

Spatial variability of surface $p\text{CO}_2$ and air-sea CO_2 flux in the Amundsen Sea Polynya, Antarctica

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Short title: Air-sea CO_2 flux in the Amundsen Sea Polynya

Abstract

Partial pressure of CO₂ ($p\text{CO}_2$) and dissolved oxygen (DO) in the surface waters of the Amundsen Sea Polynya (ASP) were measured during austral summer 2010–2011 on the Amundsen Sea Polynya International Research Expedition (ASPIRE). Surface $p\text{CO}_2$ was as low as 130 μatm , mainly due to strong net primary production. Comparing saturation states of $p\text{CO}_2$ and DO distinguished dominant factors (biological activity, temperature, upwelling, and ice melt) controlling $p\text{CO}_2$ across regions. Air-sea CO₂ flux, estimated using average shipboard winds, showed high spatial variability (-52 to 25 $\text{mmol C m}^{-2} \text{d}^{-1}$) related to these factors. The central region exhibited a high flux of -36 ± 8.4 $\text{mmol C m}^{-2} \text{d}^{-1}$, which is $\sim 50\%$ larger than that reported for the peak of the bloom in the well-studied Ross Sea, comparable to high rates reported for the Chukchi Sea, and significantly higher than reported for most continental shelves around the world. This central region ($\sim 20,000$ km^2) accounted for 85% of the CO₂ uptake for the entire open water area. Margins with lower algal biomass accounted for $\sim 15\%$ of regional carbon uptake, likely resulting from $p\text{CO}_2$ reductions by sea ice melt. During ASPIRE we also observed $p\text{CO}_2$ up to 490 μatm in a small region near the Dotson Ice Shelf with an efflux of 11 ± 5.4 $\text{mmol C m}^{-2} \text{d}^{-1}$ that offset about 3% of the uptake in the much larger central region. Overall, the 2010–2011 ASP was a large net sink for atmospheric CO₂ with a spatially averaged flux density of -18 ± 14 $\text{mmol C m}^{-2} \text{d}^{-1}$. This high flux suggests a disproportionate influence on the uptake of CO₂ by the Southern Ocean. Since the region has experienced a significant increase in open water duration (1979–2013), we speculate about whether this CO₂ sink will increase with future climate-driven change.

I. Introduction

The increase of atmospheric CO₂ as a result of human activity has drawn much attention in the past years, primarily with respect to its role in altering the Earth's climate (Manabe et al., 1980). The ocean has sequestered 25–28% of the anthropogenic CO₂ since 1960 (Le Quéré et al., 2013), acting as a carbon sink and thus playing a significant role in mitigating climate change (Sabine et al., 2004; Sarmiento et al., 2002; Solomon et al., 2007). The Southern Ocean makes a substantial contribution to this atmospheric carbon sink; over 40% of the anthropogenic CO₂ in the ocean has been absorbed south of 40°S (Sallée et al., 2012).

High-latitude oceans are capable of taking up massive amounts of atmospheric CO₂ 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 in the deep ocean and thus the global atmospheric CO₂ level (Takahashi et al., 2009; Sigman and Boyle, 2000; Sigman et al., 2010). The CO₂ sink in the Southern Ocean is affected by rates of upwelling, wind speed (McNeil et al., 2007; Le Quéré et al., 2007; Lovenduski et al., 2008), biological uptake (Arrigo et al., 1999; de Baar et al., 1995), and ice melt (Ishii et al., 2002; Fransson et al., 2011). Yet the specific role of the Southern Ocean in future atmospheric CO₂ uptake is still uncertain due to spatial and temporal variability in the biological and solubility pumps and to under-sampling in critical regions such as coastal Antarctic polynyas (Arrigo et al., 2008a; Carrillo et al., 2004).

Polynyas are recurring areas of open ocean surrounded by sea ice and characterized by high energy and material transfers between the atmosphere and the polar ocean (Smith and Barber, 2007). The open water area typically expands in spring and summer (e.g., Arrigo and van Dijken, 2003), but is mostly ice-covered in autumn and winter, although small winter coastal polynyas are responsible for significant heat exchange and dense water formation in the coastal

Antarctic (e.g., Chapman, 1999; Barber and Massom, 2007). Polynyas are often areas of high biological production during summer, facilitating substantial CO₂ exchange with the atmosphere (Yager et al., 1995; Miller and DiTullio, 2007). Sea ice can restrict air-sea gas exchange and limit the equilibration between surface waters and the atmosphere (Hood et al., 1999; Tortell et al., 2011). Sea ice, however, is also habitat for microorganisms performing both photosynthesis and respiration, as well as a site for calcium carbonate precipitation and dissolution, all of which can influence gas exchange and affect surface ocean CO₂ concentrations (Gosink et al., 1976; Miller et al., 2011; Rysgaard et al., 2007; Fransson et al., 2011).

The Amundsen Sea, located in the South Pacific sector of the Southern Ocean (Figure 1), is one of the least explored areas in Antarctica due to its remote location and historically heavy sea ice cover. It is characterized by a continental shelf that widens from west to east, and deepens toward the continent via a deep trough system that influences ocean circulation and ice sheet dynamics in the region (Nitsche et al., 2007; Wåhlen et al., 2010; Jacobs et al., 2012). It is distinguished by its thick but variable multiyear (perennial) sea ice, interspersed with areas of seasonal sea ice and a number of coastal polynyas (Arrigo et al., 2012), the Amundsen Sea Polynya (ASP) being the largest (Stammerjohn et al., 2014). Among all Antarctic polynyas, the ASP is the fourth largest (with a 1997–2010 average area of $27,300 \pm 8,700 \text{ km}^2$ during the open period from October 1 to March 31, and maximum open area of $\sim 80,000 \text{ km}^2$; Arrigo et al., 2012). From 1997 to 2010, the ASP opened to $> 10,000 \text{ km}^2$ for an average of 132 ± 17.5 ($n = 14$) days per year (Arrigo et al., 2012). The eastern ASP has experienced a rapid increase in seasonal open water duration (currently 2.6 months longer than in 1979; Stammerjohn et al., 2014), and is also flanked by some of the world's fastest melting glacial ice (Rignot et al., 2013;

Mouginot et al., 2014), including the Pine Island, Thwaites, Crosson, Dotson, and Getz Ice Shelves.

The ASP is estimated by satellite to be the most productive polynya in the Southern Ocean (per unit area) on average, with the highest interannual variability (Arrigo and van Dijken, 2003). Average primary production in summer typically exceeds $1 \text{ g C m}^{-2} \text{ d}^{-1}$ (Lee et al., 2013; Alderkamp et al., 2012), much higher than offshore waters of the open Southern Ocean ($0.2\text{--}0.4 \text{ g C m}^{-2} \text{ d}^{-1}$; Arrigo et al., 2008b). Only a few in situ biogeochemical studies have been conducted in the ASP, primarily in the past few years. Tortell et al. (2012) reported measurements of surface water $p\text{CO}_2$ and DO in the ASP during January–February 2009, with sea-air CO_2 exchange averaging $-41.9 \mu\text{mol m}^{-2} \text{ d}^{-1}$ in the open waters of the polynya, and argued on that basis that the ASP alone contributes 5% of the Southern Ocean CO_2 flux.

