SPATIAL VARIABILITY AND MAGNITUDE OF SURFACE pCO_2 AND AIR-SEA CARBON FLUXES IN THE AMUNDSEN SEA POLYNYA, ANTARCTICA

by

LINQUAN MU

(Under the Direction of Patricia L. Yager)

ABSTRACT

The Amundsen Sea Polynya (ASP) is one of the most biologically productive regions in the Southern Ocean characterized by high air-sea CO_2 gradients and carbon fluxes. In this study, partial pressure of CO_2 (pCO_2) in the surface waters of the ASP was determined during the early austral summer. Air-sea carbon flux was estimated using average shipboard wind measurements and compared with other studies in the same and nearby areas. The saturation states of surface pCO_2 and dissolved oxygen (DO) are compared to distinguish the dominant factors (including biological activity, temperature, upwelling and sea ice coverage) determining pCO_2 across different regions of the polynya. Overall, the study indicates that the entire ASP is a large net sink for atmospheric CO_2 with high spatial variability, and provides further insights to the patterns of carbon cycling in a climate-sensitive Antarctic polynya.

INDEX WORDS: Amundsen Sea Polynya; pCO_2; Air-sea exchange; Carbon flux; Dissolved oxygen; Biogeochemical cycle

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B.S., East China Normal University, China, 2011

A Thesis Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2014

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May 2014

ACKNOWLEDGEMENTS

I want to thank everyone who has been involved in my entire master's thesis work, the first and foremost of which has to be my adviser Dr. Patricia Yager. Tish provided me with the valuable opportunity to study oceanography with her, and supported me throughout my master degree. She is the most patient, encouraging, and helpful adviser I could have hoped for. I want to thank her for all the advice and instructions she gave me not only on my thesis work, but more importantly on how to think as a science student. It has been a privilege to have worked with and studied from Tish.

I would like to thank Dr. Wei-Jun Cai for teaching me the essence of chemical oceanography. I would also like to thank Dr. Brian Hopkinson who taught me marine biology and gave me the useful suggestions on my thesis from a biological perspective. Thank you to the entire Marine Sciences faculty, staff, and graduate student for making my graduate school experience complete.

Thanks to the entire ASPIRE team for such an extraordinary project. I want to thank Sharon Stammerjohn for being a co-author of my manuscript and the effort put in on oxygen data processing. I would also like to acknowledge Rob Sherrell, Anna Alderkamp, Kate Lowry, and everybody else on the team. Knowing what everyone does in the group is very beneficial and it broadens my horizon as well. Also thanks to the National Science Foundation (Office of Polar Programs, Antarctic Organisms and

Ecosystems; ANT-0839069) for funding this research, which would not have been possible otherwise. Thanks also to T. Takahashi and C. Sweeney for installation and maintenance of the underway $p\mathrm{CO_2}$ system onboard RVIB *Nathaniel B. Palmer* and initial data processing for NBP 10-05. We also thank Raytheon Polar Services team for onboard logistics, and the captain and crew of the NBP during ASPIRE.

Thanks to the Yager team throughout these years (Colin, Ben, Andrew, Alice, Paul and everyone else). It has been a pleasure to have talked and worked with all of you. A special thanks to Colin, who has always been nice and helpful to me and managed to help me in a variety of circumstances.

Last but not least, I would like to thank my parents for coming to visit me during my graduation ceremony and my friends who bring happiness and encouragement to my life.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

This thesis is written as a manuscript that has been submitted to the journal *Elementa*, and is therefore formatted as a single chapter (Chapter 2). This introduction focuses in more detail on previous literature and broader implication.

Since the beginning of the industrial revolution in late 18th century, great amount of carbon dioxide (CO_2) has been released into the atmosphere owing to human activities. The increase of atmospheric CO_2 as a result of anthropogenic emissions has drawn much attention in the past years, primarily with respect to its role in altering the earth's climate. (*Manabe et al.*, 1980). Despite the fact that CO_2 has a relatively long residence time in the atmosphere, it is increasing at less than half the rate of human emissions (*Schimel et al.*, 2001). This slower growth rate is partially because the ocean sequesters 20 to 35 percent of the anthropogenic CO_2 release, acting as a "sink" (*Sabine et al.*, 2004; *Sarmiento et al.*, 2002). The ocean therefore plays a significant role in mitigating the effects of excess CO_2 emissions on the climate and slowing down the global warming process (*Solomon et al.*, 2007).

The Southern Ocean makes a substantial contribution to the atmospheric carbon sink, as over 40% of the anthropogenic CO_2 in the ocean has been absorbed south of 40 °S (*Sallée et al.*, 2012). Its responses to climate change and the efficiency of the biological pump are predicted to have great influence on the carbon sequestration in the deep sea, and thus the long-term global atmospheric CO_2 level (*Takahashi et al.*, 2009; *Sigman and*

Boyle, 2000; *Sigman et al.,* 2010; *Yager et al.,* 2012). Many studies have focused on the role of the Southern Ocean as a sink for atmospheric CO_2, yet they showed poor agreement in terms of the extent of the sinks due to undersampling in critical regions, such as coastal Antarctic polynyas (*Arrigo et al.*, 2008).

Polynyas are defined as the seasonally ice-free ocean surrounded by ice, where most energy and material transfer between the atmosphere and the polar ocean occur (*Smith and Barber,* 2007), including air-sea CO_2 exchange. Antarctic polynyas are amongst the most biologically productive regions in the Southern Ocean, making them disproportionally important in sequestering atmospheric CO_2 despite their relatively small sizes (*Yager et al.,* 2012). In order to fully understand the Southern Ocean's role in regulating atmospheric CO_2, these highly productive waters need to be accounted for in future oceanic carbon budgets and biogeochemical cycling.

In the past decades, several large-scaled and long-term interdisciplinary projects have made significant contributions to the understanding of Antarctic carbon biogeochemical cycling and CO_2 budget (*Ducklow et al.*, 2006). Some of the studies involved include the Palmer Long-Term Ecological Research (PAL-LTER) Program (*Ross et al.*, 1996), the Joint Global Ocean Flux Study (JGOFS) Southern Ocean Program (*Smith et al.*, 2000), and the ROAVERRS Program in the Ross Sea (*Arrigo et al.*, 1998). One of the ongoing objectives of the Palmer-LTER Program is to estimate the impact of annual advance and retreat of sea ice as a major physical determinant of spatial and temporal variability of primary production within an area west of the west Antarctic Peninsula (WAP). (*Smith et al.,* 1998; *Ross et al.,* 1996). Effort has also been made to explore the major physical and biological variables controlling the air-sea CO_2 flux, such as heating and cooling, ice advance and retreat, photosynthesis and respiration (*Carrillo et al.*, 2004). The Southern Ocean Program of JGOFS emphasized the importance of sea ice variability in controlling primary production and air-sea CO_2 fluxes (*Smith et al.*, 2000). Finally, the Ross Sea is one of the most studied regions with respect to high-latitude carbon cycling in Antarctica. Studies in the Ross Sea have focused on estimating carbon fluxes and biological production, as well as their sensitivity to climatological variables such as sea ice coverage (*Sweeney et al.*, 2000 & 2003; *Arrigo and van Dijken*, 2007). *Arrigo and van Dijken* (2007) showed that over a 6-year period (1997-2003), the interannual variability in air-sea CO_2 flux and primary production was strongly influenced by the rapidly changing sea ice cover, and that the net annual air-sea CO_2 exchange could be reduced by as much as 95% due to heavy sea ice during 2000-2003. *Sweeney* (2003) studied the annual cycle of CO_2 and O_2 in the surface of the Ross Sea by analyzing the balance of carbon and oxygen budgets, and also estimated the impact of ice coverage on air-sea CO_2 exchange. Results corresponded well with the "rectification" hypothesis first raised in *Yager et al.* (1995), which suggested that climate-driven decreases in seasonal ice coverage in areas might promote a greater sink for CO_2.

