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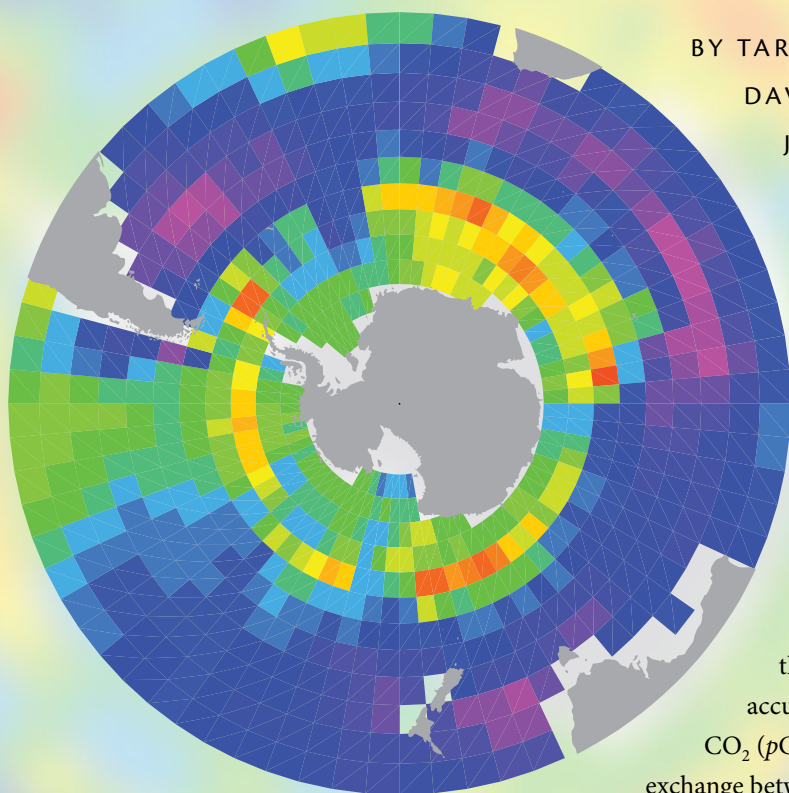
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# THE CHANGING CARBON CYCLE IN THE SOUTHERN OCEAN



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**ABSTRACT.** Various human activities, including fossil fuel combustion and forest clearing, emit about eight petagrams (or billion tons) of carbon in the form of  $\text{CO}_2$  into the atmosphere annually. The global ocean absorbs about two petagrams of  $\text{CO}_2$ , and about a half of that amount is absorbed by the Southern Ocean south of  $30^\circ\text{S}$ , thus slowing the rapid accumulation of  $\text{CO}_2$  in the atmosphere. Partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) is a measure of the chemical driving force for the  $\text{CO}_2$  exchange between the ocean and the atmosphere. This paper discusses its space and time distribution over the Southern Ocean. The major sink zone for atmospheric  $\text{CO}_2$  is located in a latitude belt between  $30^\circ\text{S}$  and  $50^\circ\text{S}$ , where the biological utilization of  $\text{CO}_2$  and cooling of warm subtropical waters flowing southward produce low seawater  $p\text{CO}_2$ . Strong winds in this zone also enhance the ocean's uptake. Although the source-sink conditions vary over a wide range through the seasons in the areas south of  $50^\circ\text{S}$ , this zone is a small sink on an annual average. Winter observations show that surface water  $p\text{CO}_2$  values in the source region for Antarctic Intermediate Water have increased at a rate faster than the atmospheric increase rate, suggesting that the ocean  $\text{CO}_2$  sink intensity has been weakening for several decades and has changed from a net sink to a net source since 2005. The results of ocean general circulation-biogeochemistry model studies are found to be consistent with the observations.

## INTRODUCTION

The Southern Ocean is a major region for the formation of deepwater masses that fill the ocean basins, and it is an important conduit for exchange of heat, momentum, and dissolved gases between the atmosphere and the ocean interior. The global ocean is currently absorbing annually about 2 Pg of carbon (1 Pg = 1 petagram =  $10^{15}$  grams = 1 billion tons) from the air in the form of  $\text{CO}_2$  gas, and the Southern Ocean south of 30°S takes up about 1 Pg of carbon. Thus, the Southern Ocean's significant role in the uptake and long-term storage of anthropogenic  $\text{CO}_2$  emitted to the atmosphere affects Earth's climate.

