

RESEARCH LETTER

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Key Points:

- The water column in Ryder Bay is a net, annual sink of atmospheric CO₂
- Seasonal sea ice increases the strength of the ocean CO₂ sink in Ryder Bay
- Large uncertainty remains regarding the effect of sea ice on gas exchange

Supporting Information:

- Text S1

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The seasonal cycle of ocean-atmosphere CO₂ flux in Ryder Bay, west Antarctic Peninsula

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Abstract Approximately 15 million km² of the Southern Ocean is seasonally ice covered, yet the processes affecting carbon cycling and gas exchange in this climatically important region remain inadequately understood. Here, 3 years of dissolved inorganic carbon (DIC) measurements and carbon dioxide (CO₂) fluxes from Ryder Bay on the west Antarctic Peninsula (WAP) are presented. During spring and summer, primary production in the surface ocean promotes atmospheric CO₂ uptake. In winter, higher DIC, caused by net heterotrophy and vertical mixing with Circumpolar Deep Water, results in outgassing of CO₂ from the ocean. Ryder Bay is found to be a net sink of atmospheric CO₂ of 0.59–0.94 mol Cm⁻² yr⁻¹ (average of 3 years). Seasonal sea ice cover increases the net annual CO₂ uptake, but its effect on gas exchange remains poorly constrained. A reduction in sea ice on the WAP shelf may reduce the strength of the oceanic CO₂ sink in this region.

1. Introduction

The Southern Ocean south of 44°S is responsible for approximately 25–30% of the global ocean uptake of anthropogenic carbon [Fletcher *et al.*, 2006; Lenton *et al.*, 2013], but accurately quantifying this sink and understanding the processes behind it remains challenging. The net ocean-atmosphere CO₂ flux of the high-latitude, seasonally ice-covered Southern Ocean is especially difficult to quantify due to a scarcity in observational data, particularly during the ice-covered winter months [Bakker *et al.*, 2014]. Not only does ice cover hinder data collection and therefore limit the scope of observational flux estimates, but it also adds complexity to the carbon cycle through its effect on gas exchange, vertical stability, and biological production.

Estimates of CO₂ uptake by the high-latitude Southern Ocean vary between models, inversions, and observations. Most recent estimates characterize the high-latitude Southern Ocean as a small sink or a small source of CO₂ to the atmosphere [Gruber *et al.*, 2009; Takahashi *et al.*, 2009; Lenton *et al.*, 2013]; however, they are largely based on the open ocean and do not account for the variability and importance of the coastal ocean which may be a strong sink of CO₂ [Arrigo *et al.*, 2008]. Furthermore, many ocean biogeochemical models fail to capture the magnitude of the seasonal cycle at high latitudes, the main mode of variability in this region [Lenton *et al.*, 2013]. This inability to reconcile modeled and observed CO₂ fluxes highlights our poor understanding of the high-latitude carbon cycle and limits confidence in our ability to predict future changes to Southern Ocean CO₂ uptake.

Recent work suggests that the Southern Ocean carbon sink may be weakening, and this has been attributed to increased upwelling of dissolved inorganic carbon (DIC) caused by increased Southern Ocean winds associated with a more positive Southern Annular Mode (SAM) [Lenton and Matear, 2007; Le Quéré *et al.*, 2007; Lovenduski *et al.*, 2008]—a climatic change that is known to include an anthropogenic component [Thompson and Solomon, 2002]. However, due to a lack of observational data in this region, our mechanistic understanding of the variability in the ocean-atmosphere flux of CO₂ remains weak. A better understanding of the processes driving seasonal and interannual variability in carbon flux is required to strengthen our predictions of future carbon uptake by the Southern Ocean. This is true especially for the productive coastal waters, which are the focus of this paper.