Carbon fluxes in western Antarctic polynyas are largely driven by climate-sensitive mechanisms. The magnitude of the CO_2 sink in a polynya depends not only on CO_2 biogeochemistry and the season (as in temperate waters), but also on the timing for ice cover and formation of the polynya (*Miller and DiTullio, 2007*). During the past two decades, studies show that western Antarctica has experienced significant surface warming and highly variable changes in summer sea ice cover, where ice shelves and marine glaciers are retreating at rapid rates (*Stammerjohn et al.*, 2008; *Scambos et al.*, 2003; *Cook et al.,* 2005). For instance, the Amundsen Sea polynya (ASP) has experienced ~3-4 fewer days of sea ice cover each year over the course of 25 years, therefore the polynya presently is having ~3 more months of open water than 25 years ago (*Stammerjohn et al.*, 2008). It is not exactly clear how and to what extent the carbon flux will be affected, but there is no doubt climate-sensitivity related to the melting of sea ice will play a dominant role in the scenario.

Within the area greatly affected by rapid climate changes, the Amundsen Sea located off western Antarctica encompasses two polynyas, the Amundsen Sea polynya, ~27,000 km^2, and the Pine Island polynya, ~18,000 km^2 (*Arrigo et al.,* 2012). Particularly, the ASP is the most productive polynya (per unit area) in the Antarctica, with the greatest interannual variability (*Arrigo and van Dijken,* 2003). Until recently the ASP has been one of the least explored areas in Antarctica due to its remote location and harsh weather. In 2010-11, the Amundsen Sea Polynya International Research Expedition (ASPIRE; cruise track shown in Figure 1) enabled the as yet most complete exploration of carbon cycling in this region. The expedition mainly aimed at various climate-sensitive processes driving the productivity and carbon sequestration of the Amundsen Sea polynya, so as to explain why it is so much more productive than other polynyas (*Yager et al.*, 2012). The RVIB *Nathaniel B. Palmer* departed Punta Arenas, Chile on Nov. 26, 2010 and arrived at McMurdo Station, Antarctica on Jan. 16, 2011. It made its way into the Amundsen Sea polynya during December of 2010, measuring variables needed to estimate the carbon budget. This study on the spatial variability and magnitude of air-sea CO_2 flux is based on the samples collected and measurements made during this expedition.

CHAPTER 2[1]

SPATIAL VARIABILITY OF SURFACE $p\mathrm{CO_2}$ AND AIR-SEA CO_2 FLUX IN THE AMUNDSEN SEA POLYNYA, ANTARCTICA

[1] L-Q, Mu, S. E. Stammerjohn, K. Lowry, and P. L. Yager, Submitted to journal *Elementa*.

2.1. ABSTRACT

Partial pressure of CO_2 (pCO_2) in the surface waters of the Amundsen Sea Polynya (ASP) was measured during the early austral summer (NBP10-05, December 14, 2010 to January 3, 2011). Air-sea CO_2 flux was estimated using average shipboard wind measurements for the observation period (8.6 ± 3.5 m/s). The region shows high spatial variability related to physical and biological processes. Surface pCO_2 in the central polynya was as low as 140 μatm, mainly due to the uptake of CO_2 by strong phytoplankton productivity. The central productive region exhibited a very high spatially averaged air-sea influx of -44.4 ± 15.5 mmol m^{-2} d^{-1}. In contrast, we observed pCO_2 values of 480 μatm in the southeast ASP near the Dotson Ice Shelf (with an efflux of 11.7 ± 7.3 mol m^{-2} d^{-1}) due to upwelling of deep water. Accounting for this spatial variability and assuming a 132-day annual ice-free period, the net carbon uptake by the ASP is 3.2 ± 2.6 mol m^{-2} a^{-1}, about two times higher than the annual per unit area CO_2 flux in the Ross Sea (-1.5 ± 1.5 mol m^{-2} a^{-1}). Further, the saturation states of surface pCO_2 and dissolved oxygen (DO) are compared to distinguish the dominant factors (including biological activity, temperature, upwelling and sea ice coverage) determining pCO_2 across different regions of the polynya. Most of these controls on the gas concentration and flux are climate sensitive. Overall, the analysis indicates that the ASP is a large net sink for atmospheric CO_2. We speculate about whether this sink will increase with climate-driven changes in the ASP region.

2.2. INTRODUCTION

High-latitude oceans are capable of taking up massive amounts of atmospheric CO_2 due to high biological productivity and low temperature. The response of the Southern Ocean to climate change and the efficiency of the biological pump influence the degree to which atmospheric carbon is sequestered to the deep ocean and thus the global atmospheric CO_2 level (*Takahashi et al.,* 2009; *Sigman and Boyle,* 2000). The CO_2 sink in the Southern Ocean is affected by rates of upwelling and high wind speeds (*McNeil et al.,* 2007; *Le Queue et al.,* 2007; *Lovenduski et al.*, 2008), high biological uptake (*Arrigo et al.,* 1999; *de Baar et al.,* 1995), sea ice coverage (*Ishii et al.,* 2002), and other physical and biological transformations. Yet the specific function of the Southern Ocean in atmospheric CO_2 drawdown is still uncertain due to spatial and temporal variability in biological and solubility pumps and undersampling in critical regions (*Carrillo et al.,* 2004).

Since vast regions of the Southern Ocean are covered with sea ice most of the year, polynyas, defined as seasonally ice-free ocean surrounded by ice, are characterized by high air-sea energy and material transfers, including air-sea CO_2 exchange. As these seasonal polynyas are open to their greatest extent during the summer and early fall, winter sea ice may rectify the carbon drawdown by covering most of the sea surface. (*Yager et al.,* 1995). The seasonal melting of sea ice in an otherwise ice-covered sea allows high rates of air-sea CO_2 exchange, thus making Antarctic polynyas important for biogeochemical cycling of carbon (*Miller and DiTullio,* 2007).

The Amundsen Sea Polynya (ASP; Figure 1) is one of the least explored areas in Antarctica due to its remote location and harsh weather. Among all Antarctic polynyas, the ASP is the fourth largest (up to 38,000 km^2 on average; with maximum area ~80,000 km^2) and estimated to be the most productive per unit area on average, but with high interannual variability (*Arrigo and van Dijken,* 2003). Average primary production in summer typically exceeds 1 g C m^{-2} d^{-1}, much higher than offshore waters of the open Southern Ocean (0.2 - 0.4 g C m^{-2} d^{-1}; *Arrigo et al.,* 2008). In general, interannual variability in air-sea CO_2 flux and primary production are strongly influenced by rapidly changing sea ice coverage, as observed in both the Ross Sea (*Sweeney et al.,* 2000; 2003*; Arrigo and van Dijken,* 2007) and the west Antarctic Peninsula (*Ducklow et al.,* 2007). However, few in-situ studies have been conducted in the ASP because of its inaccessibility. From December 2010 to January 2011, a multidisciplinary team of oceanographers examined the controls and fate of the massive phytoplankton bloom of the ASP (Figure 1; *Yager et al.* 2012). Here we estimate the magnitude and variability of surface pCO_2 and of air-sea CO_2 flux as well as its sensitivity to physical and biological drivers in the ASP region, and compare these features to nearby coastal Antarctic regions.

2.3. STUDY SITE AND METHODS

Site Description

The Amundsen Sea is located in the South Pacific sector of western Antarctica, off Marie Byrd Land, and is characterized by a relatively narrow continental shelf (*Nitsche et al. 2007*), a large amount of perennial sea ice, and a number of coastal polynyas located nearby (*Arrigo and van Dijken,* 2003). During the austral summer 2010-2011, the multidisciplinary Amundsen Sea Polynya International Research Expedition (ASPIRE; Figure 1) had the opportunity to explore this region extensively onboard the

RVIB *Nathaniel B. Palmer* (NBP) (*Yager et al.,* 2012). Ice concentration values were extracted from daily unprojected AMSR-E 12.5 km satellite images and also measured shipboard using standard techniques (*Worby et al.*, 1999).At the start of our expedition in mid-December 2010, the open water region (<50% sea ice according to satellite) was approximately 41,000 km^2 and the stations we then sampled had been open for an average of 49 $\pm$24 days. Total sea ice cover at the end of our expedition in early January 2011 was ~63,000 km^2, and the maximum open water area observed that summer was ~78,000 km^2 in mid January2011 (after ASPIRE departed).