The difference between the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) in seawater and that in the overlying air determines the direction of  $\text{CO}_2$  transfer across the sea surface. Two opposing processes primarily govern  $\text{CO}_2$  chemistry in seawater: sinking of biological products from the photic zone to deep-ocean regimes (i.e., the biological pump), and upward transport by upwelling deep waters of  $\text{CO}_2$  and nutrients formed by the decomposition of biological debris. Thus, understanding the ocean's uptake rates of atmospheric  $\text{CO}_2$  requires knowledge of ocean circulation dynamics as well as production and respiration dynamics in a wide range of ecosystems. A large number of observational and model studies have been conducted in recent years. The observational studies are based on the sea-air  $p\text{CO}_2$  difference (Takahashi et al., 2009),  $^{13}\text{C}/^{12}\text{C}$  mass balance (Quay et al., 2003), atmospheric oxygen and  $\text{CO}_2$  changes (Bender et al., 2005; Manning and Keeling, 2006), and  $\text{CO}_2$  change in the ocean (Sabine et al., 2004). The model studies include coupled Ocean

General Circulation-Biogeochemistry models (OGCM) (Mikaloff-Fletcher et al., 2006; Sarmiento and Gruber, 2006; Jacobson et al., 2007; Lenton and Matear, 2007; Gruber et al., 2009; Le Quéré et al., 2010), and inversion of atmospheric  $\text{CO}_2$  data using Atmospheric General Circulation models (AGCM) (Gurney et al., 2008). Gruber et al. (2009) reviewed the estimates for  $\text{CO}_2$  uptake flux over the contemporary global ocean obtained by four groups of independent methods: inversion of the ocean data using 10 OGCMs, 13 ocean forward models (OCMIP-2), inversion of atmospheric  $\text{CO}_2$  data (Gurney et al., 2008), and sea-air  $p\text{CO}_2$  difference (Takahashi et al., 2009). Although the mean air-to-sea flux estimates for the contemporary global ocean obtained by these methods are in general agreement at  $1.5 \pm 0.5 \text{ Pg C yr}^{-1}$ , notable discrepancies are found in the Southern Ocean. The ocean inversion methods suggest a relatively uniform weak sink in the areas south of 58°S, whereas the sea-air  $p\text{CO}_2$  difference ( $\Delta p\text{CO}_2$ ) data in these areas suggest a  $\text{CO}_2$  source. Processes governing atmosphere-ocean interactions in the Southern Ocean region are complex

because of the large seasonal variability in temperature, wind regimes, ice/water conditions, and biological activities. Although significant progress has been made in recent years due to improved research facilities, observations are still limited because of operational difficulties related to hostile weather conditions, and observation-based estimates are subject to considerable uncertainty. Model results are also subject to uncertainties because of limited time-space resolutions and imperfections in the parameterizations for various processes, including eddy mixing, ice formation, and biological processes.

In this article, we review recent progress in biogeochemical studies on the carbon cycle with emphasis on the temporal and spatial variability of  $p\text{CO}_2$  in Southern Ocean surface water. Here, the Southern Ocean is defined as the oceanic areas south of 30°S that include a major sink zone for atmospheric  $\text{CO}_2$  centered at 40°S. First, we review climatological mean distribution of surface water  $p\text{CO}_2$  and net sea-air  $\text{CO}_2$  flux. Second, we discuss the change in surface water  $p\text{CO}_2$  and the intensity of the ocean  $\text{CO}_2$  sink in circumpolar waters.

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## SEA-AIR CO<sub>2</sub> TRANSFER OVER THE SOUTHERN OCEAN

Before we discuss CO<sub>2</sub> exchange over the Southern Ocean, we briefly review relevant oceanographic information. Because  $p\text{CO}_2$  is the primary quantity measured by our group, we next discuss the time-space distribution of surface water  $p\text{CO}_2$ , and then present the net sea-air CO<sub>2</sub> flux.