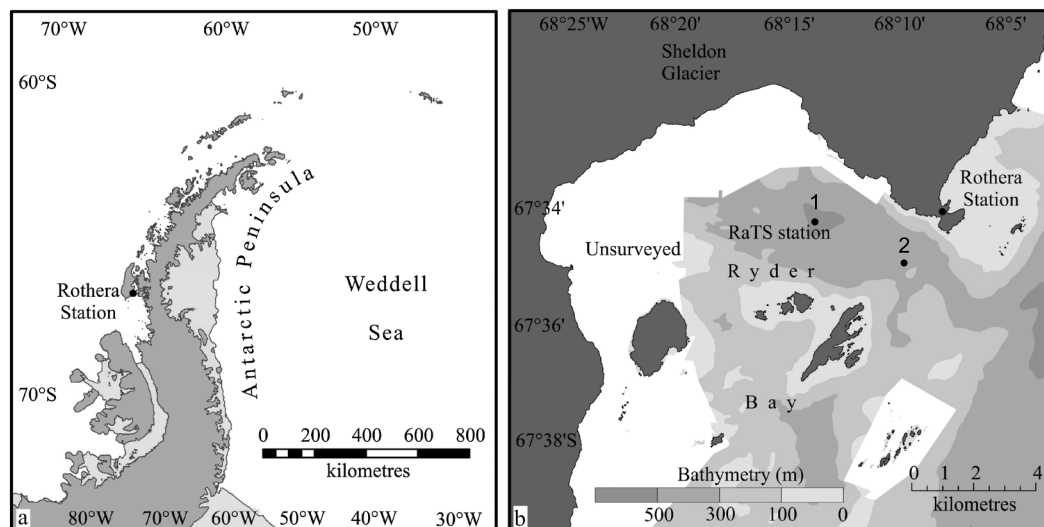


Figure 1. (a) Location of Rothera on Adelaide Island at the west Antarctic Peninsula. (b) Location of RaTS sites 1 and 2 in Ryder Bay. Modified from Venables *et al.* [2013].

2. Methods

2.1. Sampling and Analyses

Discrete samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were collected from 15m depth at the Rothera Time Series site (RaTS), located in Ryder Bay, about 4km offshore on the west Antarctic Peninsula (Figure 1). Sampling was undertaken from a rigid inflatable boat or through a hole in the ice approximately weekly in summer and biweekly in winter, weather and ice permitting. If partial ice cover prevented access to the main RaTS site, then a secondary site was used (Figure 1). Collection of inorganic carbon samples began in December 2010 and continued until February 2014. Samples were collected in 250 ml or 500 ml borosilicate glass bottles, spiked with mercuric chloride and sealed with greased stoppers. They were transported back to the University of East Anglia, UK, at the end of each field season for analysis. DIC was measured by coulometry [Johnson *et al.*, 1985] following standard operating procedure (SOP) 2 of Dickson *et al.* [2007], and TA was measured by potentiometric titration [Mintrop *et al.*, 2000] following SOP 3b of Dickson *et al.* [2007]. DIC and TA were measured using two VINDTAs (versatile instrument for the determination of titration alkalinity, version 3C, Marianda, Germany). Instruments were calibrated using certified reference materials from the Scripps Institution of Oceanography. Sea ice type and fraction of ice cover were visually estimated by marine assistants at Rothera. While these sea ice estimates are inherently somewhat subjective, the Rothera data have been found to agree well with wider-scale satellite estimates [Wallace, 2007]. Temperature, salinity, and pressure were measured during full depth (500m at site 1) conductivity, temperature, depth (CTD) casts [Venables *et al.*, 2013].

