ flux was larger in 2002 than in 2000, as is clear from the standard deviations (Table 3). In 2002, large positive CO$_2$ fluxes were also observed during leg 5, when observations were made near the mouth of the Mackenzie River (Fig. 1b'), whereas in 2000, such a large positive CO$_2$ fluxes were not observed.

In summary, the area overall acted as a moderate sink for atmospheric CO$_2$, although sea-to-air CO$_2$ fluxes were observed locally.

4 Discussion

As reported in Sect. 3.1, the dynamic range of surface water $p$CO$_2$ was larger than that of atmospheric CO$_2$, implying that spatial variations of $\Delta p$CO$_2$ were controlled chiefly by the variations in surface water $p$CO$_2$. Hence, it is important to elucidate the cause of the spatial variations in surface water $p$CO$_2$ to assess where future sinks or sources of atmospheric CO$_2$ might exist, when an ice-free period becomes longer as expected.

As a possible cause of the spatial variations in $p$CO$_2$, we first examine biological processes (production and remineralization), using observed and calculated chemical properties, and demonstrate that these effects cannot primarily account for the distribution of surface water $p$CO$_2$ (Sect. 4.1). Next, we investigate spatial variations in $p$CO$_2$ in relation to water mixing, especially river discharge, which is a dominant process in the study area (Sect. 4.2). Then, we discuss differences in calculated air-sea fluxes of CO$_2$ between 2000 and 2002, and between the areas east and west of 150°W. We also estimate the CO$_2$ fluxes in the area as a whole (Sect. 4.3). Lastly, we evaluate
the capacity of the study area as a CO$_2$ sink on the basis of the so-called buffer factor (Sect. 4.4).

4.1 Biological processes

Because of the high biological productivity of coastal regions (Codispoti et al., 1986) and the patchiness of biological activity (Valiela, 1995), biogeochemical processes can cause high spatial variations in pCO$_2$. For example, from spring to summer, the drawdown of pCO$_2$ in the Chuckchi Sea, to the west of the Beaufort Sea, is known to be related to biological production (Bates et al., 2005).

A simple method of estimating biological production is to calculate net community production (NCP; mg C m$^{-2}$ d$^{-1}$), which can be estimated from convenient chemical properties such as dissolved oxygen, nitrate, and TCO$_2$. In fact, NCP has been repeatedly used to quantify biological production (Codispoti et al., 1986; Murata et al., 2002; Bates et al., 2005). If it is calculated from TCO$_2$, NCP is obtained by dividing the drawdown of TCO$_2$ normalized to a salinity of 35 ($\Delta$nTCO$_2$) by the duration (days) of production. NCP becomes positive when net autotrophic processes exceed net heterotrophic processes (Hansell and Carlson, 1998). In the study area, $\Delta$nTCO$_2$ can be estimated from the difference of nTCO$_2$ between the surface and the temperature minimum layer (TML) in the upper ocean, because the temperature minimum water is regarded as a remnant of winter water (Coachman et al., 1975; Midorikawa et al., 2002). Using this method, NCP from the end of the previous winter to the observation time is roughly estimated by assuming a constant decrease of nTCO$_2$ in the surface layer from winter to spring. However, during this study (Fig. 5), nTCO$_2$ in the surface layer was consistently higher than that in the TML; that is, no drawdown of nTCO$_2$ relative to the TML value was observed in the layers above the TML in the study area. This result implies that the surface water pCO$_2$ in the study area is little controlled by biological production during CO$_2$-rich conditions in wintertime followed by drawdown of CO$_2$ in the subsequent season, as is often found elsewhere, such as in the northwestern North Pacific (Murata et al., 2002) and the Southern Ocean (Ishii et al., 1998).
As we discuss in Sect. 4.2, higher concentrations of nTCO$_2$ were associated with river discharge. Thus, we discuss here the possibility that biological processes in the river discharge are a factor causing the observed spatial variations of surface water $p$CO$_2$.