### General Structure of the Upper Waters

The oceanographic features in the Southern Ocean are primarily zonal due to strong, persistent westerly winds blowing around the Antarctic Continent. Several oceanographically distinct zones are separated by fronts where water properties change (Orsi et al., 1995): from north to south, these are the Subtropical Front (STF), the Subantarctic Front (SAF), the Polar Front (PF), the

Antarctic Divergence (AD), and the Continental Water Boundary (CWB). The Antarctic Circumpolar Current (ACC) includes the waters south of STF and north of CWB. Figure 1a shows the approximate positions of these fronts. In the high-latitude areas (60°S–70°S), high-salinity water (Lower Circumpolar Deep Water, LCDW, with a salinity of ~ 34.68) upwells along the Antarctic Divergence (AD). As the upwelled water drifts northward, it is altered by exchange with air, and it is subducted along the Polar Front (PF; 50°S–60°S). In general, high-latitude Southern Ocean surface waters are high in nutrients and CO<sub>2</sub> but low in chlorophyll concentrations (called HNLC conditions), with the exception of local waters in the coastal zone around Antarctica. The high concentrations of nutrients and CO<sub>2</sub> are due to the wintertime convective mixing of Upper Circumpolar Deep Water (UCDW) rich

in CO<sub>2</sub> and nutrients as well as northward Ekman transport of the upwelled deep waters. In the vicinity of the Sub-Antarctic front (SAF; 50°S–55°S), low-salinity Intermediate Water (AAIW, temperatures 3°–5°C, salinity about 34.3) is formed and sinks to the base of the main thermocline (~ 900 m deep). Further north, along the Subtropical Front (~ 40°S), the sub-Antarctic surface water that is replete with nutrients but low in chlorophyll (i.e., HNLC) converges with warm subtropical surface water that is depleted in nutrients. In the resulting high primary productivity zone that is clearly visible in satellite color images (Moore and Abbott, 2000), surface water  $p\text{CO}_2$  is reduced, creating a strong CO<sub>2</sub> sink zone centered around 40°S in the Atlantic, Indian, and most of the Pacific Oceans. These waters (Mode Water) sink to mid-depth and transport atmospheric CO<sub>2</sub> to the subsurface regime.