During the austral summer of 2010–2011, a multidisciplinary team of oceanographers embarked on the Amundsen Sea Polynya International Research Expedition (ASPIRE) to examine the controls and fate of the massive *Phaeocystis antarctica* bloom of the ASP (Figure 1; Yager et al., 2012; Alderkamp et al., 2014; Schofield et al., 2014; Williams et al., 2014; Yager et al., unpublished) during its initial buildup in early summer. Here, we examine the distribution and variability of surface $p\text{CO}_2$ and air-sea CO_2 flux, assess the sensitivity to physical and biological drivers in the ASP region, and compare our findings with previous studies to estimate the global importance of this climate-sensitive region.

2. Study Site and Methods

From December 2010 to January 2011, the ASP region was explored extensively by the ASPIRE team onboard the RVIB *Nathaniel B. Palmer* (NBP; Figure 1; Yager et al., 2012). The cruise track focused on the highly productive central region, but in an effort to link observations

with processes, the influences on the polynya from the coastal margins, particularly the Getz Ice Shelf (GIS), Dotson Ice Shelf (DIS), and the Thwaites Iceberg Tongue (TIT), were also explored. Here we focus on underway data collected from the NBP in the open waters (< 50% sea ice cover) of the polynya (December 14, 2010, to January 3, 2011; 72.6–74.3°S, 110–119°W).

Ice concentration and open water

For navigation and planning purposes during the field expedition, sea ice concentration images from Moderate Resolution Imaging Spectroradiometer (MODIS) Terra (250 m resolution) were collected and delivered to the ship electronically from the Antarctic Geospatial Information Center (AGIC), Department of Geology and Geophysics, University of Minnesota. Additionally, ice concentrations were obtained from both *in situ* field observations and satellite remote sensing images for use in data analysis, as described below.

Throughout the sampling period, visual observations of sea ice concentration were recorded using standardized protocols (Worby and Allison, 1999). These shipboard measurements were used to determine the “open water” sections of the cruise track for which underway data are presented, with open water defined as ice concentration < 50%.

While field observations provided sea ice concentrations for the exact location of our cruise track as it was sampled, satellite remote sensing techniques were also used in this analysis. Daily ASMR-E satellite images (12.5 km resolution) were obtained for the 2010–2011 season to provide an assessment of ice conditions over the larger ASP region and in the months prior to and after our sampling period. Using satellite-derived sea ice concentrations for a patch of ocean surrounding each station, we calculated the open water duration (or number of open water days) as the total number of days the location had < 50% ice concentration from the date of first

opening until (and including) the date of sampling. Additionally, we plotted the time course of sea ice concentration around each station and compared it to the measurement of ocean color by MODIS Aqua (1.24 km) to determine the approximate time needed for bloom development. Finally, we estimated the total open water area within the ASP region as all waters that were ice-free, using a stricter threshold of < 10% ice concentration to define ice-free waters. This method and the geographic constraints used to define the ASP region are consistent with calculations of polynya open water area employed by Arrigo et al. (2012).

Parameters at the sea surface

Surface seawater was sampled from the main underway seawater system onboard NBP which draws from a nominal depth of 5 m and pumps the seawater directly (with a minimum of 90° turns) to the Hydro Lab on the main deck (3 m above sea level) where it is analyzed. The 15-cm diameter piping is made of a non-metallic, chemically resistant material that maintains structural integrity under low temperatures and minimizes algal and bacterial growth. Sea surface temperature (SST) and salinity (SSS) were recorded every 10 seconds using an onboard thermo-salinograph (SBE-45 Micro TSG, SeaBird Inc., Bellevue, WA). The precision of temperature and salinity data were 0.002°C and 0.005, respectively.

The NBP carried a $p\text{CO}_2$ measurement system from Lamont-Doherty Earth Observatory (LDEO) that was linked to the underway seawater system. The LDEO system continuously measured sea surface mole fraction of CO_2 ($x\text{CO}_2$ in ppm), using a showerhead equilibrator and a non-dispersive infrared CO_2 gas analyzer, and recorded data as part of the Research Vessel Data Acquisition System (RVDAS). Precision of the system was $\pm 1.5 \mu\text{atm}$; accuracy was maintained using a 4th order calibration curve on voltages from 5 CO_2 gas standards run every 75 min. The CO_2 concentrations in the gas mixtures were calibrated using SIO standards determined by C. D.

Keeling's group using the manometric method. See Sutherland et al. (2011) for further details regarding the CO₂ measurement system.

The partial pressure of CO₂ in surface water at the temperature of equilibration ($p\text{CO}_{2(\text{eq})}$, in μatm) was converted from measured $x\text{CO}_2$ (Jiang et al., 2008):

$$p\text{CO}_{2(\text{eq})} = x\text{CO}_{2(\text{water})} \times (P_{\text{eq}} - P_{\text{v}}) \quad (1)$$

$$\ln P_{\text{v}} = 24.4543 - 6745.09/T_{\text{eq}} - 4.8489 \times \ln(T_{\text{eq}}/100) - 0.000544 \times S \quad (2)$$

where $x\text{CO}_{2(\text{water})}$ is the measured mole concentration of CO₂ (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, $p\text{CO}_2$ in the equilibrator $p\text{CO}_{2(\text{eq})}$ was corrected to surface water $p\text{CO}_{2(\text{water})}$ at in situ temperature (Takahashi et al., 1993):

$$p\text{CO}_{2(\text{water})} = p\text{CO}_{2(\text{eq})} \times \exp(0.0423 \times [T_{\text{in situ}} - T_{\text{eq}}]) \quad (3)$$

For comparison to other data sets such as chlorophyll *a* fluorescence, the influence of temperature on in situ $p\text{CO}_2$ was removed by applying the same equation to convert to a single sea surface temperature ($T = -1^\circ\text{C}$):

$$p\text{CO}_{2(\text{T})} = p\text{CO}_{2(\text{water})} \times \exp(0.0423 \times [T_{\text{T}} - T_{\text{in situ}}]) \quad (4)$$

Atmospheric $x\text{CO}_2$ was measured onboard NBP by the same system that measured sea surface $x\text{CO}_2$, but ship contamination was difficult to remove objectively. In this study, therefore, we interpolated between available hourly air $x\text{CO}_2$ observations during the time of ASPIRE from the NOAA/ESRL network (Thoning et al., 2013) at American Samoa (389.06 ± 0.56 ; $n = 366$) and South Pole Station (387.30 ± 0.13 ; $n = 484$). Thus, $x\text{CO}_{2(\text{atm})}$ was assumed to be 388 ppm. As

described above, $p\text{CO}_2$ in the atmosphere at equilibration ($p\text{CO}_{2(\text{atm})}$, in μatm) was calculated by equations (1) and (2) with $x\text{CO}_{2(\text{atm})}$, sea surface temperature $T_{\text{in situ}}$, and assuming the barometric pressure at sea surface was the same as that measured in the lab by the barometer on the $p\text{CO}_2$ system P_{eq} (range of 975–992 mbar).