To investigate biological activity affecting distributions of surface water $p$CO$_2$, we plotted the TCO$_2$ to TAlk ratio (TCO$_2$/TAlk) as a function of salinity (Fig. 6). The TCO$_2$/TAlk ratio is usually determined by in situ changes in TCO$_2$, that is, production and remineralization of organic matter. We found that the ratio generally decreased linearly with increasing salinity, although two trends (i.e., a break in the slope at a salinity of about 22) can be seen in 2000 (Fig. 6a), and considerable variation from the expected trend are seen in 2002 (Fig. 6b). The anomalously higher TCO$_2$/TAlk ratios found at lower salinity, that is, near the mouth of the Mackenzie River (Fig. 6b), may imply the presence of water (river discharge) with a larger degree of net heterotrophy. Biological activity in the river, for example, in the delta (Emmerton et al., 2008) could possibly cause net heterotrophy. However, the generally conservative changes in the TCO$_2$/TAlk ratio (Fig. 6) indicate that net heterotrophic processes do not continue after the low-salinity river water mixes with the coastal region waters.

The nitrate-depleted (nitrate-limited) conditions widely observed in the surface layer of the Arctic Ocean (Sakshaug, 2003; Dittmar and Kattner, 2003) also support the inference that biological processes do not control the distribution of surface water $p$CO$_2$.

In summary, biological activity was not a primary factor explaining the observed distributions of surface water $p$CO$_2$.

4.2 Water mixing

Spatial variations of summertime surface water $p$CO$_2$ in the area west of 150° W can be well accounted for by water mixing and cooling of a water mass (Murata and Takizawa, 2003). It is thus possible that the same processes are dominant in the area east of 150° W. To confirm this, we created separate temperature-salinity ($T/S$) diagrams for 2000 and 2002 (Fig. 7).
In general, two types of water mixing can occur. One (type A) is the mixing of waters with high temperature and low salinity, or waters with low temperature and high salinity. The other (type B) is the mixing of high-temperature waters with low-temperature waters, with relatively small variation of salinity. Type A mixing is typical where river discharge to high-latitude seas occurs (Murata, 2006, Else et al., 2008), whereas type B mixing results from the cooling of a water mass (Murata and Takizawa, 2003). The low-temperature water in type B mixing is likely to be derived from melting ice, as it is generally close to the freezing point for a given temperature and salinity.

In the Beaufort Sea, the patterns of water mixing differed between 2000 and 2002. In both 2000 and 2002, type B mixing was seen at relatively high latitudes: on leg 3 in 2000 and legs 1 and 2 in 2002 (Fig. 7). Type A mixing, in contrast, was observed at relatively low latitudes, in particular in the area near the mouth of the Mackenzie River (2002 legs 3 and 5), where type A mixing was clearly dominant (Fig. 7b).

To examine the effects of water mixing on surface water $pCO_2$, we estimated $pCO_2$ values calculated from two apparent end members by assuming conservative mixing. Values of the two end members for temperature and salinity were visually selected from the $T/S$ diagrams (Fig. 7) and are listed in Table 4. From each pair of $T$ and $S$ end-member values, together with corresponding values of TCO$_2$ and TAlk, we computed surface water $pCO_2$ in relation to salinity at four intermediate points, assuming conservative mixing (Fig. 8). The calculated $pCO_2$ values well reproduced the observed $pCO_2$ distributions. In 2002, however, a number of measured surface water $pCO_2$ values deviated from those computed from the water mixing. These values correspond to the scattered data points at salinity and temperature ranges from 18 to 26 and 0 to 2°C, respectively in the $T/S$ distributions (Fig. 7b). More shipboard observations covering a more extensive area of the coastal region were made in 2002 than in 2000 (Fig. 1), which probably resulted in encounters with more different water mixings.

The dynamic ranges of $T$ and $S$ seen in the $T/S$ diagrams on some legs (Fig. 7) might lead us to expect large changes in $pCO_2$ when, in fact, the changes in $pCO_2$ were small. For instance, type B water mixing in 2000 resulted in little variation of
surface water $p$CO$_2$ (mixing b; Fig. 8) despite large changes of temperature and salinity (Table 4). This occurs because $p$CO$_2$ depends not only on temperature and salinity but also on TCO$_2$ and TAlk (Takahashi et al., 1993), and river discharge is usually rich in both TCO$_2$ and TAlk. If it is assumed that the relationships of temperature, salinity, TCO$_2$, and TAlk with $p$CO$_2$ (Takahashi et al., 1993) hold true in the coastal region, the increments of $p$CO$_2$, from a beginning value of 270 µatm, due to the changes of temperature, salinity, TCO$_2$, and TAlk between the end members of mixing b (Table 4) are calculated to be 19, 18, −80, and 35 µatm, respectively, for a net increment of −8 µatm, implying only a small net change in $p$CO$_2$. This result demonstrates that small changes in $p$CO$_2$ can occur as a result of water mixing.