2.2. Ocean-Atmosphere CO₂ Flux

The ocean-atmosphere flux of CO₂ was calculated for each day during the study period using equation (1). A negative value signifies an uptake from the atmosphere by the ocean.

$$\text{CO}_2 \text{ flux} = s \cdot \Delta f\text{CO}_2 \cdot k \tag{1}$$

where s is the solubility of CO₂ at in situ temperature and salinity, calculated using the equation of Weiss [1974], $\Delta f\text{CO}_2$ is the difference in the fugacity of CO₂ between seawater and the air, and k is the gas transfer velocity. Water $f\text{CO}_2$ was calculated from DIC, TA, silicate, and phosphate measurements using the CO2SYS program [Van Heuven *et al.*, 2011]. Total alkalinity data are presented in the supporting information. Seawater temperature and salinity, seawater $f\text{CO}_2$, and open water fraction were linearly interpolated into daily vectors. Atmospheric $f\text{CO}_2$ was calculated from the dry mole fraction of CO₂ ($x\text{CO}_2$) using the coefficients of Weiss [1974], and water vapor pressure was calculated following Weiss and Price [1980]. Atmospheric $x\text{CO}_2$ data are from weekly flask samples from Palmer Station, approximately 400km northeast of Rothera [Dlugokencky *et al.*, 2014]. These discrete flask data were interpolated and smoothed using a

weighted linear least squares method. Daily averaged wind speed and sea level pressure were measured at Rothera. Wind speed has been corrected from the measurement height of 42 m to 10 m above sea level following *Fairall et al.* [2011].

2.3. Ice Cover and Gas Transfer Velocity

Gas transfer velocity (k) and its relationship with ice cover were calculated using two separate methods. First, k was calculated from wind speed using the parameterization of *Wanninkhof et al.* [2013]. As in previous studies, the gas transfer velocity was scaled linearly with sea ice cover by multiplying k by the fraction of open water. Even at 100% ice cover, there is likely to be some gas exchange with the atmosphere due to leads, fractures, and brine channels [*Semiletov et al.*, 2004; *Loose and Schlosser*, 2011], so, consistent with other studies [*Bates et al.*, 2006; *Mucci et al.*, 2010; *Roden et al.*, 2013], we have set the minimum open water fraction to 0.01. A scenario with no ice is also considered in which k is not modified by ice cover and also a scenario in which brash and grease ice do not affect k . The second method for calculating gas transfer velocity is a recently published parameter model for gas exchange in the sea ice zone [*Loose et al.*, 2014]. This model relates k to wind speed through mean squared wave slope and also includes shear-driven and convection-driven turbulence. The k derived from both methods was corrected to the Schmidt number following *Wanninkhof* [1992]. Full details of gas flux calculations are given in the supporting information.

2.4. Uncertainties

Uncertainties were calculated from the measurement uncertainty of DIC, TA, silicate, phosphate, and atmospheric CO₂; the uncertainty of the carbonate system dissociation constants [*Millero*, 2007]; and the uncertainty of the parameterization of the gas transfer velocity [*Wanninkhof*, 2014]. The propagation of uncertainties using a Monte Carlo approach is described in Appendix A.

3. Results and Discussion

3.1. Seasonal and Interannual Variability

The 3 years of DIC data presented here (Figure 2) display a clear, highly asymmetric, seasonal cycle with an amplitude of $\sim 200 \mu\text{mol kg}^{-1}$. DIC decreases sharply during December/January due to the rapid increase of biological production, and summer months are characterized by low and variable DIC values. There is a gradual increase from around April to maximum DIC concentrations of $\sim 2200 \mu\text{mol kg}^{-1}$ in September. This increase during autumn and winter is caused by net heterotrophy and mixing with relatively old, carbon-rich Circumpolar Deep Water (CDW) as the mixed layer deepens. The rapid spring DIC drawdown is preceded by a more gradual decrease corresponding to reduced sea ice cover (Figure 2), an increase in photosynthetically active radiation, and a shoaling and warming mixed layer. The gradual decrease prior to the main spring bloom is therefore likely to be caused by the onset of algal production in the water column and ice but may also be influenced by ikaite dissolution during ice melt (see section 3.2).