Underway surface dissolved oxygen (DO) was measured with an oxygen Optode (Model # 3835; AADI Inc., Attleboro, MA; precision $< 1 \mu\text{mol L}^{-1}$) and surface chlorophyll a fluorescence (Chl a) was measured with an ECO-AFL/FL Fluorometer (Wet Labs, Philomath, OR). The Optode DO measurements were calibrated with titrated samples using the Winkler method. An RMA regression ($n = 100$; $r^2 = 0.996$) gave standard errors for the slope and y-intercept of $< 1\%$ and 6.5% , respectively. Chlorophyll a calibrations at sea were problematic, so we report uncalibrated fluorescence values here for comparison purposes only.

Discrete seawater samples were also collected from below the surface, using a conventional CTD-rosette, and analyzed for nutrients, total dissolved inorganic carbon and alkalinity, chlorophyll a , and dissolved oxygen (see Yager et al., unpublished).

Processes controlling $p\text{CO}_2$ distribution

Surface $p\text{CO}_2$ and DO saturation states were compared in accordance with the method described in Carrillo et al. (2004) to determine the qualitative importance of changes in temperature and biological processes on $p\text{CO}_2$:

$$p\text{CO}_{2_sat} = (p\text{CO}_{2(\text{water})} / p\text{CO}_{2(\text{atm})}) \times 100\%, \quad (5)$$

$$\text{DO}_{_sat} = (\text{DO} / \text{DO}^*) \times 100\%, \quad (6)$$

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 DO

equilibrates with the atmosphere much faster than $p\text{CO}_2$, the effects of gas exchange on the data distribution can also be modeled using the Carrillo et al. (2004) approach.

We also calculated the theoretical distribution of $p\text{CO}_2_{sat}$ and DO_{sat} that would be observed if Winter Water (WW) was subject to primary production and warming. Properties for WW were derived from ASPIRE measurements made at the base of the deep mixed layer (~ 100 m) in the polynya region (temperature, $T = -1.8^\circ\text{C}$; salinity, $S = 34.1$; total dissolved inorganic carbon, $\text{DIC} = 2215 \mu\text{mol kg}^{-1}$; total alkalinity, $\text{ALK} = 2291 \mu\text{mol kg}^{-1}$; dissolved oxygen, $\text{DO} = 290 \mu\text{mol L}^{-1}$; nitrate, $\text{NO}_3 = 31 \mu\text{mol L}^{-1}$; phosphate, $\text{PO}_4 = 2 \mu\text{mol L}^{-1}$, silicate, $\text{SiO}_4 = 90 \mu\text{mol L}^{-1}$; Yager et al., unpublished). We applied a photosynthetic quotient (PQ) of 1.25 mol O_2 evolved per mol DIC removed (e.g., Tortell et al., 2011) and used elemental stoichiometry observed in the upper 100 m of the ASP (C:Si:N:P = 116:13:16:1; Yager et al., unpublished; results were not significantly different if traditional Redfield values were used), reflecting a mixed bloom of diatoms and *Phaeocystis antarctica* (Arrigo et al., 1999). We allowed nitrate drawdown to contribute to changes in total alkalinity (1:1; Wolf-Gladrow et al., 2007) and included phosphate and silicate in our calculations of the carbonate system. Changes were made stepwise to the above inventories; $p\text{CO}_2$ was calculated using CO2calc (Robbins et al., 2010; based on CO2SYS, Lewis and Wallace, 1998), with Mehrbach constants refit by Dickson and Millero (1987) and Dickson (1990). We calculated $p\text{CO}_2_{sat}$ and DO_{sat} as described above. We also calculated similarly the $p\text{CO}_2_{sat}$ and DO_{sat} expected from these photosynthetic impacts plus warming (PQ + warming) to the maximum SST observed in the ASP (+0.1°C).

Additionally, we applied a simple two-endmember mixing model to investigate the $p\text{CO}_2$ and DO saturation states ASPIRE observed. In this case, we mixed Antarctic Surface Water (AASW) from the central polynya ($T = -0.2^\circ\text{C}$, $S = 33.8$, $\text{DIC} = 2041 \mu\text{mol kg}^{-1}$, $\text{ALK} = 2344$

$\mu\text{mol kg}^{-1}$, $\text{DO} = 490 \mu\text{mol L}^{-1}$, $\text{NO}_3 = 6 \mu\text{mol L}^{-1}$, $\text{PO}_4 = 0.8 \mu\text{mol L}^{-1}$, $\text{SiO}_4 = 67 \mu\text{mol L}^{-1}$; Yager et al., unpublished) with WW (as above). From values along each mixing line, we then calculated $p\text{CO}_2$ using CO2calc, and $p\text{CO}_2_{\text{sat}}$ as described above, and compared them to calculated values for DO and DO_{sat} . We assumed that DO mixed linearly as a mass property (as is done with apparent oxygen utilization, AOU, calculations; e.g., Craig, 1971). The resulting mixing-only relationship was not distinguishable from the PQ curve (data not shown).

To model the predicted effects of sea ice melt on the carbonate system (Rysgaard et al., 2007), we added $56 \mu\text{atm } p\text{CO}_2$ (a value determined recently for the ASP region; Fransson et al., 2011) to every observation and compared the distribution to DO, which is not affected by carbonate dissolution. Because of the heterogeneity of sea ice in this region, we might expect some variation in this contribution, but the authors did not report variation (Fransson et al., 2011).

Wind speed and transfer velocity

Underway wind speed was measured by an anemometer (RM Young 5106) located in the ship's Aloft Observation Station (about 25 m above the sea surface) and corrected for ship motion during the cruise. We also corrected the data to a height of 10 m (u_{10}) by a factor of 0.91 according to Thomas et al. (2005; see also Crusius and Wanninkhof, 2003, and Benschop, 1996).

In the absence of meteorological buoy or station observations in the region, we assumed the underway wind speeds were representative of the entire ASP region (reasonable given the relatively small size of the ASP). This assumption was tested by comparing ASPIRE data (December 14, 2010, to January 3, 2011) to wind data collected by other expeditions to the same general area but with different dates and cruise tracks (NBP 09-01, *DynaLiFe*, January 11 to

February 15, 2009, Tortell et al., 2011; *Araon*, January 2010, and *Araon*, February–March 2012, data courtesy of the Korean Polar Research Institute).

Temporally-averaged, height-corrected shipboard wind speed (u_{10}) during the sampling period in the polynya was used to derive the CO₂ transfer velocity k for long-term averaged winds (Wanninkhof, 1992):

$$k = 0.39 \times u_{10}^2 \times (Sc/660)^{-0.5} \quad (7)$$

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

Air-sea CO₂ flux

The sea surface $p\text{CO}_2$ gradient ($\Delta p\text{CO}_2$, relative to the atmosphere), temperature, salinity, wind speed, and sea level pressure were used to calculate the air-sea CO₂ flux (Wanninkhof, 1992) over the study area. The air-sea CO₂ flux ($\text{mmol C m}^{-2} \text{ d}^{-1}$) was determined as:

$$F = k \times K_0 \times [p\text{CO}_{2(\text{water})} - p\text{CO}_{2(\text{atm})}] \quad (8)$$

where K_0 is the solubility of CO₂ in the seawater, which is a function of temperature and salinity (Weiss, 1974). Air-sea CO₂ flux was spatially interpolated over the polynya region using the underway data from the ship track and the DIVA gridding method built into Ocean Data View 4 (Schlitzer, 2014; <http://odv.awi.de>). A spatially-averaged flux was then calculated for the entire open-water region as well as for sub-regions such as the central polynya and the southeast region near the DIS.