In conclusion, river discharge is the most important factor accounting for the distributions of surface water $p$CO$_2$ in the area east of 150° W. This feature of the $p$CO$_2$ distribution is in distinct contrast to that in the area west of 150° W, where no influence of river discharge was detected (Murata and Takizawa, 2003).

4.3 Air-to-sea flux of CO$_2$

On the basis of the observations during the two years, we investigated spatial variations in the air-sea flux of CO$_2$ in coastal regions east of 150° W in the Canadian Beaufort Sea, where the influence of river discharge was dominant. In this section, we first discuss differences in the CO$_2$ fluxes between 2000 and 2002 (Sect. 4.3.1). Second, we investigate differences in the CO$_2$ fluxes between the areas east and west of 150° W (Sect. 4.3.2). Then, we attempt to estimate air-to-sea CO$_2$ fluxes in an extended area in the ice-free season, and we compare the results with those obtained by previous studies (Sect. 4.3.3).

4.3.1 Differences between 2000 and 2002

Although the mean CO$_2$ flux did not show large differences between 2000 and 2002, distinct differences in the variability of the CO$_2$ flux were observed between the two
years. Variability was larger in 2002 (Sect. 3.2), probably because the wind speed frequency distributions differed (Fig. 9). The wind speed frequency distribution in 2000 was unimodal, with one peak at the wind speed class of 6–7 m s\(^{-1}\), whereas the distribution in 2002 was bimodal, with peaks at wind speed classes of 4–5 and 12–13 m s\(^{-1}\). This difference in the wind speed frequency distributions is reflected in the frequency distributions of the CO\(_2\) fluxes (Fig. 10). In 2000 (Fig. 10a), the CO\(_2\) fluxes were concentrated in a few frequency classes, whereas in 2002, they showed a wider range (Fig. 10b). In spite of this difference, 86% and 76% of the total CO\(_2\) flux ranged from −30 to 0 mmol m\(^{-2}\) d\(^{-1}\) in 2000 and 2002, respectively, resulting in the nearly equal means of the CO\(_2\) flux.

4.3.2 Differences between the areas east and west of 150° W

To compare the CO\(_2\) fluxes in the area east of 150° W with those observed west of 150° W, we calculated the CO\(_2\) fluxes from data obtained west of 150° W during cruises MR00-K06 and MR02-K05. The CO\(_2\) fluxes during MR00-K06 were previously calculated by Murata and Takizawa (2003). However, we recalculated them, because Murata and Takizawa (2003) used averaged wind speeds to calculate the CO\(_2\) fluxes, which moderated their spatial and temporal variability.

The averaged CO\(_2\) fluxes in the area west of 150° W (Table 5) were almost equivalent to those in the area east of 150° W (Table 3). Furthermore, the shapes of the CO\(_2\) flux frequency distributions were similar between east and west of 150° W (compare Fig. 10a and b with Fig. 10c and d, respectively); the CO\(_2\) fluxes mostly range from −30 to 0 mmol m\(^{-2}\) d\(^{-1}\) in both areas. The frequencies of CO\(_2\) fluxes outside this range were quite small. These findings indicate that the absorption of CO\(_2\) by the ocean was almost equivalent between the areas.

Although the high-frequency parts of the distributions displayed an overall accordance, extreme CO\(_2\) flux values were positive east of 150° W, whereas west of 150° W, they were negative. Positive extreme values were observed chiefly in 2002, and co-
incided with the elevated surface water $pCO_2$ values (Fig. 3a), which were probably caused by upwelling of subsurface waters rich in CO$_2$. Vertical distributions of water temperature and salinity at the time of the large positive CO$_2$ fluxes indicate that upwelling of lower temperature and saltier water brought up water rich in CO$_2$ (Fig. 11). Upwelling conditions, however, returned shortly (after about 2 h) to the usual conditions (higher temperature and lower salinity water; Fig. 11). Williams et al. (2008) reported that conditions favorable to upwelling often occur in the area, depending on wind direction, supporting our inference. In fact, changes in wind direction were recorded during the cruise. On the other hand, the large negative CO$_2$ fluxes west of 150°W were probably associated with decreases in surface water $pCO_2$ caused by water mixing and cooling (Murata and Takizawa, 2003; Bates, 2006), together with high wind speeds.