Here we report underway data collected from the NBP in the open waters of the polynya (December 14, 2010 - January 3, 2011; 72.6 - 74.3 °S, 110 - 119 °W; Ice cover < 70% according to shipboard observations). We used a higher open water criteria for underway open water observations to account for the change in scale between satellite and shipboard observations of ice.

Open water duration (or open water days) was computed from satellite observations for the number of days that each station had less than 50% ice cover, including the day that we sampled it. The uncertainty was calculated as the standard deviation of the number of open water days when calculated with a range of sea ice concentration thresholds (10 - 90%).

Measurement of parameters at sea surface

Surface seawater was sampled from the NBP's main uncontaminated seawater system. Sea surface temperature (SST) and salinity (SSS) were recorded every 10 seconds using an onboard SeaBird CTD (SBE-45 Micro TSG, SeaBird Inc., Bellevue, WA). The accuracies of temperature and salinity were 0.002 ℃ and 0.005, respectively.

The NBP carries a pCO_2 measurement system from Lamont-Doherty Earth Observatory (LDEO). xCO_2 was continuously measured using a showerhead equilibrator and a non-dispersive infrared CO_2 gas analyzer, and recorded by the Research Vessel Data Acquisition System (RVDAS). Further details regarding the CO_2 measurement system can be found on LDEO website (http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/text/NBP10_5_data_report.pdf)

The partial pressure of CO_2 in surface water at the temperature of equilibration ($pCO_{2(eq)}$, in μatm) was converted from measured xCO_2 (*Jiang et al.*, 2008):

$$pCO_{2(eq)} = xCO_{2(water)} \times (P_{eq} - P_v) \tag{1}$$

$$\ln P_v = 24.4543 - 6745.09/T_{eq} - 4.8489 \times \ln(T_{eq}/100) - 0.000544 \times S \tag{2}$$

where $xCO_{2(water)}$ is the measured mole concentration of CO_2 (ppm), P_{eq} is the barometric pressure at equilibration (atm), and P_v is the water vapor pressure at 100% humidity calculated using the temperature at equilibration T_{eq} (K) and salinity S (*Weiss and Price*, 1980).

Given the temperature difference between the equilibrator and the sea surface, pCO_2 in the equilibrator $pCO_{2(eq)}$ was corrected to surface water $pCO_{2(w)}$ at in-situ temperature (*Takahashi et al.*, 1993):

$$pCO_{2(water)} = pCO_{2(eq)} \times \exp(0.0423 \times (T_{in\text{-}situ} - T_{eq})) \tag{3}$$

Similarly, partial pressure of CO_2 in the atmosphere at equilibration ($pCO_{2\,(atm)}$, in μatm) was calculated by equations (1) and (2) with $xCO_{2(atm)}$, sea surface temperature $T_{in\text{-}situ}$, and assuming the barometric pressure at sea surface is the same as P_{eq}. In this study $xCO_{2(atm)}$ is assumed constant at the 388 ppm, which is an interpolation between the

American Samoa and the South Pole Station observations from the NOAA/ESRL network (*Thoning et al.*, 2013) during the time of the ASPIRE expedition.

Underway dissolved oxygen (DO) and chlorophyll *a* fluorescence (chl *a*) at surface were measured with an Oxygen Optode (AADI Inc., Attleboro, MA) and an ECO-AFL/FL Fluorometer (Wet Labs, Philomath, OR), respectively. The optode DO measurements were calibrated by titrated samples using Winkler method (n = 100).

Surface $p\mathrm{CO_2}$ and DO saturation states were compared in accordance with the method described in *Carrillo et al.* (2004) to determine the relative importance of changes in temperature and biological processes on the $p\mathrm{CO_2}$:

$$p\mathrm{CO_2}\_sat = (p\mathrm{CO_{2(water)}} / p\mathrm{CO_{2(atm)}}) \times 100\%, \tag{4}$$

$$\mathrm{DO}\_sat = (\mathrm{DO} / \mathrm{DO^*}) \times 100\%, \tag{5}$$

where DO* is the solubility of O_2 for standard air pressure, and was corrected to in-situ temperature and salinity using the equations in *Garcia and Gordon* (1992). Because there is evidence that waters upwelling near the ice shelf are moving north and shoaling as they move into the center of the productive polynya (*Yager et al.*, 2012), we also applied a simple two-endmember mixing model to investigate some of the $p\mathrm{CO_2}$ and DO saturation states we observed.

Air-sea CO_2 flux

The sea surface $p\mathrm{CO_2}$ gradient (relative to the atmosphere), temperature, salinity, wind speed, and sea level pressure were used to calculate the daily averaged air-sea CO_2 flux (*Wanninkhof*, 1992).

Underway wind speed u_{10} was measured by an anemometer (RM Young 5106) and corrected for ship motion during the cruise. Temporally averaged shipboard wind speed during the sampling period in the polynya was used to derive the CO_2 transfer velocity k (*Wanninkhof*, 1992):

$$k = 0.39 \times u_{10}^2 \times (Sc/660)^{-1/2} \quad (6)$$

where Sc is the Schmidt number, a function of sea surface temperature (*Wanninkhof*, 1992).

Thus the average air-sea CO_2 flux (mmol m^{-2} d^{-1}) is expressed as:

$$F = k \times K_0 \times [pCO_{2(water)} - pCO_{2(atm)}] \quad (7)$$

where K_0 is the solubility of CO_2 in the seawater which is a function of temperature and salinity (*Weiss*, 1974).

Air-sea CO_2 flux was spatially interpolated over the polynya region using the underway data. The interpolation was made in Ocean Data View 4 (*Schlitzer*, 2011; http://odv.awi.de).

2.4. RESULTS

Large spatial variability of surface water pCO_2 was observed in the ASP (Figure 2a). The central polynya showed very low pCO_2 ranging from 130 to 200 μatm, indicating a strong undersaturation of pCO_2. In contrast, the area off the Dotson Ice Shelf showed supersaturated pCO_2 with an average of 430 μatm.

During the cruise, surface chlorophyll *a* concentration (chl *a*) was found to be high through much of the ASP (Figure 2b), verified by discrete measurements exceeding 30 mg m^{-3}. Upon entering the polynya in mid-December, we observed low values (< 1 mg m^{-3}) in the sea ice zone bordering the polynya to the west and east. Intermediate values were observed in mid-December in the western polynya. Highest values (> 20 mg

m^{-3}) were observed in the central polynya, north of 73 °40'S, at stations sampled after December 20. High phytoplankton biomass was associated with low (< 10 μmol L^{-1}) nitrate concentrations that showed significant nitrate depletion from pre-season surface concentrations of ~ 31 μmol L^{-1} (*Yager et al.*, 2012).

The distribution of surface DO shows a pattern similar to chl *a* (Figure 2c). DO at the surface ranges from 230 μmol L^{-1} to 490 μmol L^{-1} (or 65% - 130% saturation). DO supersaturation was largely observed in the central polynya typically exceeding 125%, corresponding well with the maximum chl *a*. DO undersaturation (60% - 80%) was found along the sea ice zone to the east, and the region near the ice shelf to the south. The western polynya was close to full DO saturation (90% - 110%).

A logarithmic regression between pCO_2 and chl *a* yielded a strong relationship ($r^2 = 0.89$, n = 6500, p<0.01; Figure 3), while a strong linear association between surface pCO_2 and DO saturation states was also observed during the entire cruise ($r^2 = 0.95$, n = 6500, p<0.01; Figure 4a). Areas of surface ocean pCO_2 supersaturation and DO undersaturation were found in the low productivity waters near the ice shelf, while areas of pCO_2 undersaturation and DO supersaturation were encountered in highly productive central polynya. pCO_2_*sat* typically decreased with increasing distance from both the ice shelf and the sea ice margin.