Total annual flux was roughly estimated by multiplying this spatially-averaged flux by the 1997–2010 average open water period (days) and the average open water area of the polynya (Arrigo et al., 2012), assuming that the flux ASPIRE measured is representative of the entire open water season. When averages were calculated, they are reported with ± 1 standard deviation and the total number (n) of observations.

3. Results

Ice concentration and open water

The springtime polynya opened initially from the southeastern region near the TIT and DIS, with daily open water area in October 2010 averaging $5190 \pm 3090 \text{ km}^2$ ($n = 31$; Figure 2). In early November, the open water region began to expand rapidly toward the north into the sea ice pack and toward the east near the GIS (Figure 2A). By mid November and early December, the polynya had grown to about $25,000 \text{ km}^2$ (Figures 2B, C, and F). As the NBP entered the polynya in mid-December 2010 for ASPIRE, the open water area was $41,400 \text{ km}^2$ (Figures 2D, F). Total polynya area at our departure from the region in early January was $63,300 \text{ km}^2$, with the open water area significantly expanded to both the north and west compared to when we first arrived (Figures 2E, F). The average of daily open water area estimates during the measurement period was $48,000 \pm 10,400 \text{ km}^2$ ($n = 21$). The maximum open water area that summer was $\sim 78,000 \text{ km}^2$ in mid-January 2011 (after the NBP departed). Over the entire austral spring-summer season of ASPIRE (October 1, 2010, to March 31, 2011), the mean daily open water area of the ASP was $28,200 \pm 22,100 \text{ km}^2$ ($n = 182$ days), similar to the 1997–2010 average reported by Arrigo et al. (2012).

Stations visited during the cruise had been open for an average of 49 ± 24 ($n = 57$) days prior to our sampling. By comparing AMSRE (12.4 km^2) and MODIS Aqua (1.24 km^2) observations, we were able to estimate that the length of time between the disappearance of sea ice and the observation of increasing ocean color (bloom "spin up") was ~ 20 days for most stations.

Parameters at the sea surface

Large spatial variability of surface water $p\text{CO}_2$ was observed across the ASP (Figure 3A). As the NPB entered the polynya in the west (near 118°W) in mid-December (see Figure 1), undersaturated $p\text{CO}_2$ values near $300 \mu\text{atm}$ were observed across the western region and near the Getz Ice Shelf (GIS). As the NBP departed in early January, traveling again through the western region ($\sim 116^\circ\text{W}$) of the polynya, low $p\text{CO}_2$ values of $\sim 200 \mu\text{atm}$ were observed, suggesting a drawdown of $\sim 100 \mu\text{atm}$ over about 20 days. Over the entire time we sampled there, the central polynya ($73.0\text{--}73.7^\circ\text{S}$) showed strong undersaturation of $p\text{CO}_2$ with low values ranging from 130 to $200 \mu\text{atm}$. Somewhat higher $p\text{CO}_2$ values were observed in the sea ice zone bordering the polynya, especially near the TIT in the northeast. The area near the DIS showed strongly supersaturated $p\text{CO}_2$ values of $\sim 430 \mu\text{atm}$, with the very highest value ($490 \mu\text{atm}$) at the western edge of the ice sheet where a large northward current ($0.2\text{--}0.3 \text{ m s}^{-1}$) of iron-rich, oxygen-poor, modified Circumpolar Deep Water (mCDW) was observed exiting just below the ice shelf at $150\text{--}400 \text{ m}$ (Sherrell et al., 2014).

During the cruise, surface Chl *a* was found to be highest across the central ASP, north of 73.7°S (Figure 3B). Relatively low levels of Chl *a* fluorescence were observed near the GIS, DIS, and TIT. Peak fluorometric and HPLC measurements of Chl *a* on discrete surface water samples from the central region were $\sim 20 \text{ mg m}^{-3}$ (Alderkamp et al., 2014), so the numeric values from the underway fluorometer are likely too high to be used as mg m^{-3} , but good for relative comparisons.

The distribution of surface DO (Figure 3C) exhibited a pattern similar to Chl *a*. DO at the surface ranged from 230 to $490 \mu\text{mol L}^{-1}$ (or 65 to 130% saturation). As the NBP entered the open water area on December 14, the western portion of the polynya exhibited DO

concentrations between 350 and 400 $\mu\text{mol L}^{-1}$ and was near DO saturation (90–110%). The highest DO values ($> 400 \mu\text{mol L}^{-1}$) were observed in the central polynya, typically exceeding 125% saturation and corresponding well with maximum Chl *a*. DO values were lowest (230–350 $\mu\text{mol L}^{-1}$) near the DIS, especially at the western edge where $p\text{CO}_2$ was highest.

The lowest $p\text{CO}_2$ observations tended to occur in warmer, low-salinity surface waters where high DO was also observed (Yager et al., 2012). Significant correlations were found between $p\text{CO}_2$ and sea surface temperature (SST; $R = 0.50$, $n = 6500$) and between $p\text{CO}_2$ and sea surface salinity (SSS; $R = -0.57$, $n = 6500$), but the relationships were non-linear (Figures 4A and 4B). Chl *a* and $p\text{CO}_2$ were more closely correlated ($R = -0.87$; $n = 6500$; Figure 4C). This correlation did not improve significantly when $p\text{CO}_2$ was corrected to a single temperature ($p\text{CO}_{2(T)}$, where $T = -1^\circ\text{C}$). The best linear relationship with $p\text{CO}_2$ was found when Chl *a* was log transformed ($R^2 = 0.89$, $n = 6500$, $p < 0.01$; Figure 5).

Processes controlling $p\text{CO}_2$ distribution

A strong linear association was observed between surface $p\text{CO}_2$ and DO saturation states ($R^2 = 0.95$, $n = 6500$, $p < 0.01$; Figure 6A). The distribution of observations was consistent with our model of Winter Water ($p\text{CO}_{2_sat} = 126\%$, $\text{DO}_{sat} = 75\%$) being modified by net photosynthesis alone (PQ) or by both net photosynthesis and warming (PQ + warming; Figure 6A). Underway data fell into three of the four quadrants described by Carrillo et al. (2004). The spatial distribution of data from each of the quadrants (Figure 6B) indicated that most observations in Quadrant I (corresponding to net photosynthesis) were located in the central polynya, where the maximum DO_{sat} (133%; 484 $\mu\text{mol L}^{-1}$) and minimum $p\text{CO}_{2_sat}$ (34%; 133 μatm) were observed. Saturation of $p\text{CO}_2$ ($p\text{CO}_{2_sat}$) and undersaturation of DO typically decreased with increasing distance from both the ice shelf and the northern sea ice margin.