Due to the pronounced seasonal cycle in DIC, the $\Delta f\text{CO}_2$ changes sign between winter and summer (Figure 2), making the water column a potential source of CO₂ to the atmosphere during winter and a potential sink during summer. This gradient determines the direction of the CO₂ flux, but its magnitude is strongly influenced by wind speed and ice cover. The daily ocean-atmosphere CO₂ flux, as calculated with a linear scaling between k and ice cover (Figure 3), ranges from approximately $-15 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ in summer (into the ocean) to approximately $10 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ in winter (out of the ocean). In all 3 years sampled, the summer uptake of CO₂ by the ocean is greater than the winter outgassing, making the water column in Ryder Bay a net sink of atmospheric CO₂ over an annual cycle. Summing the daily fluxes gives the cumulative ocean-atmosphere CO₂ flux (Figure 3), clearly showing a net ocean sink from all estimates. The mean net annual CO₂ uptake by the ocean from 1 January 2011 to 31 December 2013 was $0.59 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ as calculated using the linear scaling of k with ice cover (solid blue line, Figure 3) with net annual uptake ranging from $0.22 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ in 2013 to $1.03 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ in 2011. When calculated using the sea ice gas exchange model (solid red line, Figure 3), the mean net annual ocean uptake was $0.94 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ ranging from $0.47 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ in 2013 to $1.50 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ in 2011. Our estimates of net annual ocean carbon uptake using a linear k scaling are similar to the estimate of *Roden et al.* [2013], who calculated a net ocean uptake in Prydz Bay, East Antarctica of $0.54 \pm 0.11 \text{ mol Cm}^{-2} \text{ yr}^{-1}$, also using a linear scaling of k with ice cover. Our estimates are somewhat lower than the net annual CO₂ uptake of the Ross Sea, estimated using a biogeochemical model as $1.7\text{--}4.2 \text{ mol Cm}^{-2} \text{ yr}^{-1}$ [*Arrigo et al.*, 2008].

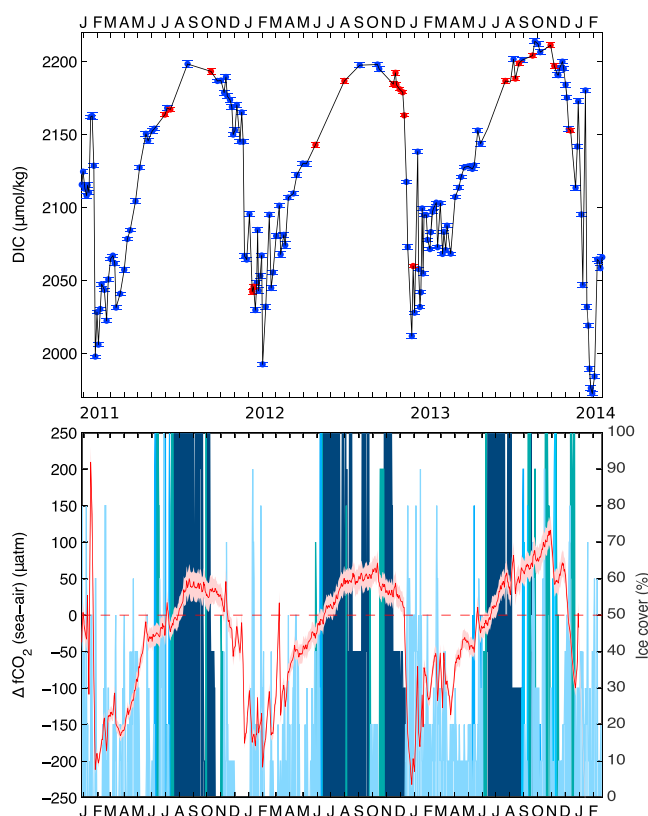


Figure 2. (top) The seasonal cycle of dissolved inorganic carbon from December 2010 until February 2014 at 15m depth at RaTS. Blue points indicate data from site 1, red from site 2. Error bars are uncertainty (2SD) based on measurement precision. (bottom) The red line represents the seasonal cycle of $\Delta f\text{CO}_2$ with the shaded region representing approximate 95% confidence from uncertainty analysis. The red dashed line shows $\Delta f\text{CO}_2 = 0$, i.e., ocean CO_2 concentration is at equilibrium with the atmosphere. Blue bars show percentage ice cover. Bar color denotes ice type with dark blue representing fast ice, turquoise representing pack ice, and light blue representing brash ice.