The underway data extended into three of four quadrants on a plot of DO_*sat* versus pCO_2_*sat*, (Figure 4a). A spatial distribution of the quadrants (Figure4b) indicates that most observations in Quadrant I (supersaturated DO and undersaturated pCO_2) were located in the central polynya, where the maximum DO_*sat* (133%; 484 μmol L^{-1}) and minimum pCO_2_*sat* (34%; 133 μatm) were observed. Observations from Quadrant III (undersaturated DO and supersaturated pCO_2) were mainly located to the southeast of the polynya near the Dotson Ice Shelf, where the highest supersaturation of pCO_2 (126%; 489 μatm) and the greatest undersaturation of DO (55%; 203 μmol L^{-1}) were recorded. Observations in Quadrant IV (both pCO_2 and DO slightly undersaturated), were found along the western inbound leg and other areas where sea ice was present (south central and eastern areas of the polynya). No observations occurred in Quadrant II with both supersaturated pCO_2 and DO.

As shown in Figure 4, the strong linear relationship between pCO_2_*sat* and DO_*sat* is offset from the origin (full saturation for both gases). We tested to see if a mixing model could account for this offset by questioning if the observations in Quadrant IV (mostly between 114 °W - 116 °W and 73.6 °S - 73.8 °S) could be a mixture of surface waters from Quadrants I and III, or a mixture of surface waters from Quadrant I and deep waters that may be upwelled near the ice shelf. Because they are conserved mass properties (and pCO_2 is not), we mixed discrete values of pH and total alkalinity (ALK) from surface and deep waters in the region (*Chierici et al.*, unpublished, *Yager et al.*, unpublished) and then calculated the resulting pCO_2 saturation states along the mixing line. The water mass properties in front of the Dotson Ice Shelf indicated upwelling of deeper water (*Randall-Goodwin et al.*, 2012), thus the pH and ALK of water from~400m depth (7.65 and 2350 μmol/kg, respectively) was used as the deep endmember, while pH and ALK from the central polynya (7.8 and 2320 μmol/kg, respectively) were used as the surface endmember. DO saturation state for these same waters was estimated from CTD profiles on the R/V *Nathaniel B. Palmer*, equipped with duel oxygen sensors. The mixing line is depicted as a blue line in Figure 4b. Both the intercept and slope of the mixing line is strongly correlated with the regression line (in red), suggesting that mixing can explain the offset from the origin of the surface pCO_2 and DO in the ASP.

An alternative hypothesis for the mixing line is related to photosynthetic carbon drawdown from winter water (i.e. the deeper endmember). A perfect pCO_2 and DO relationship as a result of pure photosynthesis and respiration of primary producers is shown in Figure 4a (line in green). The slope of this line is assumed at -1.1, negative value of the typical photosynthetic quotient for phytoplankton (*Laws*, 1991). Comparisons with the slope of mixing line at -0.54 and of the regressional line at -0.60 suggest that CO_2 drawdown from winter water is not sufficient to explain the mixing line or the regressional line.

Wind speed determines the gas transfer velocity (k) and therefore contributes to air-sea CO_2 flux in the ASP. High and variable wind speeds were observed across the ASP during ASPIRE (Figure 5) with an underway temporally averaged wind speed of 8.6 $\pm$3.5 m/s, a maximum value of 18 m/s, and a minimum near 0 m/s. In the absence of a good meteorological buoy network, we assumed the underway wind speeds measured shipboard were representative of the entire ASP region (given its relatively small size), so temporally-averaged shipboard measured wind speeds were used in determining air-sea CO_2 flux. NCEP/NCAR reanalysis wind data, which are interpolated over a much larger area of the Amundsen Sea, report the monthly average wind speed to be 5.0 $\pm$2.6 m/s (http://www.cpc.ncep.noaa.gov/products/wesley /reanalysis.html), considerably lower than our observations. This difference is not surprising given that there are few in situ meteorological data available as input to the NCEP/NCAR reanalysis data. We also compared our shipboard wind measurement with a few other recent expeditions to the polynya (i.e. Dynalife 2009, *Tortell et. al* (2012); Araon 2010-2011 and 2012, S.-H. Lee personal communication) during austral summer and found that they typically agreed with each other, with the difference between measurements of average wind speed typically lower than 7%. These favorable comparisons give us confidence to use our average wind speed observations for CO_2 flux calculations during the entire ASPIRE sampling effort.

The spatial variability of the CO_2 flux was dominated by the spatial variability in pCO_2 (Figure 6). The spatially averaged air-sea CO_2 uptake in the central polynya was estimated to be -44.4 $\pm$15.5 mmol m^{-2} d^{-1}. If we assume steady uptake throughout the summer and a 132 $\pm$18-day open water period (*Arrigo et al.,* 2012), and 21 days for the bloom to create the observed pCO_2 gradient (111 days for gas exchange), we estimate the total uptake by the highly productive central polynya (about 12,000 km^2) to be: -0.7 $\pm$ 0.2 Tg C per year. The spatially averaged efflux in the southeast near the ice shelf was 11.7 $\pm$7.3 mmol m^{-2} d^{-1}. Using a similar time period without the bloom buildup (132 days) this upwelling near the ice shelf (about 4000 km^2) would contribute to an outgassing of 0.07 $\pm$0.05 Tg C per year, counteracting about 10% of the biologically-driven drawdown in the center polynya. Spatially averaging over the entire open water region for December and early January, we calculate -24.0 $\pm$19.8 mmol m^{-2} d^{-1}, or -3.2 $\pm$ 2.6 mol m^{-2} a^{-1} if we assume a 132 days of open water.

2.5. DISCUSSIONS

Much of our current knowledge about carbon biogeochemical cycling in Antarctic polynyas comes from field studies at a few sites, most extensively in the Ross Sea and along the western Antarctic Peninsula. Extensive phytoplankton blooms occur on the Ross Sea continental shelf during spring (*Sweeney*,2003) corresponding with surface pCO_2 as low as ~180 μatm (*Sweeney et al.,* 2000). Further, the annual air-sea CO_2 flux in the Ross Sea is estimated to be -1.5 $\pm$ 1.5 mol m^{-2} a^{-1},based on studies conducted during 1996-1997 (*Sweeney,* 2003). The surface pCO_2 and air-sea CO_2 flux in the ASP, where the lowest pCO_2 observed was at ~130 μatm and a spatially averaged CO_2 flux of -3.2 $\pm$ 2.6 mol m^{-2} a^{-1}, compare reasonably well with those observed in the Ross Sea. The ASP is smaller in area, but its per area gas flux can be twice as high.

Tortell et. al (2012) also reported findings on pCO_2 and air-sea CO_2 flux in the ASP. Their research was conducted during summertime of 2009 (Jan.11 - Feb.16), a month later in the summer than our study. They reported surface pCO_2 as low as ~100 μatm and the air-sea CO_2 flux for ice-free polynya waters to be ~ -41.9 mmol CO_2 m^{-2} d^{-1}. These observations compare well with our estimation of air-sea CO_2 flux for the highly productive central ASP (-44.4 mmol CO_2 m^{-2} d^{-1}), supporting the idea that the ASP continues to grow and becomes a larger CO_2 sink throughout the summer.

Air-sea CO_2 exchange can be affected by various physical and biological processes. In polar oceans, sea surface pCO_2 and air-sea CO_2 flux are sensitive to seasonal changes in sea ice extent, sea surface and air temperature, ocean circulation, freshwater inputs, and finally the seasonal succession of marine biological production and consumption (*Bates et al.,* 2011). Our study shows that the extreme low level of surface pCO_2 in the central ASP is strongly correlated to the intense phytoplankton bloom during the austral summer, while high pCO_2 observed near the Dotson Ice Shelf south of the polynya is consistent with physical observations of deep water upwelling. Surface waters slightly undersaturated in both pCO_2 and DO are likely a result of vertical mixing between surface and subsurface waters.