Observations in Quadrant IV (both gases undersaturated) were found at the margins of the central zone, along the western inbound leg, and in other areas where some sea ice was present (south central and eastern areas of the polynya). Observations from Quadrant III (indicating net respiration) were located mainly to the southeast of the polynya near the DIS, where the highest supersaturation of $p\text{CO}_2$ (126%; 489 μatm) and the greatest undersaturation of DO (55%; 203 $\mu\text{mol L}^{-1}$) were recorded. No observations fell into the fourth quadrant designated by Carrillo et al. (2004), where both $p\text{CO}_2$ and DO are supersaturated (suggestive of warming).

A small subset of the data did not follow the PQ model; these data, located at the edge of the DIS, fell in the lower right of Quadrant III, dominated by respiration (Figure 6A). Because Chl *a* there was very low, and no other significant sources of labile organic matter were detected in this region, active microbial respiration at the surface was unlikely (see Williams et al., 2014). Instead, the low O_2 and high $p\text{CO}_2$ suggest the influence of deep water brought to the surface. The physical properties of this region indicate a much deeper mixed layer than elsewhere in the polynya (Figure 7); given the arrangement of the DIS and TIT, the offshore winds from the south may be favorable for upwelling (Figure 8). Buoyancy-driven upwelling was also likely with known interactions between warmer, saltier mCDW and ice shelf basal melt (see Jacobs et al. 2012; Yager et al., 2012; Sherrell et al., 2014). Indeed, if we plot the $p\text{CO}_2_{\text{sat}}$ and DO_{sat} for mCDW brought to surface ocean pressure (mCDW in ASP has properties of: $T = +0.7^\circ\text{C}$, $S = 34.6$, $\text{DIC} = 2255 \mu\text{mol kg}^{-1}$, $\text{ALK} = 2344 \mu\text{mol kg}^{-1}$, $\text{DO} = 200 \mu\text{mol L}^{-1}$, $\text{PO}_4 = 2.1 \mu\text{mol L}^{-1}$; $\text{SiO}_4 = 107 \mu\text{mol L}^{-1}$; Yager et al., unpublished) the DIS data suggest a mixing line between WW and mCDW (Figure 6A).

The $p\text{CO}_2_{\text{sat}}$ versus DO_{sat} data distribution was significantly offset from the origin (equilibrium saturation for both gases; Figure 6A). If we account for the effects of sea ice

alkalinity contributions in this region (Fransson et al., 2011), however, the data intersect the origin (see inset, Figure 6A). Local variations in the sea ice contribution could explain some of the scatter in the data; e.g., deviations from the PQ and PQ + warming lines. Some variation could also be attributable to air-sea gas exchange, but few data followed the expected curvature (Figure 6A), except perhaps data in the uppermost left of Quadrant I.

Wind speed and transfer velocity

Variable wind speeds were observed across the ASP during ASPIRE (Figure 9) with a shipboard average of $8.7 \pm 3.5 \text{ m s}^{-1}$ ($n = 6209$), a maximum value of 19 m s^{-1} , and a minimum of 0.2 m s^{-1} . Average wind speeds were not significantly different ($p < 0.01$) from the average winds of three other summertime ASP expeditions (*DynaLiFe* 2009, *Araon* 2010, *Araon* 2012). When height-corrected to 10 m, ASPIRE values reduce to 7.9 ± 3.2 , with maximum at 17 m s^{-1} . NCEP/NCAR reanalysis wind data (National Weather Service, 2014), which are interpolated over a much larger area of the Amundsen Sea, report monthly averaged wind speeds of $5.0 \pm 2.6 \text{ m s}^{-1}$ for December 2010 (<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 for input to the NCEP/NCAR reanalysis. Since our data agreed reasonably well with those from three other recent expeditions to the ASP, we used them here for flux estimates.

With a range in sea surface temperature from -1.8 to 0.1°C (average = -0.74 ± 0.40 ; $n = 6209$), the Schmidt number varied from 2061 to 2304 (average = 2169 ± 52 , $n = 6209$). Gas transfer velocity varied from 12.9 to 13.7 cm h^{-1} (average = $13.3 \pm 0.2 \text{ cm h}^{-1}$; $n = 6209$). Solubility of CO_2 ranged from 0.063 to 0.068 $\text{mol kg}^{-1} \text{ atm}^{-1}$ (average = $0.065 \pm 0.001 \text{ mol kg}^{-1} \text{ atm}^{-1}$; $n = 6209$).

Air-sea CO₂ flux

With $\Delta p\text{CO}_2$ values from -242 to $116 \mu\text{atm}$ (median = $-106 \mu\text{atm}$; average = $-102 \pm 99 \mu\text{atm}$; $n = 6209$), air-sea gas exchange rates ranged from -51.8 to $24.9 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (negative values indicate oceanic uptake, positive values are oceanic outgassing). The spatial variability of the CO₂ flux (Figure 10) mirrored the $p\text{CO}_2$ distribution since temperature and salinity varied comparatively little, with the highest uptake in the central polynya. Over the entire open water region from December 14 to January 3, we calculated a spatially averaged flux of $-18 \pm 14 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ($-0.21 \pm 0.17 \text{ g C m}^{-2} \text{ d}^{-1}$). Summed over the daily open water area of the polynya (average = $48,000 \pm 10,400 \text{ km}^2$) over the time of ASPIRE sampling (21 d), carbon uptake was $0.22 \pm 0.17 \text{ Tg C}$. The CO₂ flux in the central polynya was double the polynya-wide rate, at $-36 \pm 8.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ($-0.43 \pm 0.10 \text{ g C m}^{-2} \text{ d}^{-1}$) and accounted for 85% of the total uptake when summed over the central region ($\sim 20,000 \text{ km}^2$): $0.18 \pm 0.04 \text{ Tg C}$. The efflux in the southeast near the DIS was $11 \pm 5.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ($0.13 \pm 0.07 \text{ g C m}^{-2} \text{ d}^{-1}$). Covering a much smaller area (about 2000 km^2), this efflux added up to $0.01 \pm 0.003 \text{ Tg C}$, offsetting only $\sim 3\%$ of the drawdown in the center polynya over the same time period (21 d).

4. Discussion

Comparison to other regions

As the most biologically productive polynya per unit area (Arrigo and van Dijken, 2003), the ASP provides a window to investigate and better understand the sensitivities and vulnerability of biogeochemical cycling in the coastal regions of Antarctica. Our analysis confirms that the extremely low surface $p\text{CO}_2$ observed in the central ASP was driven by the intense phytoplankton bloom. With the Southern Ocean's highest algal productivity, then, it is perhaps not surprising that the carbon flux density (CO₂ flux per unit area) observed in this

productive zone during ASPIRE was greater than for most other continental shelves and comparable to the highest rates reported in other Antarctic and Arctic polynyas (Ducklow and McCallister, 2004) and the Chukchi Sea (Bates et al. 2006).