There is significant interannual variability in the ocean-atmosphere flux of CO_2 , especially in the amount of winter outgassing (Figure 3). Atmospheric CO_2 increases by roughly 2.3 ppm/yr from ~ 387 ppm in January 2011 to ~ 394 ppm in January 2014, with a seasonal amplitude of ~ 3 ppm. Despite this increase in atmospheric CO_2 during the study period, the ocean to atmosphere CO_2 flux increases through each successive winter in the three observed years, and we hypothesize that this interannual variability is caused by two main drivers. First, higher water $f\text{CO}_2$ in winter increases the concentration gradient of CO_2 between the ocean and the atmosphere (Figure 2), making the ocean a stronger potential source of CO_2 to the atmosphere. We suggest that the increase in $f\text{CO}_2$ and DIC in surface water in winter is caused by increased mixing of CDW into the surface layer, and this theory is supported by a slight increase in winter salinity from 2011 to 2013. Reduced ice cover in Ryder Bay during winter allows enhanced mixing due to the exposed water surface, and this can result in reduced stratification in the following spring [Venables and Meredith, 2014]. A decrease in ice cover could therefore affect ocean-atmosphere CO_2 fluxes by increasing the mixing of CDW into the surface and increasing surface water $f\text{CO}_2$ and DIC.

Second, a reduction in ice cover during winter, when $\Delta f\text{CO}_2$ is positive, allows more gas exchange across the air-water interface. The three consecutive winters shown here exhibit increasing $\Delta f\text{CO}_2$ and a longer period during which $\Delta f\text{CO}_2$ is positive, while ice cover is below 50%. These factors combined result in increased outgassing of CO_2 to the atmosphere and a reduced net CO_2 sink over the seasonal cycle. When the effect of ice cover on k is ignored, the water column is still found to be a net sink of atmospheric CO_2 (dashed lines, Figure 3), although the strength of this sink is reduced compared with the equivalent calculations including ice cover (solid blue and red lines, Figure 3). The role of winter sea ice cover in reducing CO_2 flux from the ocean to the atmosphere is consistent with previous observations [Gibson and Trull, 1999; Sweeney, 2003;