Carrillo et al. (2004) investigated the surface water west of the Antarctica Peninsular (WAP) and found that DO and pCO_2 varied significantly from atmospheric equilibrium suggesting a combination of physical and biological controls on DO and pCO_2 distributions (*Carrillo et al.*, 2004). Unlike our study, all four Quadrants were detected in various areas of their study region (on a Quadrant map similar to Figure 4). Their study was also later (Jan-Feb) and mostly ice-free by the time of sampling. Moreover, their study also found that observations in Quadrant I (with DO supersaturation and pCO_2 undersaturation) were mainly distributed near the coast or to the south where surface stratification was enhanced by recent glacial run-off or sea ice melt, respectively. In further contrast, their study did not include any observations in the vicinity of ice shelves (which were otherwise located south of their study region). The potential upwelling signal they observed (Quadrant III) was associated with shelf break upwelling, as opposed to the coastal upwelling we observed in the vicinity of the Dotson Ice Shelf. Temperature effects on oxygen and CO_2 saturation in surface water of the ASP were less obvious than in the WAP, presumably because the mixing between water masses was significant and outcompeted the effects by heating and cooling.

Overall, the variation of pCO_2 in the ASP is largely dominated by the intense phytoplankton bloom in the polynya. Observations in Quadrant I are mainly located in the central polynya where intense phytoplankton blooms were occurring, causing the biological drawdown of CO_2 (undersaturated pCO_2) and production of oxygen (supersaturated DO; Figure 4). The strong correlation with chl *a* confirms this relationship.

We can speculate why pCO_2 corresponds with chl *a* logarithmically rather than linearly, and why some places with low chl *a* also have low pCO_2 at surface. First, the variable range of pCO_2 at low chl *a* corresponds to either Quadrant III (high pCO_2, upwelling of deep water) or Quadrant IV (low pCO_2 due to low SST associated with actively melting sea ice), areas where low chl *a* was also observed. Second, under peak bloom conditions with very low pCO_2 and high chl *a*, chlorophyll fluorescence per unit mass of POC (particulate organic carbon) in phytoplankton was found to increase (*Sherrell et al.*, unpublished), potentially contributing to less pCO_2 drawdown during conditions of very high chl *a* and probable light limitation due to self-shading.

Observations in Quadrant III with slightly supersaturated pCO_2 and undersaturated DO are largely distributed south of the polynya near the ice shelf. Since there are no significant sources of allochthonous organic carbon in coastal Antarctica, these surface waters are probably not actively net-heterotrophic, but rather likely reflect their recent condition as deep water that has just recently come to the surface. Low levels of heterotrophic respiration in this region can be expected as a direct result of low chl *a*, and thus low in situ production. Wintertime respiration driving oversaturation under the ice (e.g. Yager et al. 1995) is an unlikely explanation since this southern region of the ASP is often open during winter and generally opens first (in early November, according to AMSR-E observations) relative to the central polynya, making it impossible to have accumulated the CO_2at the surface, under the winter sea ice. We hypothesize that the upwelled deep waters contribute to the high pCO_2 in this region, as suggested in *Randall-Goodwin et al.* (2012) and *Yager et al.* (2012).

In Quadrant IV, where both pCO_2 and DO were undersaturated, sea ice was present (or had recently melted) and surface waters were still near freezing, indicating temperature was less of a dominant control than the mixing with the newly melted sea ice. However, mixing with deeper waters may also have played a role, especially near 113.3 °W - 113.9 °W and 73.6 °S - 73.8 °S, where a large iceberg (300 m deep) was observed. Water was likely stirred by the wind-driven drift of the iceberg, enhancing vertical mixing between surface and deep water. As a result, surface pCO_2_*sat* increased (but was still undersaturated) and surface DO_*sat* decreased (becoming undersaturated) since deeper water has higher pCO_2 and lower DO.

Without pCO_2 and wind speed data from the later summer and earlier fall, we are not able to accurately calculate the annual carbon flux in the ASP. Nevertheless, it seems important to try to estimate the potential large-scale impact of the ASP on atmospheric carbon uptake. To make a crude annual flux estimate, we can propose a series of hypotheses: if we assume that the region south of the polynya by the ice shelf which we suspected to be an upwelling zone does not increase in size and that the productive summertime area increases to its average maximum extent (38,000 km^2) over 132 days (*Arrigo and Van Dijken,* 2003; *Arrigo et al.,* 2012), the annual atmospheric carbon sink into the ASP would be -2.7 $\pm$0.9 TgC. The continued bloom and reduced pCO_2 in the central polynya in January and February supported by *Tortell et al.* (2012). Compared with the Southern Ocean south of 62 °S (an area of 1.5 $\times 10^7$ km^2 and annual flux of -40 Tg C; *Takahashi et al.,* 2009), the ASP occupies only 0.25% in area, but it may account for up to 6.5% in annual carbon flux of the Southern Ocean. Therefore the ASP can be disproportionally important relative to its size for the air-sea CO_2 flux and oceanic cycling of carbon.

The high pCO_2 variability in the surface water associated with high interannual variability of productivity in the ASP may contribute to strong climate sensitivity (*Yager et al.*, 2012). Based on satellite data (*Arrigo et al.*, 2012), the temporal variation of primary production in the ASP is closely related to the timing and duration of open water in the polynya, which in turn affects the timing and duration of the phytoplankton bloom. The satellite sea ice record indicates a strong trend toward earlier sea ice retreat in the ASP region over 1979 to 2013 (Stammerjohn, unpublished data). We surmise that an earlier opening of the ASP would enhance the magnitude of the phytoplankton bloom. If this trend continues, the ASP will likely become more productive and thus a greater carbon sink in the near future if light and iron availability for phytoplankton growth also continue to increase. The sensitivity of the phytoplankton bloom to stratification created by seasonal sea ice, however, suggests the carbon sink depends on the continued longevity of the seasonal sea ice cover of the ASP.

2.6. CONCLUSIONS

Based on the spatial differences in surface pCO_2 and thus the air-sea CO_2 flux, the ASP can be generally divided into two regimes. One is in the central polynya north of 73.7 °S characterized as a large carbon sink. Sea surface pCO_2 typically reaches 150 μatm, and chl *a* concentration exceeds 20 mg m^{-3}. Close correlation between pCO_2 and both chl *a* (r^2 = 0.89, n = 6500) and dissolved oxygen concentration (r^2 = 0.95, n = 6500) suggests that the extreme sink for atmospheric CO_2 in the central polynya is mainly dominated by the massive biological uptake for carbon as a result of phytoplankton bloom. The other regime is a relatively small region along the ice shelf to the south of the polynya, characterized by high pCO_2 and low chl *a*. The primary production here is low, but the undersaturation of DO supports the idea that deep water upwelling near the ice shelf brings up relatively high pCO_2 water to outgas at the surface. We note the highly climate-sensitive nature of the processes driving this large carbon sink.

CHAPTER 3

CONCLUSIONS

Being the most biologically productive polynya (per unit area) in Antarctica with the highest interannual variability (*Arrigo and van Dijken*, 2003), the Amundsen Sea Polynya is a window to understand the biogeochemical cycling of typical coastal Antarctic polynyas. This site needs to be thoroughly studied in terms of climate-driven spatial and temporal variability of pCO_2 as well as air-sea carbon flux. This study highlights two main sections of the ASP that have different pCO_2 gradient and thus different air-sea CO_2 fluxes, dominated by massive phytoplankton uptake and respiration-controlled upwelled deep water, respectively. Higher air-sea pCO_2 gradient and larger area of the central polynya makes the entire ASP a great carbon sink.

Recent studies (*Le Quéré et al.*, 2007; *Lovenduski et al.*, 2008) show that CO_2 sink in the Southern Ocean has weakened over past decades caused by changes in patterns of wind as well as wind-driven ocean circulation, and this trend is predicted to continue in the future. Climate changes in the Antarctic are playing an increasingly significant role in regulating the size of carbon sink in the Southern Ocean. It is still unknown how and to what extent carbon flux in a western Antarctic polynya (like the ASP) can be affected by annually decreasing sea ice cover. On one hand, since polynyas are free of ice for a longer period of time, under the assumption that the flux per unit area remains constant, the total carbon uptake will be increased, making the polynyas larger carbon sinks. On the other hand, however, excess exposure of polynya may also induce excess wind-driven vertical mixing and thus a less stratified surface layer, through which the biological CO_2 uptake per unit area is reduced. In this case, the annual carbon sink may not be increased. Therefore it is uncertain how the melting sea ice affects the extent of CO_2 flux. But there is no doubt western Antarctic polynyas are highly climate-sensitive and will remain to be the foci of future carbon cycling and flux studies in the Antarctic.