Much of our current knowledge about carbon biogeochemical cycling in coastal Antarctica comes from field studies at a few sites, most extensively in the Ross Sea Polynya (RSP) and along the western Antarctic Peninsula (wAP). Extensive phytoplankton blooms occur on the Ross Sea continental shelf during spring and summer (Sweeney, 2003), corresponding with surface $p\text{CO}_2$ as low as $\sim 130 \mu\text{atm}$ (Sweeney et al., 2000). In the central region of ASP, we observed a similar minimum surface $p\text{CO}_2$ ($\sim 130 \mu\text{atm}$) but a higher spatially-averaged air-sea CO_2 flux ($-36 \pm 8.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$) than the peak flux of $\sim 24 \text{ mmol C m}^{-2} \text{ d}^{-1}$ observed in the RSP (Sweeney 2003). The ASP is smaller in area, but its early summer CO_2 flux density is at least 50% larger than peak rates in the RSP. We note, however, that Sweeney (2003) applied the NCEP-NCAR reanalysis wind speed, which may underestimate the flux.

Carrillo et al. (2004) investigated the surface waters of the Palmer LTER site along the wAP and showed that DO and $p\text{CO}_2$ varied systematically from atmospheric equilibrium, according to the relative importance of various physical and biological controls (their "four quadrant" approach). Unlike ASPIRE, LTER observations were found in all four quadrants (on a quadrant map similar to Figure 6A) and the data go solidly through the origin (100% $p\text{CO}_2_{\text{sat}}$, 100% DO_{sat}). Large temperature and gas exchange effects on oxygen and CO_2 saturation in the wAP surface waters were more obvious than in the ASP. Their study was later in the season (January–February) and the site was mostly ice-free by the time of sampling. Moreover, their study also found that observations in Quadrant I (with DO supersaturation and $p\text{CO}_2$ undersaturation) were mainly distributed adjacent to the coast or to the south (in Marguerite

Bay), where surface stratification was enhanced by recent glacial run-off or sea ice melt, respectively. Their study did not include any observations in the vicinity of ice shelves (which were located south of their study region). The strong net respiration signal they observed (Quadrant III) was associated with shelf-break upwelling, as opposed to the wind- or buoyancy-driven upwelling that we observed in the ASP in the vicinity of the DIS.

Mechanisms important to ASP CO₂ flux

Polynyas are defined by the dynamics of sea ice. In addition to biological dynamics in sea ice and the impacts of microbial photosynthesis and respiration on surface ocean $p\text{CO}_2$ and DO (e.g., Yager et al., 1995; Fransson et al., 2011), sea ice can impact surface $p\text{CO}_2$ via CaCO_3 precipitation during ice formation or dissolution during melt, in combination with brine rejection (Rysgaard et al., 2007). In a study of this effect in the pack ice surrounding the ASP during 2008–2009, Fransson et al. (2011) estimated that the dissolution of CaCO_3 during sea ice melt could explain a reduction in surface $f\text{CO}_2$ of up to $56 \mu\text{atm}$, in close agreement with results of $60 \mu\text{atm}$ obtained by Rysgaard et al. (2007) for the Arctic. Such a reduction in $p\text{CO}_2$, independent of a change in DO, is consistent with the offset in the ASPIRE data from the origin in Figure 6A. ASPIRE data therefore independently confirm the Fransson et al. (2011) estimate, although the scatter of data around the PQ and PQ + warming curves (Figure 6a) suggests some variability in the sea ice contribution. The sea ice alkalinity-driven reduction in surface $p\text{CO}_2$ (relative to O_2) also explains the data found in Quadrant IV (which in the absence of sea ice processes would indicate cooling) that we observed in the marginal zones of the ASP. Most importantly, the sea ice contribution reduces $p\text{CO}_{2_sat}$ before the phytoplankton bloom develops, reduces opportunities for springtime outgassing of wintertime respiration (from supersaturated WW), and

contributes modestly (~ 15%) to the carbon uptake in the region, supporting the idea that sea ice contributes significantly to this polar carbon pump (Rysgaard et al., 2007).

ASPIRE observations in Quadrant III (with supersaturated $p\text{CO}_2$ and undersaturated DO) were largely distributed near the DIS and TIT. Expression of wintertime respiration-driven oversaturation under the ice (e.g. Yager et al., 1995) is an unlikely explanation for these waters, because this southern region of the ASP is often partially open during winter and then fully opens in early November (see Figure 2, as well as Stammerjohn et al., 2014). As there are no significant sources of allochthonous organic carbon in coastal Antarctica, these surface waters are probably not actively net-heterotrophic (see Williams et al., 2014), but rather reflect the surfacing of long-submerged deep water through deep mixed layers or wind-driven or buoyancy-driven upwelling. Oversaturation from winter respiration may explain the Quadrant III waters near the TIT, because the sea ice interspersed in this iceberg field was observed during ASPIRE to be thick and impenetrable.

Gas exchange should leave a "fingerprint" on the quadrant plot (Figure 6A). As described by Carrillo et al. (2004), with O_2 equilibration faster than that for $p\text{CO}_2$, we would expect to see observations tipping toward the horizontal axis as individual water parcels experience gas exchange. This effect is very well illustrated in the LTER data from the wAP (Carrillo et al., 2004), but not so obvious in the ASPIRE data. Because we observed a highly linear relationship in these data, with little scatter between the model PQ curves and the 100% DO_{sat} axis, the impact of gas exchange is either indistinguishable from variability in the PQ or sea ice alkalinity contribution, or simply low compared to net photosynthesis. Most of the deviations from the model photosynthesis curve are above the line and can be explained by warming; exceptions are

the observations in the left, uppermost corner of Quadrant I that appear to "fall off" the PQ + warming line toward the 100% DO_{sat} line, probably indicating gas exchange.

Scaling up

The estimate of carbon uptake during the 21-day period of ASPIRE is quite small (0.22 Tg) compared to other large ocean carbon sinks (e.g., Takahashi et al., 2000), including the RSP (25 ± 10 Tg; Sweeney et al., 2000). The ASP, however, very likely takes up carbon outside of the ASPIRE observation window. Indeed, the AMSR-E satellite estimates of open water area show that the polynya continued to expand (Figure 2F) and MODIS Aqua ocean color time series data, processed to Level 2 for each ASPIRE station, indicate that chlorophyll *a* continued to rise for several more weeks after we sampled (data not shown). We also know that nitrate was still available at the surface ($> 7 \mu\text{M}$) when the NBP departed the region (Williams et al., 2014). With some assumptions about continuity, scaling up the flux density can be attempted both temporally (extending the bloom season) and spatially (extending the open water area). If we apply ASPIRE flux observations to the sea-ice climatology (Arrigo et al., 2012) and propagate the errors (Bevington 1969), we can extend the ASPIRE estimate to the full season using the daily average polynya flux ($-18 \pm 14 \text{ mmol C m}^{-2} \text{ d}^{-1}$) and the productive open water season (132 ± 18 d; less 20 d for spin up). This calculation results in an estimate of $-2.0 \pm 1.6 \text{ mol C m}^{-2} \text{ a}^{-1}$. The rate doubles to $-4.0 \pm 1.1 \text{ mol C m}^{-2} \text{ a}^{-1}$, if we apply the central polynya flux density. For comparison, the annual air-sea CO₂ flux in the Ross Sea is estimated to be $-1.5 \pm 1.5 \text{ mol C m}^{-2} \text{ a}^{-1}$, based on multi-season studies conducted during 1996–1997 (Sweeney, 2003).