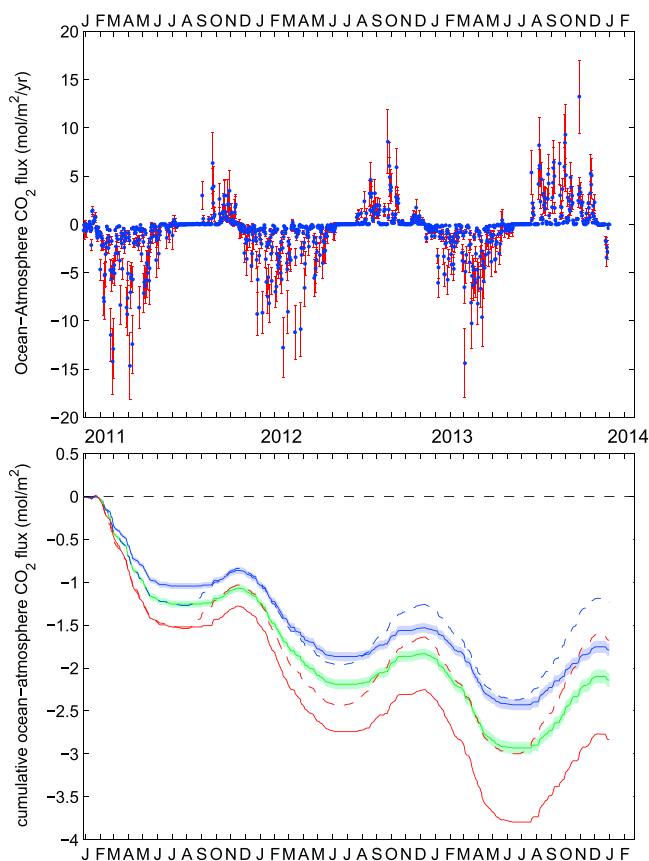


Figure 3. (top) Ocean-atmosphere CO₂ flux at RaTS, calculated using a linear scaling between k and all ice types (corresponds to solid blue line in Figure 3, bottom). Error bars represent approximate 95% confidence. (bottom) Cumulative ocean-atmosphere flux of CO₂ at RaTS. Blue line represents flux calculated following Wanninkhof *et al.* [2013] with a linear scaling of k to sea ice cover. Green line also represents flux calculated following Wanninkhof *et al.* [2013] but excluding brash ice. Shaded regions represent approximate 95% confidence, calculated as the square root of the cumulative sum of the squares. Blue dashed line represents flux calculated following Wanninkhof *et al.* [2013] assuming no ice cover. Red line represents flux calculated using the model of Loose *et al.* [2014], including all ice types. Red dashed line represents flux calculated with the model of Loose *et al.* [2014] but assuming no ice cover.

Bakker *et al.*, 2008] and supports the hypothesis that increased Antarctic sea ice cover during glacial periods could have lowered atmospheric CO₂ by reducing deep water ventilation [Stephens and Keeling, 2000].

3.2. Unresolved Complexity

Quantification of the gas transfer velocity in ice-covered or partially ice-covered waters is challenging, particularly as different ice types are likely to affect gas fluxes in different ways, and this heterogeneity is not well understood. To investigate the sensitivity of our flux estimates to different ice types, ocean-atmosphere CO₂ flux was also calculated with brash ice ignored (green line, Figure 3). This scenario results in a stronger annual ocean uptake of CO₂ than when k is affected by all ice types (solid blue line) because brash ice predominates in summer, when the $\Delta f\text{CO}_2$ is negative, so its removal allows more CO₂ flux into the water. The parameter model of Loose *et al.* [2014] (red line, Figure 3) gives higher k values and therefore a larger net annual sink than the scenario using a linear scaling of k with ice cover. This is partly caused by the way in which these two methods calculate k from wind speed. The contribution of this factor can be seen as the difference between the red and blue dashed lines which do not include ice effects. Another reason for the discrepancy between the linear scaling and the parameter model is the inclusion in the model of shear-driven and convection-driven turbulence which can increase the gas transfer velocity by 40% [Loose *et al.*, 2014]. It is important to note that the uncertainty caused by the handling of ice cover and ice type in gas flux estimates dwarfs that caused by uncertainty in the carbonate parameters and the gas transfer

velocity (shading on blue and green lines, Figure 3). More observational data, from both laboratory ice tank experiments and field studies, are needed to increase our confidence in calculating ocean-atmosphere gas flux in seasonally ice-covered waters.

As carbon samples were collected from 15 m depth, the seawater $f\text{CO}_2$ used for flux calculations may not accurately represent surface concentrations when the mixed layer shoals to above this depth in summer. Due to biological activity in the surface mixed layer, it is likely that our water $f\text{CO}_2$ is overestimated between approximately December and March, giving an underestimate of the difference between the concentration of CO_2 in the atmosphere and the sea water. The net annual ocean CO_2 uptake presented here is therefore likely to be an underestimate. Mixed layer depth data are presented in the supporting information.