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APPENDICES

FIGURES AND CAPTIONS

Figure 1

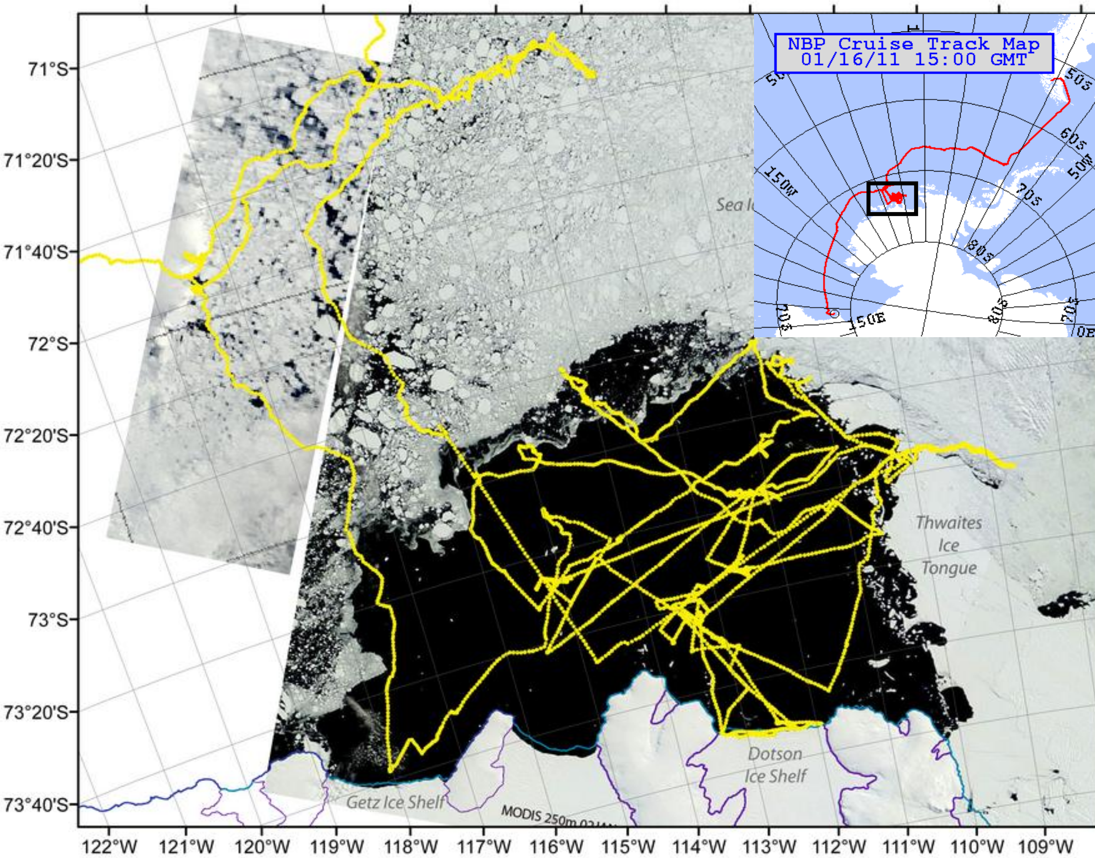
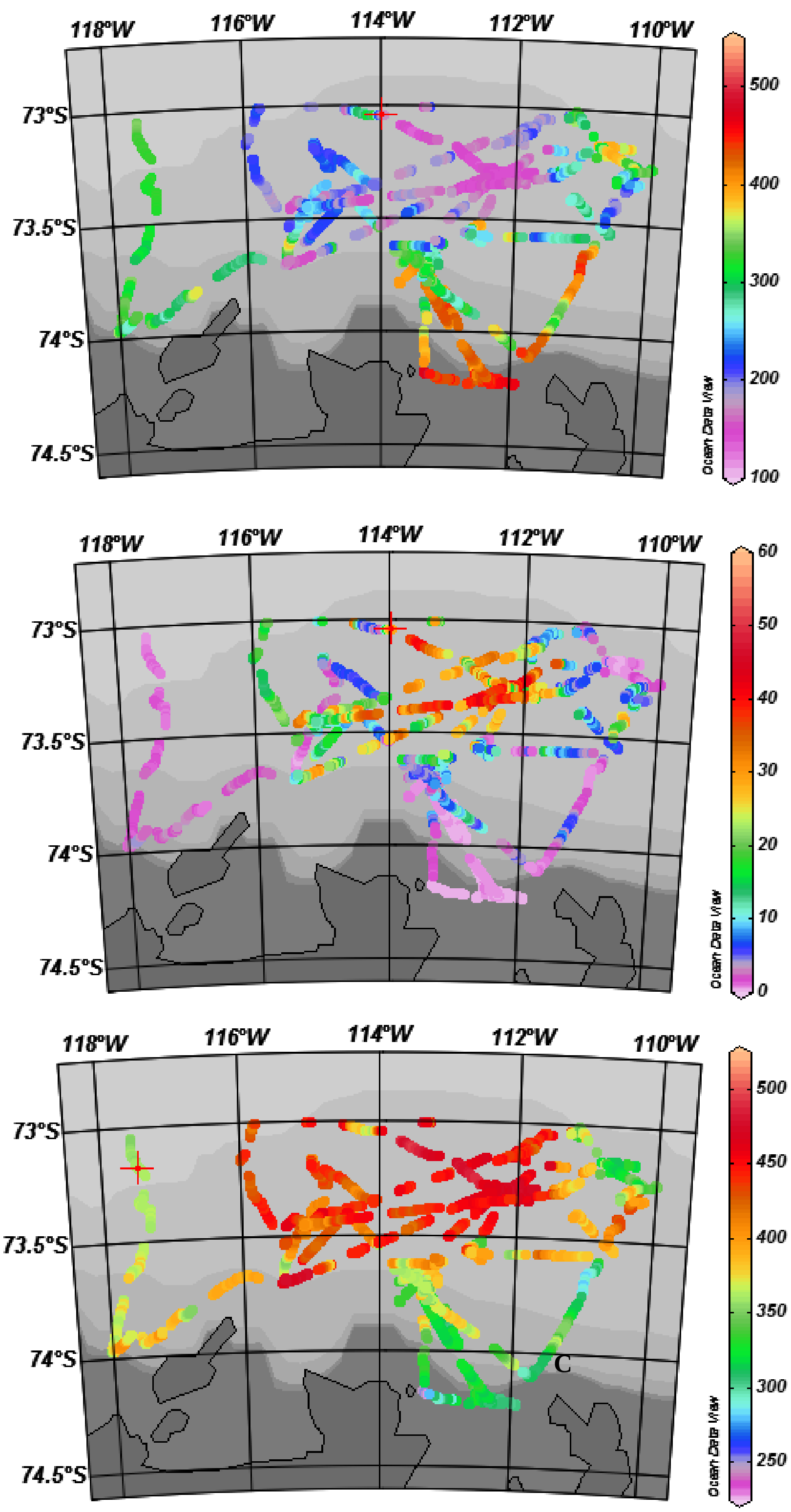


Fig.1 Cruise track within the Amundsen Sea Polynya (white dashed line) north of Dotson Ice Shelf onboard NBP10-05 (December 14, 2010 - January 3, 2011) plotted on a Moderate Resolution Imaging Spectroradiometer (MODIS) sea ice reflectance satellite image from January 2, 2011. Inset shows the area of interest on the full NBP 10-05 cruise track between Punta Arenas, Chile and McMurdo Station.

Figure 2


118°W
116°W
114°W
112°W
110°W
73°S
73.5°S
74°S
74.5°S
500
400
300
200
100
Ocean Data View
118°W
116°W
114°W
112°W
110°W
73°S
73.5°S
74°S
74.5°S
60
50
40
30
20
10
0
Ocean Data View
118°W
116°W
114°W
112°W
110°W
73°S
73.5°S
74°S
74.5°S
c
500
450
400
350
300
250
Ocean Data View

a)

b)

c)

Fig.2 Underway measurements of (a) pCO$_2$ (μatm), (b) chlorophyll a (μg L^{-1}), and (c) dissolved oxygen concentration (μmol L^{-1}) at sea surface of the polynya. Warm colors (red) indicate high values; cool colors (purple) indicate low values.