Additional justification for extending our observations into late summer can be found from Tortell et al. (2012), who report findings on *p*CO₂ and air-sea CO₂ flux in the ASP during the mid-to-late summer season of a previous year (January 11 to February 16, 2009); i.e., one

month later compared to our study, just after the peak in the *Phaeocystis antarctica* bloom (Alderkamp et al., 2012). They reported surface $p\text{CO}_2$ as low as $\sim 100 \mu\text{atm}$ and the air-sea CO_2 flux density for ice-free polynya waters to be $-41.9 \text{ mmol C m}^{-2} \text{ d}^{-1}$. At the same time, nitrate lower than that seen during ASPIRE ($7 \mu\text{M}$) was observed in a few areas of the central polynya (Alderkamp et al., 2012). The observations suggest that the bloom likely continued for at least another month after the NBP departed, supporting a continuation and enhancement of the high flux observed during ASPIRE, although it could also indicate interannual variability, known to be high in this region (Arrigo and van Dijken, 2003; Stammerjohn et al., 2014).

If we apply the spatially-averaged flux to the average open water area of the polynya ($27,300 \pm 8,700 \text{ km}^2$) and propagate the errors, the ASP CO_2 uptake scales up to $0.65 \pm 0.57 \text{ Tg C}$. Again, the rate doubles (to $1.3 \pm 0.56 \text{ Tg C}$) using the central polynya flux density. Clearly, some understanding is needed of seasonally-changing spatial distributions; our extrapolation is tenuous, as we do not know the relative contributions of the three zones over the entire season. Assuming that their relative contributions do not change, and comparing this estimate of annual uptake with that of the Southern Ocean south of 62°S (an area of $1.5 \times 10^7 \text{ km}^2$ and annual flux of -40 Tg C ; Takahashi et al., 2009), the ASP accounts for 2–3% of the annual carbon uptake by the Southern Ocean, even though the ASP occupies only 0.25% of the total area. This calculation is more conservative than the estimate by Tortell et al. (2011), yet the ASP is still clearly disproportionately important in its contribution to Southern Ocean air-sea CO_2 flux and the global carbon cycle.

Climate sensitivity?

The high $p\text{CO}_2$ variability associated with high interannual variability of productivity may contribute to strong climate sensitivity in the ASP (Yager et al., 2012). Based on satellite

data (Arrigo et al., 2012), 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 eastern ASP region over the observing period of 1979 to 2013 (Stammerjohn et al., 2014). Because the ASPIRE data offer a first glimpse at early season conditions, we can make some inferences about future carbon cycling in this region.

Specifically, an earlier sea ice retreat would not necessarily increase phytoplankton productivity if the system were still light limited. In that case, buildup of wintertime respiration (indicated by supersaturated $p\text{CO}_2$ and undersaturated DO in WW) could outgas if sea ice were simply exported from the region by winds to expose open water. Depending on the wind speed, however, equilibration with the atmosphere could take several weeks. Although there are satellite observations of a small, wind-driven ASP in the winter, the dense pack ice offshore would prevent a much larger wind-driven opening. Instead, the polynya likely opens initially by wind-driven exposure, but grows via solar warming of low-albedo surface water and subsequent sea ice melt (e.g., Minnett, 1995). What we see currently in the early-season ASP is a reduction in both surface salinity and $p\text{CO}_2$ by the freshwater and alkalinity of the sea ice melt itself, and a switch from oceanic outgassing to oceanic uptake before the phytoplankton bloom begins. We note that the $p\text{CO}_2$ reduction of $56 \mu\text{atm}$ due to sea ice melt according to Fransson et al. (2011) is for the entire 70-m mixed layer and assumes complete melting of the sea ice column; only a partial melt into the surface layers would be needed to reduce surface $p\text{CO}_2$ and prevent CO_2 outgassing.

When combined, Figures 2 and 3A reveal the close connection between surface $p\text{CO}_2$ and the timing of sea ice melt observed during ASPIRE. The polynya first opened in the eastern ASP

(east of $\sim 115^\circ\text{W}$) in early November, allowing for a longer season of phytoplankton growth and the almost $200 \mu\text{atm}$ differential in $p\text{CO}_2$ between the central and western polynya (west of $\sim 115^\circ\text{W}$), which was just opening when we arrived in mid-December. Furthermore, we observed temporal $p\text{CO}_2$ variation when we resampled some areas: the western ASP at the beginning of the cruise (December 14, 2010; the westernmost leg of the cruise track at $\sim 117.5^\circ\text{W}$) was slightly undersaturated in $p\text{CO}_2$ ($\sim 330 \mu\text{atm}$), presumably due to newly exposed water; during the final period of the cruise (December 24, 2010) in a nearby area (cruise leg at $\sim 116^\circ\text{W}$), $p\text{CO}_2$ was substantially more undersaturated ($\sim 200 \mu\text{atm}$) due to a longer open water period. As in the Weddell Sea (Bakker et al. 2008) and many other polynyas (Miller and DiTullio, 2007), the seasonal pattern of melting sea ice plays a crucial role in affecting $p\text{CO}_2$, and thus the air-sea CO_2 flux in the ASP.

How even near future regional sea ice changes might affect CO_2 fluxes in this critically important region is uncertain. We speculate that an earlier opening of the ASP could extend the productive season and enhance the magnitude of the phytoplankton bloom, if enough light and iron are available. In this event, the ASP could become a greater carbon sink in the near future. However, extending the open water season too much could reduce sea ice melt-induced stratification and enhance light limitation (Schofield et al., 2014), suggesting that the ASP carbon sink also depends on the continued longevity of the surrounding seasonal marginal ice zone.

Recent studies (Le Quéré et al., 2007; Lovenduski et al., 2008) indicate that the Southern Ocean CO_2 sink has weakened over the past three decades (1979–2004) due to large-scale changes in winds and in the wind-driven ocean circulation. This trend is predicted to continue into the future. Climate changes in the Antarctic are playing an increasingly significant role in regulating the size of the carbon sink in the Southern Ocean. There is no doubt that Antarctic

polynyas are highly climate-sensitive, with some undergoing radical changes like the ASP and Mertz Glacier Polynya (Shadwick et al., 2013); they should continue to be foci of future studies of biogeochemical cycling in the Antarctic.

5. Conclusions

As the most biologically productive polynya per unit area in Antarctic waters, with the highest interannual variability (Arrigo and van Dijken, 2003), the ASP provides a window to investigate and better understand the sensitivities and vulnerability of biogeochemical cycling in the coastal regions of Antarctica. With ASPIRE, we were able to identify three main regions of the ASP having different $p\text{CO}_2$ concentrations and thus different air-sea CO_2 fluxes: a large central zone dominated by a massive phytoplankton bloom, low $p\text{CO}_2$, and high rates of CO_2 uptake; a small near-ice-shelf zone dominated by deep mixed layers, high $p\text{CO}_2$, and outgassing; and a third marginal ice zone with relatively low biological productivity but undersaturated $p\text{CO}_2$, resulting from sea ice melt-driven reductions in $p\text{CO}_2$. Currently, the regional impact of the ASP is dominated by the phytoplankton bloom, making the ASP a significant carbon sink relative to other continental shelves and a disproportionate contributor to the overall Southern Ocean carbon uptake. As the net impact of the ASP on future global carbon cycling depends on the climate sensitivity and temporal distribution of these three zones, a better seasonal understanding of these distinctive regions is greatly needed.