4.3.3 Air-to-sea CO$_2$ fluxes and comparison with previous studies

As discussed in Sect. 4.2, surface water $pCO_2$ in the area east of 150°W showed spatial variability associated with river discharge, but that in the area west of 150°W did not (Murata and Takizawa, 2003). In spite of the different mechanisms causing spatial variability, the means and frequency distributions of the CO$_2$ fluxes were similar between the two areas (Sect. 4.3.2). Therefore, we adopted values of −30 to 0 mmol m$^{-2}$ d$^{-1}$ as representative CO$_2$ flux values for the region as a whole (165°–130°W; 70°–73°N). Our observations were made chiefly in September, when the ice-free area is at its maximum. Bates (2006) estimated CO$_2$ fluxes during spring (May–June) to summer (July–August) to be −30 to −90 mmol m$^{-2}$ d$^{-1}$, using observations made in 2002. On the basis of observations made in August–September 1996, Pipko et al. (2002) reported that surface water $pCO_2$ in the Chukchi Sea was mainly undersaturated in CO$_2$ with respect to the atmosphere and that the averaged CO$_2$ flux was −12.2 mmol m$^{-2}$ d$^{-1}$. These results indicate that the region as a whole acts as a sink for atmospheric CO$_2$ throughout the year, if the air-sea flux of CO$_2$ during the ice-covered season is neglected.
They also imply that on a seasonal time scale, no mechanisms causing CO$_2$ source conditions exist in the region, although source conditions occur over a shorter (meso) time scale near the mouth of the Mackenzie River (Sect. 4.3.2). However, because of the low frequency of sea-to-air CO$_2$ fluxes (Fig. 10), for estimations on a seasonal or annual basis, these CO$_2$ fluxes can be ignored. From the estimated CO$_2$ flux of $-10.2 \pm 7.7 \text{ mmol m}^{-2} \text{ d}^{-1}$, calculated from all flux values from $-30$ to $0 \text{ mmol m}^{-2} \text{ d}^{-1}$, the area of the combined region ($= 411,000 \text{ km}^2$), and the assumed ice-free period ($= 100 \text{ days}$), we estimated the uptake of CO$_2$ in the entire region during the ice-free period to be $5.0 \pm 3.8 \text{ Tg C}$.

The CO$_2$ flux estimated in the present study ($-10.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) is close to that ($-12.2 \text{ mmol m}^{-2} \text{ d}^{-1}$) reported by Pipko et al. (2002), but smaller than those ($-30$ to $-90 \text{ mmol m}^{-2} \text{ d}^{-1}$) reported by Bates (2006), both of whom based their calculations on the formulation of W92. The different results probably reflect seasonal differences. The observations of the present study and those of Pipko et al. (2002) were obtained in late summer, while those of Bates (2006) were obtained from spring to early summer. In spring to early summer, enhanced biological activity such as blooms operate to reduce surface water $p$CO$_2$ considerably, causing larger air-to-sea CO$_2$ fluxes.

The CO$_2$ flux estimated in the present study is also close to values found in other high-latitude marginal seas: $-1.94 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Borges et al., 2005) and $-12 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Cai et al., 2006).

4.4 Capacity of the Beaufort Sea as a CO$_2$ sink

The buffer factor, that is, the ratio of the change in $p$CO$_2$ to that in TCO$_2$, generally ranges from 9 to 13 in open oceans (Takahashi et al., 1993; Sabine et al., 2004) and is often used to evaluate oceanic capacity as a CO$_2$ sink: the lower the buffer factor, the larger the potential for CO$_2$ uptake. In fact, more anthropogenic CO$_2$ is stored in the subtropical oceans, where the buffer factor is lower, than in the polar oceans, where the buffer factor is higher (Sabine et al., 2004). In this section, we use the buffer factor
to evaluate the capacity of the study area as a CO$_2$ sink during the ice-free season.

To estimate the buffer factor, we first computed $p$CO$_2$ at an average temperature and a salinity of 35 from nTCO$_2$ and TA$_{alk}$ normalized to a salinity of 35 (nTA$_{alk}$), using the same combination of constants as used for the TA$_{alk}$ calculation (Sect. 2.2). Then, we calculated the natural logarithms of nTCO$_2$ ($\ln$(nTCO$_2$)) and of the calculated $p$CO$_2$ ($\ln$(pCO$_2$)). Distributions of the $\ln$(pCO$_2$) as a function of the $\ln$(nTCO$_2$) are illustrated in Fig. 12a and b. The buffer factor corresponds to the slope of the regression line.