Figure 3

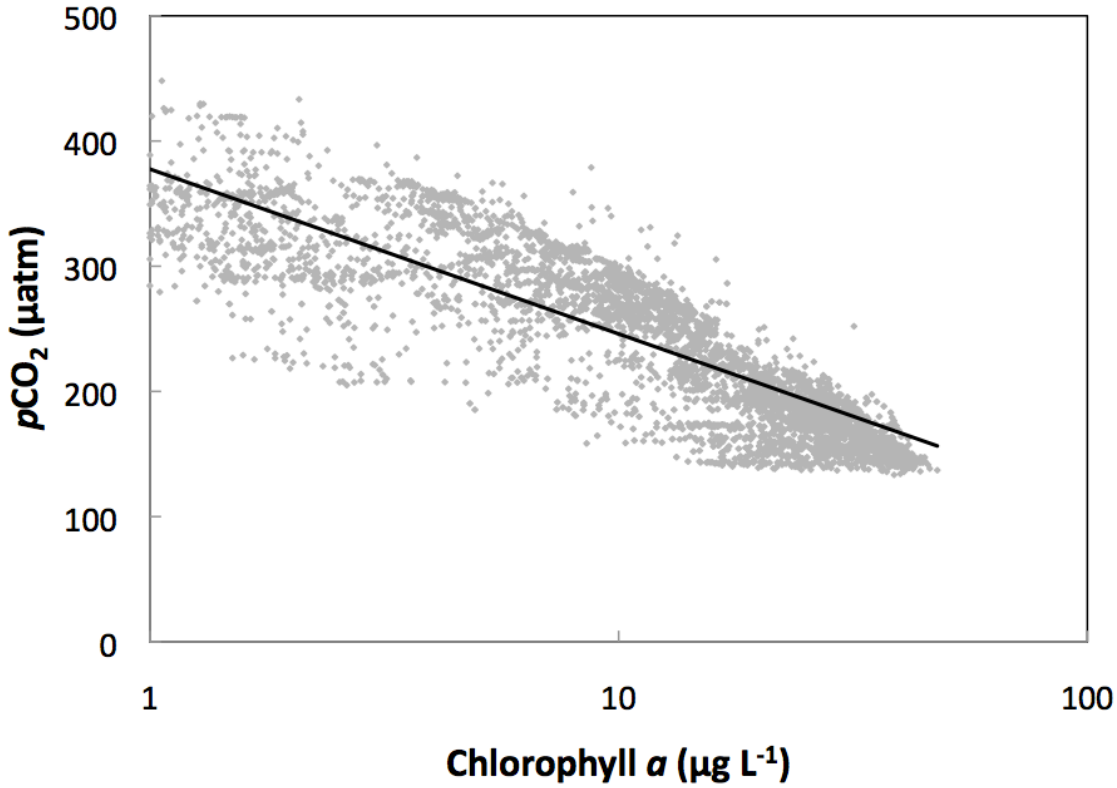


Fig.3 Relationship of pCO_2 with chlorophyll *a* (log scale). R^2 = 0.89; n = 6500.

Figure 4a

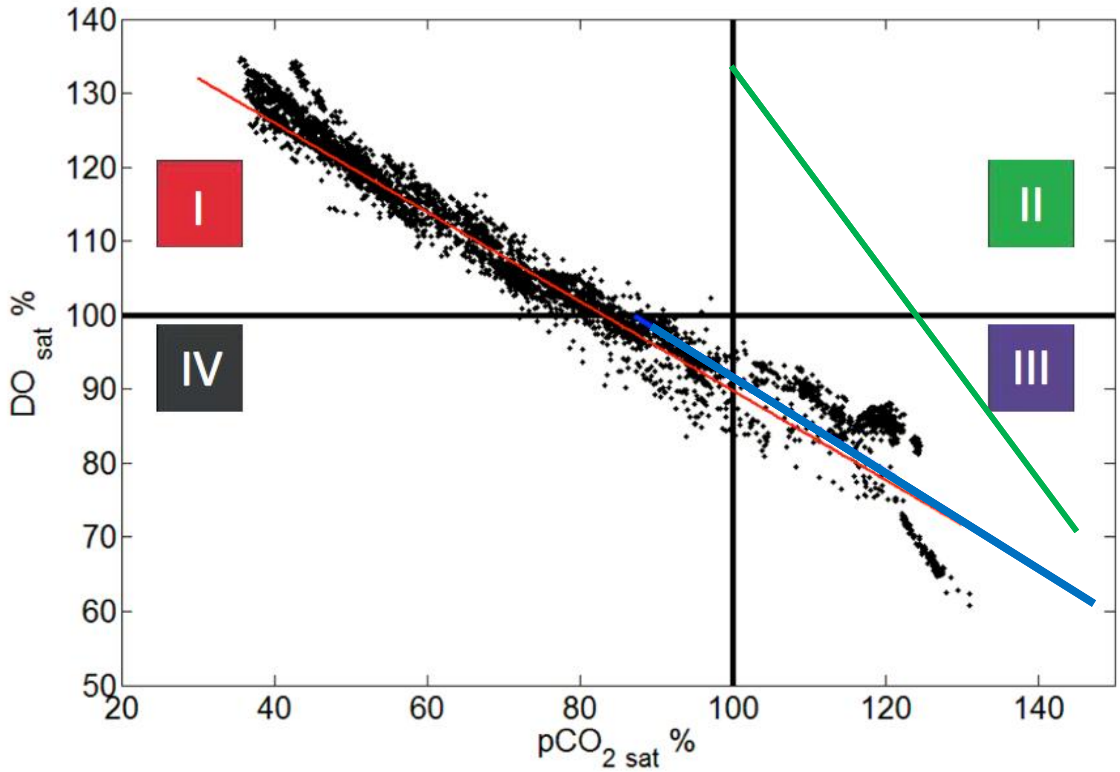


Fig.4a pCO_2 saturation (%) against DO saturation (%). Crossbar represents 100% saturation levels of pCO_2 and DO. Based on these levels, the figure is divided into 4 quadrants. Quadrant I (upper left; excess DO, depleted pCO_2) reflects photosynthesis; Quadrant III (lower right; depleted DO and excess pCO_2) reflects respiration; Quadrant IV (lower left, undersaturated DO and pCO_2) typically indicates cooling. The red line is a linear regression, and the blue line is the mixing line of deep and surface water masses, suggesting that mixing, rather than cooling, explains the surface waters in Quadrant IV. Slope of the regressional line s = -0.603; R^2 = 0.96; n = 6500. The green line is the ideal line depicting photosynthesis and respiration of autotrophs, the slope of which is 1.1.