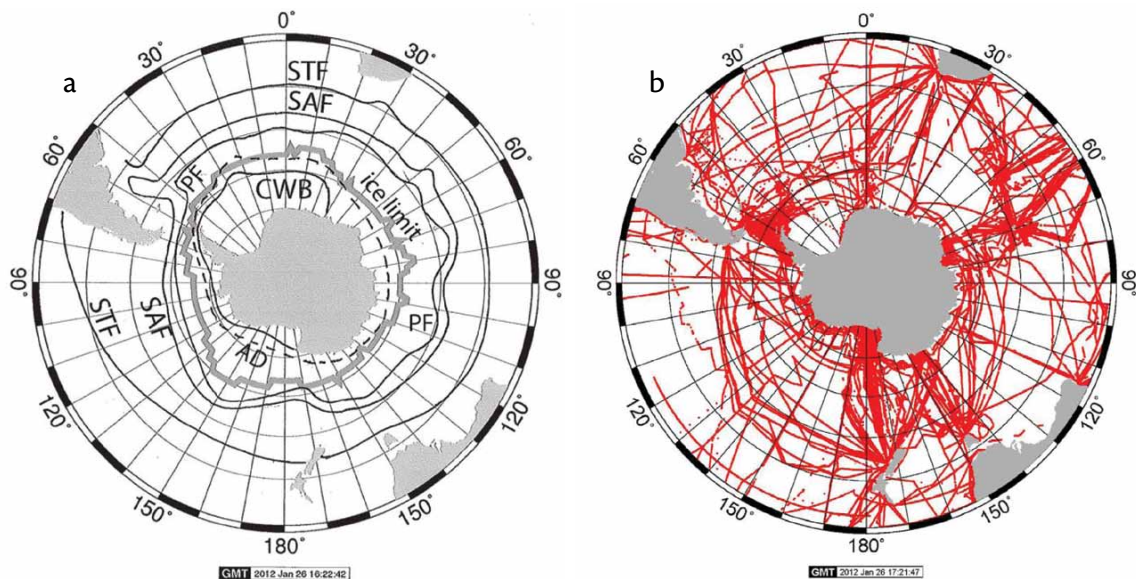


Figure 1. (a) Zonal structure of Southern Ocean surface waters (based on Orsi et al., 1995), showing the approximate locations of fronts: STF = Subtropical Front. SAF = Subantarctic front. PF = Polar Front. AD = Antarctic Divergence. CWB = Continental Water Boundary. Winter ice limit is indicated with a broad gray curve. (b) Locations of surface water  $p\text{CO}_2$  measurements between 1960 and 2011 over the Southern Ocean. Approximately 2.1 million  $p\text{CO}_2$  measurements were made during this period; the data (Takahashi et al., 2011) are available at the Carbon Dioxide Information and Analysis Center at Oak Ridge National Laboratory (CDIAC; [http://cdiac.ornl.gov/oceans/LDEO\\_Underway\\_Database](http://cdiac.ornl.gov/oceans/LDEO_Underway_Database)).

## CO<sub>2</sub> Partial Pressure in Surface Water

In seawater, CO<sub>2</sub> molecules exist in three forms: as CO<sub>2</sub> molecules in an aqueous environment ([CO<sub>2</sub>]<sub>aq</sub> or [H<sub>2</sub>CO<sub>3</sub>]) and as two ionized forms ([HCO<sub>3</sub><sup>-</sup>] and [CO<sub>3</sub><sup>=</sup>]). The sum of these species is referred to as the total concentration of CO<sub>2</sub> dissolved in seawater (TCO<sub>2</sub>), which is measured as the total amount of CO<sub>2</sub> extracted from an acidified seawater sample. In surface ocean waters, about 1% of TCO<sub>2</sub> exists as [CO<sub>2</sub>]<sub>aq</sub>, about 4% as [CO<sub>3</sub><sup>=</sup>], and 95% as [HCO<sub>3</sub><sup>-</sup>]. Of these, [CO<sub>2</sub>]<sub>aq</sub> is the only species involved in the exchange of CO<sub>2</sub> between the sea and the overlying air. The partial pressure of seawater CO<sub>2</sub> is a measure of [CO<sub>2</sub>]<sub>aq</sub>, and represents the driving force for the transfer of CO<sub>2</sub> gas across the sea-air interface. The difference between *p*CO<sub>2</sub> in seawater and air ( $\Delta p\text{CO}_2$ ) determines the direction and magnitude of the net CO<sub>2</sub> flux across the interface. When the *p*CO<sub>2</sub> in seawater is greater than that in the overlying air ( $\Delta p\text{CO}_2 > 0$ ), the net flux is from sea to air; when  $\Delta p\text{CO}_2 < 0$ , the net flux is from air to sea. The net sea-air flux may be estimated by multiplying the sea-air *p*CO<sub>2</sub> difference by the gas transfer coefficient across the sea surface.

## Observations of Surface Water *p*CO<sub>2</sub>

Figure 1b shows the locations of where surface water *p*CO<sub>2</sub> data have been collected over the Southern Ocean since the 1960s. The observations were made using a gas-seawater equilibrator coupled with a CO<sub>2</sub> analyzer (gas chromatograph or IR analyzer) that was calibrated using three or more certified CO<sub>2</sub>-air reference gas mixtures by the Climate Monitoring

and Diagnostics Laboratory of the National Oceanic and Atmospheric Administration (NOAA), Boulder, CO. Equilibrators (bubbler, membrane, or shower types; e.g., Chipman et al., 1993; Hales et al., 2004; Newberger, 2004) were operated either in a seawater flow-through mode for continuous underway measurement of water samples pumped from an intake located a few meters below the sea surface, or in a discrete water mode for water samples collected in nonmetallic sampling bottles. Seawater temperature and salinity and equilibration pressure and temperature are recorded and used for computing in situ *p*CO<sub>2</sub> values. The overall precision of the *p*CO<sub>2</sub> data is estimated to be  $\pm 2 \mu\text{atm}$ .