In both years, the calculated buffer factor east of 150° W was 1.5. The buffer factor west of 150° W, however, calculated by the same method (Fig. 12c and d), was 6.9 in 2000 and 5.2 in 2002, although the fit of the regression lines is relatively poor. Furthermore, two separate trends can be discerned visually in 2002, suggesting the presence of different water masses in the area. Bates (2006) reported low buffer factors of ~3.5–6.5 in the area of 170°–150° W, 65°–75° N in summer 2002, which are close to the values that we obtained in the area west of 150° W. The buffer factors obtained in the area east of 150° W are much lower, implying that there is a higher potential sink for atmospheric CO$_2$ in that area.

The difference in the buffer factors between the areas probably originates from differences in water masses. As discussed so far, the area east of 150° W is influenced by river discharge, but not the area west of 150° W (Murata and Takizawa, 2003). Thus the extremely low buffer factors obtained east of 150° W probably reflect the carbonate system of water masses affected by river discharge. The extremely low values were probably caused by a decrease in nTCO$_2$ with little change in nTA$_{alk}$, which are features of biological production (decreases of nTCO$_2$) along with an absence of calcification (no changes of nTCO$_2$). Bates (2006) similarly explained the low buffer factor in the area west of 150° W. As examined in Sect. 4.1, biological activity was not efficient in the area east of 150° W, although biological activity occurring in upstream of rivers may cause the buffer factor to be low in the area.
5 Concluding remarks

We discussed spatial variations of surface water $pCO_2$ and the air-sea flux of CO$_2$ in coastal regions of the Canadian Beaufort Sea. The spatial variations in $pCO_2$ were primarily associated with water mixing, related chiefly to river discharge. Biological processes seemed to be of minor importance during this late summer season. Overall, the area acted a moderate sink for atmospheric CO$_2$.

The influence of river discharge was well confirmed by vertical distributions of nTCO$_2$, nTAlk, and other physical and chemical properties. Namely, distinct vertical gradients in these properties were found in the top few tens of meters. These vertical gradients, however, also raise some questions, because similar vertical gradients in these properties often occur also in the top few meters, implying that their values at the sea surface may differ from those a few meters below. For air-sea exchange, values at the sea surface are important. During the cruises, we collected surface water samples at nearly 0 m by using a bucket. At one CTD station (69°45.04′ N; 138°09.44′ W), for instance, surface salinity, water temperature, TCO$_2$, and TAlk by bucket sampling were 17.80, 2.1°C, 1860.9 µmol kg$^{-1}$, and 1941.1 µmol kg$^{-1}$, respectively. Using these values, we calculated surface water $pCO_2$ to be 284.6 µatm. The observed surface water $pCO_2$, in water sampled from about 4 m depth, was 333.1±3.3 µatm. This difference of about 48 µatm is not negligible. We cannot explain why a large vertical difference in $pCO_2$ existed between the sea surface and the depth of approximately 4 m. Nevertheless, since the water temperature and salinity values obtained by the bucket sampling were not markedly different from the averaged values of the continuous measurements, which were 2.00°C and 17.21, respectively, biological processes in the thin surface layer may possibly account for the difference in $pCO_2$ within the top 4 m.

The vertical difference in $pCO_2$, which has been left unexamined so far, probably affects the calculated air-sea flux of CO$_2$. Further studies are necessary to investigate this point.
Acknowledgements. We thank the officers and crew of the R/V Mirai for exceptional support during the cruises. We also give special thanks to the staff of Marine Works Japan, who worked as physical and chemical oceanography marine technicians on board the R/V Mirai, and who also worked to ensure that the data obtained by the shipboard observations were of the first quality.

References


Dickson, A. G.: Standard potential of the reaction: AgCl(s) + 1/2H$_2$(g)=Ag(s) + HCl(aq), and the


Table 1. Comparison between atmospheric CO$_2$ in the area east of 150° W during cruises MR00-K06 ($n$=248) and MR02-K05 ($n$=429), and the monthly mean (± standard deviation) atmospheric CO$_2$ in September, measured at Point Barrow (71° 32’ N, 156° 60’ W) (Tans and Conway, 2005).