Figure 4b

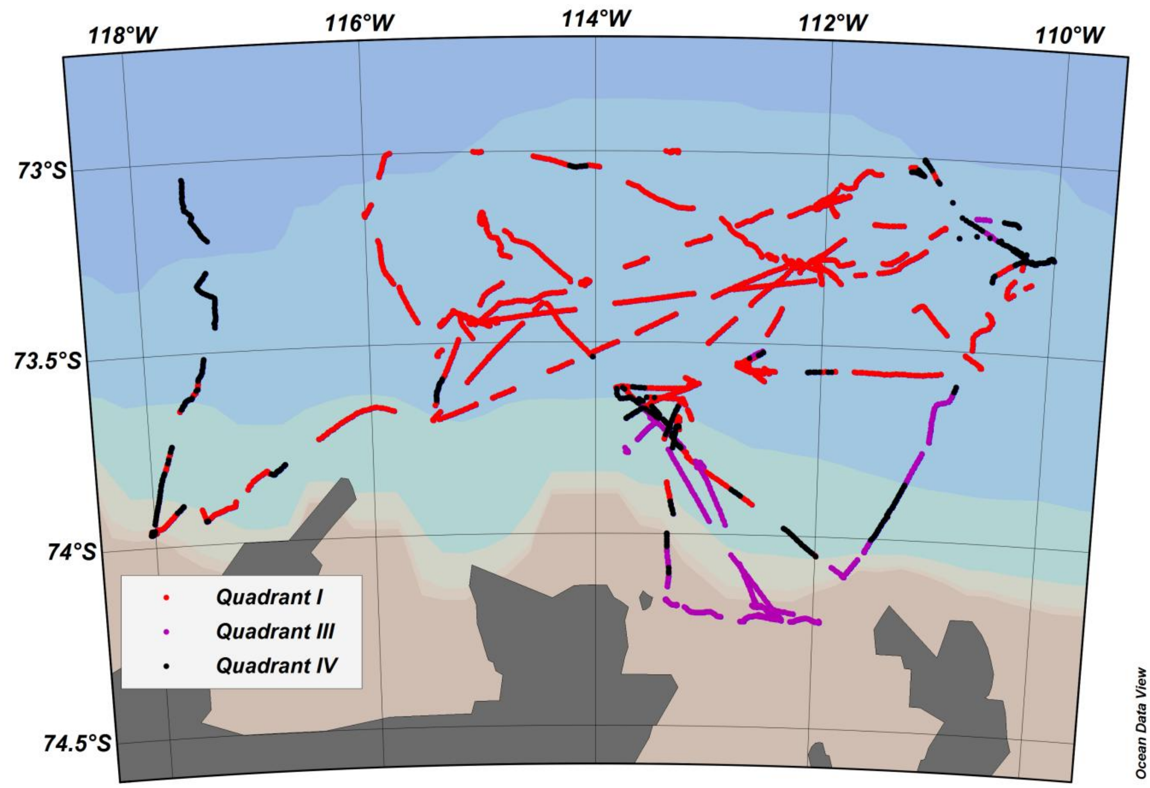


Fig.4b Spatial distribution of the three quadrants with data points (I is red, III is purple, IV is black).

Figure 5

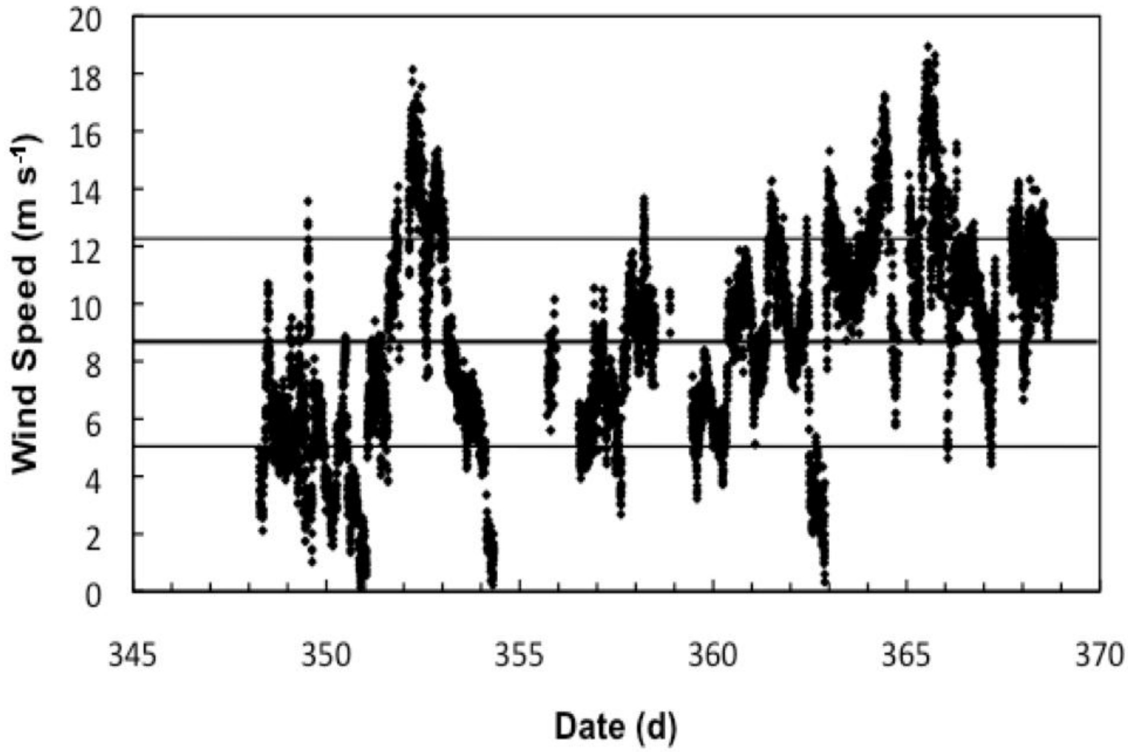


Fig.5 Time series of shipboard wind speed (m s^{-1}) showing the average and standard deviation for the cruise period (8.6 $\pm$3.5 m s^{-1}; n = 6500). The temporally averaged wind speed and the variance involved are shown on the figure as three straight lines.

Figure 6

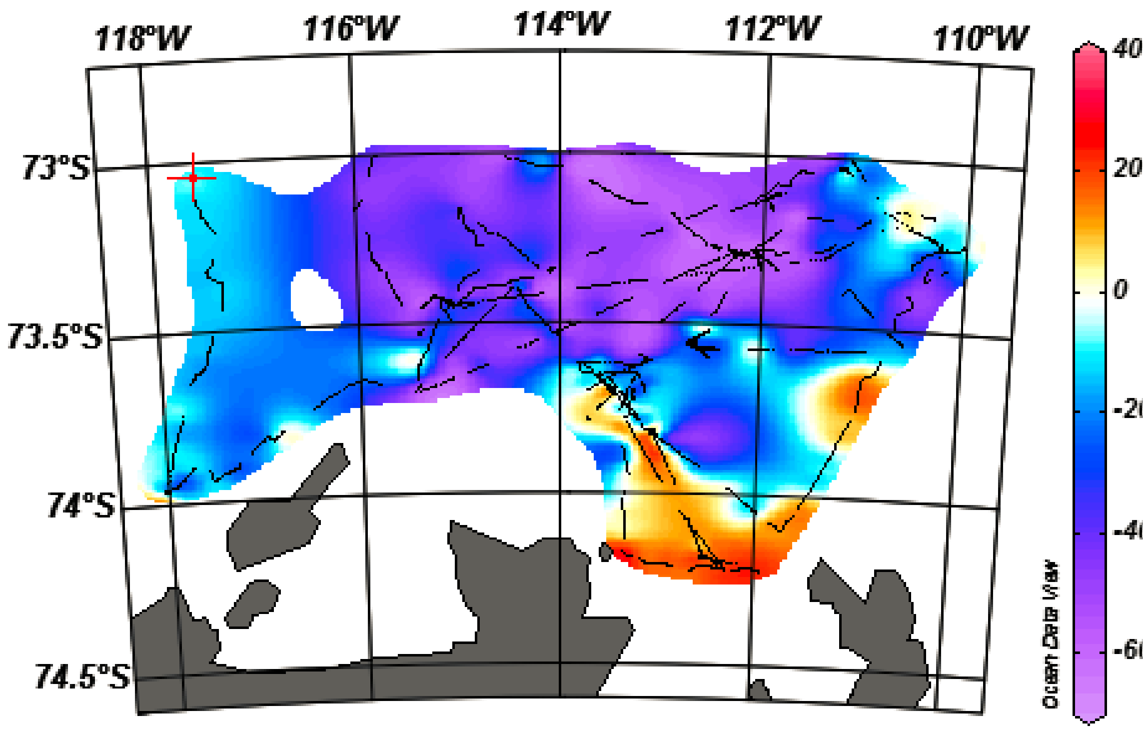


Fig.6 Spatial distribution of air-sea CO_2 flux (mmol C m^{-2} d^{-1}) based on pCO_2 gradient and average shipboard wind speed (ODV DIVA Gridding). Positive values imply flux out of the ocean, while negative values imply flux into the ocean.