Sea ice does not simply act as a cap to ocean-atmosphere gas exchange; sea ice-atmosphere CO_2 exchange has been observed in both the Arctic and Antarctic [Gosink *et al.*, 1976; Semiletov *et al.*, 2004; Delille, 2006; Zemmelen *et al.*, 2006; Miller *et al.*, 2011; Nomura *et al.*, 2013]. The estimates of CO_2 flux presented here do not account for these ice-atmosphere interactions and so may overestimate or underestimate the net annual sink of the water column. Although sea ice has been demonstrated to act as both a source and a sink of CO_2 over the seasonal cycle [Delille *et al.*, 2014], we have applied the maximum flux of CO_2 from Antarctic sea ice to the atmosphere of $1.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ observed by Delille *et al.* [2014] in order to obtain a first-order estimate of the maximum possible reduction in CO_2 sink strength caused by ice cover. Multiplying the percentage cover of fast or pack ice in Ryder Bay during the study period by this value results in a weakening of the net annual sink of atmospheric CO_2 of approximately $0.2 \text{ mol m}^{-2} \text{ yr}^{-1}$.

As well as modulating gas exchange via physical processes, sea ice also affects CO_2 flux through its effect on carbonate chemistry. The precipitation of the hydrated calcium carbonate mineral ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) in sea ice increases CO_2 in brine, and its dissolution on ice melt reduces CO_2 of the seawater [Rysgaard *et al.*, 2011]. Although no carbon measurements in sea ice were made here, ikaite has been observed in Antarctic sea ice [Dieckmann *et al.*, 2008] and has been found to significantly increase brine pCO_2 during precipitation and decrease brine pCO_2 on dissolution [Papadimitriou *et al.*, 2004; Delille *et al.*, 2007; Geilfus *et al.*, 2012]. Rysgaard *et al.* [2012] found the dissolution of ikaite during sea ice melt to correspond to an air-sea CO_2 uptake of $\sim 3.9 \text{ mol Cm}^{-2} \text{ yr}^{-1}$, given a reduction in ice thickness of 0.2 m/week. This process is of a significant magnitude compared to the ocean-atmosphere CO_2 fluxes presented here (Figure 3). It is likely that some of the increase in water pCO_2 observed during winter in Ryder Bay is caused by the release of high CO_2 brine from sea ice and, similarly, that some of the $f\text{CO}_2$ decrease observed in spring is caused by ikaite dissolution. However, the quantification of the impact of ice formation/melt on carbonate chemistry in Ryder Bay is complicated by the fact that an observed change in ice cover is not directly related to ice formation/melt as much of the brash and pack ice may be blown in/out of the bay rather than forming/melting in situ [Meredith *et al.*, 2010]. Biological production by ice algae was also not quantified here and it almost certainly contributes to reducing DIC and $f\text{CO}_2$ in the surface layer, thereby affecting the ocean-atmosphere CO_2 flux in spring.

3.3. Future Implications

The mechanistic understanding of observed variability in the ocean CO_2 uptake that we have developed has significant implications for how we can expect the carbon sink in this region to behave in the future. The west Antarctic Peninsula has been one of the most rapidly warming regions in the world over the last 50 years [Vaughan *et al.*, 2003; Meredith and King, 2005] with an associated rapid decrease in sea ice cover [Stammerjohn *et al.*, 2008; Li *et al.*, 2014]. On a larger scale, and contemporaneous with this, there has been a strengthening of zonal winds south of 45°S , which is projected to increase in future [Le Quéré *et al.*, 2007], and modeling studies suggest that this will increase the upwelling of carbon-rich deep water in the Southern Ocean, slowing the increase in the carbon sink expected with rising atmospheric CO_2 levels [Lenton and Matear, 2007; Lovenduski *et al.*, 2008]. Decadal changes in the properties and production of dense water around Antarctica have also been observed [Meredith *et al.*, 2014; Purkey and Johnson, 2012; Lavergne *et al.*, 2014], emphasizing further the potential sensitivity of the Southern Ocean carbon sink to climatic change. The observations presented here support the theory that reduced winter ice cover and increased surface DIC concentrations in future will reduce the rate at which the region takes up atmospheric CO_2 . Furthermore, a reduction in the spring phytoplankton bloom in Ryder Bay following winters with reduced sea ice