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Period (UTC)</th>
<th>xCO$_2$ (ppmv)</th>
<th>pCO$_2$ (µatm)</th>
<th>CO$_2$ at Point Barrow (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR00-K06</td>
<td>1–22 Sep 2000</td>
<td>363.2±1.8</td>
<td>361.0±1.8</td>
<td>361.90</td>
</tr>
<tr>
<td>MR02-K05</td>
<td>15–30 Sep 2002</td>
<td>367.0±1.4</td>
<td>364.7±1.4</td>
<td>365.29</td>
</tr>
</tbody>
</table>
Table 2. Means (± standard deviation), maxima, and minima of surface water $pCO_2$ during MR00-K06 ($n=855$) and MR02-K05 ($n=1711$).

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Period</th>
<th>Mean (µatm)</th>
<th>Max. (µatm)</th>
<th>Min. (µatm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR00-K06</td>
<td>13–22 Sep 2000</td>
<td>292.1±22.1</td>
<td>395.4</td>
<td>261.2</td>
</tr>
<tr>
<td>MR02-K05</td>
<td>15–30 Sep 2002</td>
<td>306.5±27.6</td>
<td>490.0</td>
<td>252.6</td>
</tr>
</tbody>
</table>
**Table 3.** Means of $\Delta p$CO$_2$ and the CO$_2$ fluxes in the area east of 150° W.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>$\Delta p$CO$_2$ (µatm)</th>
<th>CO$_2$ flux (mmol m$^{-2}$ d$^{-1}$)</th>
<th>W92$^1$</th>
<th>LM86$^2$</th>
<th>WM99$^3$</th>
<th>N00$^4$</th>
<th>H06$^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR00-K06</td>
<td>−68.3±22.2</td>
<td>−15.0±11.3</td>
<td>−8.6±5.9</td>
<td>−13.8±14.1</td>
<td>−11.9±8.5</td>
<td>−12.3±9.2</td>
<td></td>
</tr>
<tr>
<td>MR02-K05</td>
<td>−58.2±27.6</td>
<td>−16.8±20.0</td>
<td>−9.1±10.6</td>
<td>−18.9±28.9</td>
<td>−13.0±14.9</td>
<td>−13.7±16.3</td>
<td></td>
</tr>
</tbody>
</table>

1 Wanninkhof (1992)
2 Liss and Merlivat (1986)
3 Wanninkhof and McGillis (1999)
4 Nightingale et al. (2000)
5 Ho et al. (2006)
Table 4. End-member values of water temperature ($T$), salinity ($S$), TCO$_2$, and TAlk for various types of conservative water mixing.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Mixing</th>
<th>$T$ ($^\circ$C)</th>
<th>$S$</th>
<th>TCO$_2$ (µmol kg$^{-1}$)</th>
<th>TAlk (µmol kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR00-K06</td>
<td>a</td>
<td>2.432 (−0.979)</td>
<td>15.43 (24.84)</td>
<td>1867.9 (1798.1)</td>
<td>1924.5 (1875.9)</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>−0.420 (1.268)</td>
<td>26.61 (28.42)</td>
<td>1817.0 (1899.3)</td>
<td>1914.6 (2024.9)</td>
</tr>
<tr>
<td>MR02-K05</td>
<td>c</td>
<td>3.765 (−0.382)</td>
<td>11.48 (28.46)</td>
<td>1677.2 (1691.4)</td>
<td>1724.3 (1748.6)</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>2.488 (−0.382)</td>
<td>16.40 (28.46)</td>
<td>1691.4 (1930.6)</td>
<td>1748.6 (2048.4)</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>2.907 (−0.972)</td>
<td>23.97 (25.99)</td>
<td>1684.1 (1802.5)</td>
<td>1767.1 (1879.7)</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>1.331 (−1.000)</td>
<td>26.04 (26.04)</td>
<td>1784.7 (1784.7)</td>
<td>1863.2 (1863.2)</td>
</tr>
<tr>
<td></td>
<td>g</td>
<td>1.297 (1.220)</td>
<td>14.56 (23.35)</td>
<td>1715.1 (1686.6)</td>
<td>1754.3 (1758.0)</td>
</tr>
</tbody>
</table>