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Contributions

- Contributed to conception and design: PY and SS
- Contributed to acquisition of data: PY, SS, KL
- Contributed to analysis and interpretation of data: LM, PY, SS, KL
- Drafted and or revised the article: LM, PY, SS, KL
- Approved the submitted version for publication: LM, KL, SS, PY

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Competing interests

The authors have no competing interests or conflicts of interest.

Data accessibility statement

Original $p\text{CO}_2$ data is publically available at Lamont Doherty Earth Observatory:

http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/Palmer_data/1005SFC.PRT

All other data are publically available from BCO-DMO: <http://www.bco-dmo.org/project/2132>

Figure Titles and Legends

Figure 1 - ASPIRE sampling region and cruise track

Ship track of ASPIRE (NBP10-05) within the Amundsen Sea Polynya region overlaid on a Moderate Resolution Imaging Spectroradiometer (MODIS) Terra satellite image from January 2, 2011. Open water is dark, sea ice to the north and west is light gray, and the Getz Ice Shelf (GIS), Dotson Ice Shelf (DIS), and Thwaites Iceberg Tongue (TIT) in the south are white. Inset indicates the study area (black square) in the South Pacific sector of west Antarctica. The ship track before December 14 is dark blue; for December 14–20, light blue; December 21–27, green; December 28 to January 3, yellow; and after January 4, red. Data from sections of the ship track in heavy sea ice cover were not included in the open water analyses.

Figure 2 - The opening of the Amundsen Sea Polynya in 2010–2011

MODIS Terra images (250 m resolution; collection date below each map) show the ASP region before and during ASPIRE (A–E). Black is open water; white is either sea ice, glacial ice, or cloud cover (somewhat distinguishable by texture); coastal features as identified in Figure 1. Original MODIS images (A–E) courtesy of L. Schoeller (AGIC). Images A–E are noted by red arrows on a plot of daily open water area through time (October 1, 2010, to April 1, 2011) as determined by AMSR-E (described in Methods).

Figure 3 - Underway observations during ASPIRE

Underway measurements of $p\text{CO}_2$ (μatm) (A), chlorophyll a fluorescence (mg m^{-3}) (B) and dissolved oxygen concentration ($\mu\text{mol L}^{-1}$) (C) are shown for sea surface of the polynya. Warm colors (red) indicate high values; cool colors (purple) indicate low values. Dashed white line is the periphery of the open water region on January 2, 2011. Continent is dark gray; glacial ice sheets are white. Bathymetric contours (Nitsche et al., 2007) step from darkest gray for the deepest zone (> 1000 m) near the coast, to intermediate shades of grays for trough areas (750–1000 m) extending north, predominant troughs (500–750 m), and shallower shelf areas (250–500 m), to lightest gray for shallowest areas (0–250 m) near the coast.

Figure 4 - Relationships between $p\text{CO}_2$ and other underway measurements

Underway measurements of $p\text{CO}_2$ (μatm , $n = 6209$) are plotted against sea surface temperature (SST, $^{\circ}\text{C}$) (A), salinity (unitless) (B), and chlorophyll a fluorescence (relative units) (C).

Figure 5 - Relationship between $p\text{CO}_2$ and chlorophyll a

Underway measurements of $p\text{CO}_2$ (μatm) are plotted against chlorophyll a fluorescence (relative units, log scale): $R^2 = 0.89$; $n = 6500$.

Figure 6 - Carrillo-style plot of saturation states of $p\text{CO}_2$ and oxygen

Percentages of dissolved oxygen saturation (DO_sat) are plotted against percentages of $p\text{CO}_2$ saturation (A). Crossbar represents 100% saturation levels of $p\text{CO}_2$ and DO; it divides the figure into four quadrants. Of these, Quadrant I (upper left; excess DO, depleted $p\text{CO}_2$) suggests net

photosynthesis, Quadrant III (lower right; depleted DO and excess $p\text{CO}_2$) suggests net respiration, and Quadrant IV (lower left, undersaturated DO and $p\text{CO}_2$) suggests cooling. The modeled effects of photosynthesis (PQ, green curve) and photosynthesis plus warming (PQ + Warming, blue curve) on Winter Water (WW) endmember (pink) are plotted over the observations. The subset of observations from near the DIS are also shown (lower right) along with the mCDW endmember. Inset upper right shows the data distribution following a $56 \mu\text{atm}$ adjustment in $p\text{CO}_2$ from sea ice alkalinity contributions. Spatial distribution of data are shown by quadrant, where Quadrant I is red, III is purple, and IV is black (B). Bathymetry, coasts, and sea ice edge are the same as in Figure 3.

Figure 7 – Thicker mixed layer depth near the Dotson Ice Shelf

Close-up of cruise track map (A) color-coded for measurements of $p\text{CO}_2$ (μatm) shows location (red outline) of Dotson Ice Shelf stations expanded below (coasts and bathymetry as in Figure 3). Cross sections of water properties (low values are cool, purple; high values are warm, red) for the upper 400 m are shown moving (left to right) from the ice shelf to the north-northwest for sigma-theta (kg m^{-3} ; = (density – 1) / 1000) (B), potential temperature ($^{\circ}\text{C}$) (C), and salinity (unitless) (D). Mixed layer depth at Station 11 near the ice shelf is significantly thicker (~ 100 m) than at Station 8 ~ 5 km north (stations shown in expansion of A).

Figure 8 - Regional wind directions

Regional monthly views of winds and sea ice concentration in 2010–2011 are shown for the greater Amundsen Sea region. The vectors are the NCEP/NCAR Reanalysis 10-m winds; color shading shows GSFC Bootstrap SSM/I sea ice concentrations where dark blue is open water and white is complete sea ice cover. The solid red and green contours outline the 15 and 75% sea ice

concentrations, respectively. The ASP/DIS region generally experiences offshore (southerly) winds, which could facilitate upwelling.

Figure 9 - Shipboard wind speed

Measurements of shipboard wind speed (m s^{-1}) at the 25 m height of the ship's mast are plotted against time, showing the average and ± 1 standard deviation for the sampling period ($8.6 \pm 3.5 \text{ m s}^{-1}$; $n = 6500$) as three horizontal lines. Wind speeds ranged from 0.2 to 18.9 m s^{-1} . The average dropped to $7.9 \pm 3.2 \text{ m s}^{-1}$ when corrected to 10 m height. Gaps indicate transits into sea ice-covered regions.

Figure 10 - Air-sea CO_2 flux density

Spatial distribution (ODV DIVA Gridding) of air-sea CO_2 flux ($\text{mmol C m}^{-2} \text{ d}^{-1}$), based on $p\text{CO}_2$ gradient, gas exchange coefficients, and average shipboard wind speed, is shown for the Amundsen Sea Polynya. Positive values (warm, red) imply carbon flux out of the ocean (outgassing), while negative values (cool, purple) indicate carbon flux into the ocean (uptake). Coasts and sea ice cover (dashed black line) are as in Figure 3.