Table A1. Uncertainties Associated With Measured Parameters, Carbonate System Constants, and the Gas Transfer Velocity

Parameter	Uncertainty (1 SD)	Unit	Source
DIC	2.2	$\mu\text{mol kg}^{-1}$	Long-term precision of CRM analyses
TA	1.3	$\mu\text{mol kg}^{-1}$	Long-term precision of CRM analyses
Silicate	2.6	%	Precision quoted by analyst
Phosphate	2.7	%	Precision quoted by analyst
pK1	0.0055	-	Constant from Goyet and Poisson [1989]; uncertainty from Millero [2007]
pK2	0.01	-	Constant from Goyet and Poisson [1989]; uncertainty from Millero [2007]
Atmospheric CO ₂	0.23	ppm	RMSE of the smoothed, interpolated data versus the measured values at Palmer station.
Gas transfer velocity	20	%	Wanninkhof [2014]

cover has been found [Venables *et al.*, 2013], and it has been suggested that a continued reduction in WAP sea ice cover is likely to lead to reduced phytoplankton blooms in the region. A reduction in winter sea ice would therefore not only increase winter outgassing but would also reduce summer uptake of CO₂ by the ocean, further reducing the net annual CO₂ sink.

Appendix A: Uncertainties

Uncertainties were calculated using a Monte Carlo approach to ensure that all nonlinearities in the carbon system calculations were accounted for in error propagation. This is hard to achieve using formal error propagation. The propagation of uncertainties was divided into two steps. First, the uncertainty on water $f\text{CO}_2$ for each measurement of DIC and TA was calculated as follows: 10^5 parameter value sets were created including the parameters DIC, TA, silicate, phosphate, pK1, and pK2. For each parameter, values were determined by random sampling from a distribution based on the measured value (or calculated value in the case of carbonate system constants) as the population mean with a standard deviation based on the measurement or parameter uncertainty (see Table A1). The CO2SYS program was run on each set of parameter values to determine a probability density function (pdf) for $f\text{CO}_2$, twice the standard deviation of which was taken as a measure of that data point's uncertainty. The errors on measured values and carbonate system constants used in the uncertainty analysis (see Table A1) were assumed to be normally distributed. One standard deviation was used to define the characteristics of the distribution of each of the input parameters in the uncertainty analysis. Two standard deviations (approximately 95% confidence) is quoted when referring to calculated uncertainties.

The second step was the calculation of uncertainty on the daily calculated ocean-atmosphere flux. Following interpolation of all input parameters on a daily basis, the uncertainty on each daily calculated flux was calculated as follows: 10^5 parameter value sets were created for water $f\text{CO}_2$, air $f\text{CO}_2$, and k as described above. The uncertainty on water $f\text{CO}_2$ was taken from the previous step, the uncertainty on air $f\text{CO}_2$ is described in Table A1, and the uncertainty on k was taken as 20% [Wanninkhof, 2014] and given a uniform distribution. The ocean-atmosphere flux was calculated for each set of values as above, and twice the standard deviation of the resulting pdf was taken as a measure of the uncertainty of that day's flux. The uncertainty on the cumulative flux was calculated as the square root of the sum of the squares of the uncertainties up to and including each point which assumes randomly distributed rather than systematic uncertainty. Uncertainties were only quantified for the fluxes calculated following Wanninkhof *et al.* [2013] with a linear scaling of ice cover and k . The uncertainty on the fluxes calculated following Loose *et al.* [2014] was not quantified as the uncertainties in this new model are not well understood.

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