Values in parentheses indicate the second end-member are first end member values; values without parentheses are the first end-member values.
Table 5. Means of $\Delta p$CO$_2$ and the CO$_2$ fluxes in the area west of 150° W.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>$\Delta p$CO$_2$ (µatm)</th>
<th>CO$_2$ flux (mmol m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W92$^1$</td>
<td>LM86$^2$</td>
</tr>
<tr>
<td>MR00-K06</td>
<td>$-102.6\pm34.0$</td>
<td>$-16.8\pm14.4$</td>
</tr>
<tr>
<td>MR02-K05</td>
<td>$-70.0\pm27.4$</td>
<td>$-17.3\pm23.4$</td>
</tr>
</tbody>
</table>

1 Wanninkhof (1992)  
2 Liss and Merlivat (1986)  
3 Wanninkhof and McGillis (1999)  
4 Nightingale et al. (2000)  
5 Ho et al. (2006)
Fig. 1. Cruise areas during (a) MR00-K06 (2000) and (b) MR02-K05 (2002). Solid circles show points where surface water $pCO_2$ was sampled. The locations of CTD water sampling stations in 2000 and 2002, from which the data in Figs. 5 and 11 were obtained, are indicated by red and light-green squares, respectively. This map was created with ODV Software (Schlitzer, 2001). The numbers in panels (a') and (b') indicate leg numbers and are associated with the numbers of Figs. 2, 3, 4, and 7. Arrows in the panels indicate the sailing direction.
Fig. 2. (a) Distributions of (a) surface water pCO$_2$, and (b) surface water TCO$_2$, (c) surface water TAlk, (d) SST, and (e) SSS as a function of sequential day during cruise MR00-K06. The distributions of each property are shown in different colors, according to portions (legs 1–3) of the cruise, which correspond to the observation points in Fig. 1a’. In panel (a), the horizontal line indicates the mean atmospheric pCO$_2$ (361.0 µatm).
Fig. 3. Distributions of (a) surface water \( p\text{CO}_2 \), (b) surface water TCO\(_2\), (c) surface water TAlk, (d) SST, and (e) SSS as a function of sequential day during cruise MR02-K05. The distributions of each property are shown in different colors, according to legs 1–6 of the cruise, which correspond to the observation points in Fig. 1b’. In panel (a), the horizontal line indicates the mean atmospheric \( p\text{CO}_2 \) (364.7 \( \mu \text{atm} \)).
Fig. 4. Distributions of the CO$_2$ fluxes calculated based on the W92 formulation as a function of sequential day for (a) MR00-K06 and (b) MR02-K05. The distributions of the CO$_2$ fluxes during legs 1–3 of MR00-K06 and legs 1–6 of MR02-K05 correspond to the observation points shown in panels (a') and (b') in Fig. 1, respectively.
Fig. 5. Vertical distribution of nTCO$_2$ during MR00-K06 (squares) and MR02-K05 (crosses). Arrows indicate the temperature minimum layer in each vertical profile. The observation points are shown in Fig. 1.
Fig. 6. Distributions of TCO$_2$/TAlk as a function of salinity for (a) MR00-K06 and (b) MR02-K05.
Fig. 7. T/S diagrams for (a) MR00-K06 and (b) MR02-K05. The distributions are divided according to the cruise legs, shown by different colors, as in Fig. 1a' and b'. The solid line in each panel indicates the freezing point at a given temperature and salinity. The broken lines show the two mixing types (A and B) schematically.
Fig. 8. Distributions of observed (crosses) and calculated (colored symbols labeled with letters a–g) $pCO_2$ as a function of salinity for (a) MR00-K06 and (b) MR02-K05. Calculated $pCO_2$ values are based on the conservative mixing of two end members, which are given in Table 4.
Fig. 9. Frequency distributions of wind speed for (a) MR00-K06 and (b) MR02-K05.
Fig. 10. Frequency distributions of the CO$_2$ fluxes calculated based on the W92 formulation in the area east of 150° W for (a) MR00-K06 and (b) MR02-K05, and the area west of 150° W for (c) MR00-K06 and (d) MR02-K05. For frequencies less than 10, the columns are labeled with the number of observations for clarity.
Fig. 11. Vertical distributions of (a) temperature, (b) salinity, and (c) calculated $p$CO$_2$ under upwelling (solid circles) and usual (squares) conditions. The observation points are shown in Fig. 1.
Fig. 12. Buffer factors calculated from the slopes of regression lines of ln(pCO₂) regressed on ln(nTCO₂) for the area east of 150° W during (a) MR00-K06 and (b) MR02-K05, and for the area west of 150° W during (c) MR00-K06 and (d) MR02-K05.