## Climatological Mean Distribution of Surface Water *p*CO<sub>2</sub>

Figure 2 displays monthly distribution maps for the climatological mean sea-air *p*CO<sub>2</sub> difference for the reference year 2000. Here, we briefly describe the method used for constructing these maps. Because *p*CO<sub>2</sub> has increased with time in response to the increase in atmospheric CO<sub>2</sub>, data obtained in different years and months are corrected to a reference year 2000 using a mean rate of  $1.5 \mu\text{atm yr}^{-1}$ , which is assumed to be equal to the mean atmospheric CO<sub>2</sub> increase. The corrected *p*CO<sub>2</sub> values are binned into  $4^\circ \times 5^\circ$  boxes, and monthly mean values for each box are computed. Because fewer than 50% of the boxes have observations, they are interpolated using a two-dimensional diffusion-advection transport equation to fill all the boxes. The sea-air *p*CO<sub>2</sub> differences ( $\Delta p\text{CO}_2$ ) are computed using atmospheric *p*CO<sub>2</sub> values that are calculated

from zonal mean atmospheric CO<sub>2</sub> concentrations in dry air for the year 2000 (GLOBALVIEW, 2006) and monthly mean values for barometric pressure and water vapor pressure at the sea surface. The computational details are described in Takahashi et al. (2009), and the climatological mean values in each box are available at <http://www.ldeo.columbia.edu/res/pi/CO2>.

Figure 2 shows that a strong CO<sub>2</sub> sink zone (blue color with negative  $\Delta p\text{CO}_2$ ) is located near 40°S during the austral winter months (June through October). Its formation is attributed primarily to high productivity in the high-chlorophyll zone observed by satellites over the same latitudes (see Plates 3 and 6 in Moore and Abbott, 2000). However, the collocation of the CO<sub>2</sub> sink zone and the high-productivity zone is only qualitative because seawater *p*CO<sub>2</sub> is governed by net community production, which includes primary production as well as the respiration, recycling, and export of organic carbon from the mixed layer. Peaking of the sink intensity in August and September suggests that winter cooling of surface water plays an important role in the formation of the sink. As the season progresses, the CO<sub>2</sub> sink zone moves southward due mainly to increased photosynthesis under longer daylight hours and warmer temperatures. The biological drawdown effect is clearly seen in the areas north of the Weddell and Ross Seas, where satellites observe high concentrations of chlorophyll (see Plate 3 of Moore and Abbott, 2000). Boutin et al. (2008) measured sea-air *p*CO<sub>2</sub> difference continuously in the zone between the PF and the SAF (40°S–55°S) in the Pacific and Indian Ocean sectors using the CARIOCA

(Carbon Interface Ocean Atmosphere) drifter buoys during all seasons from 2001 to 2006, observing that the waters in these areas are mostly undersaturated with a mean  $\Delta p\text{CO}_2$  of  $-19 \mu\text{atm}$ . Their mean value is similar to our climatological mean within about  $2 \mu\text{atm}$ .

In the permanently open ocean zone

(POOZ) of the ACC between  $50^\circ\text{S}$  and  $60^\circ\text{S}$ ,  $\Delta p\text{CO}_2$  is generally small (light blue and green in Figure 2) because of the competing effects of temperature and  $\text{TCO}_2$  on seawater  $p\text{CO}_2$ : summertime photosynthesis reduces  $\text{TCO}_2$  and  $p\text{CO}_2$ , counteracting  $p\text{CO}_2$  increase due to warming, whereas wintertime

cooling counteracts the increasing effect on  $p\text{CO}_2$  of upwelled high  $\text{TCO}_2$  deep waters. In the Indian Ocean sector between  $50^\circ\text{S}$  and  $58^\circ\text{S}$ , Metzl et al. (2006) measured  $p\text{CO}_2$ ,  $\text{TCO}_2$ , alkalinity, and the concentrations of chlorophyll, silicate, and nitrate during January and August cruises in

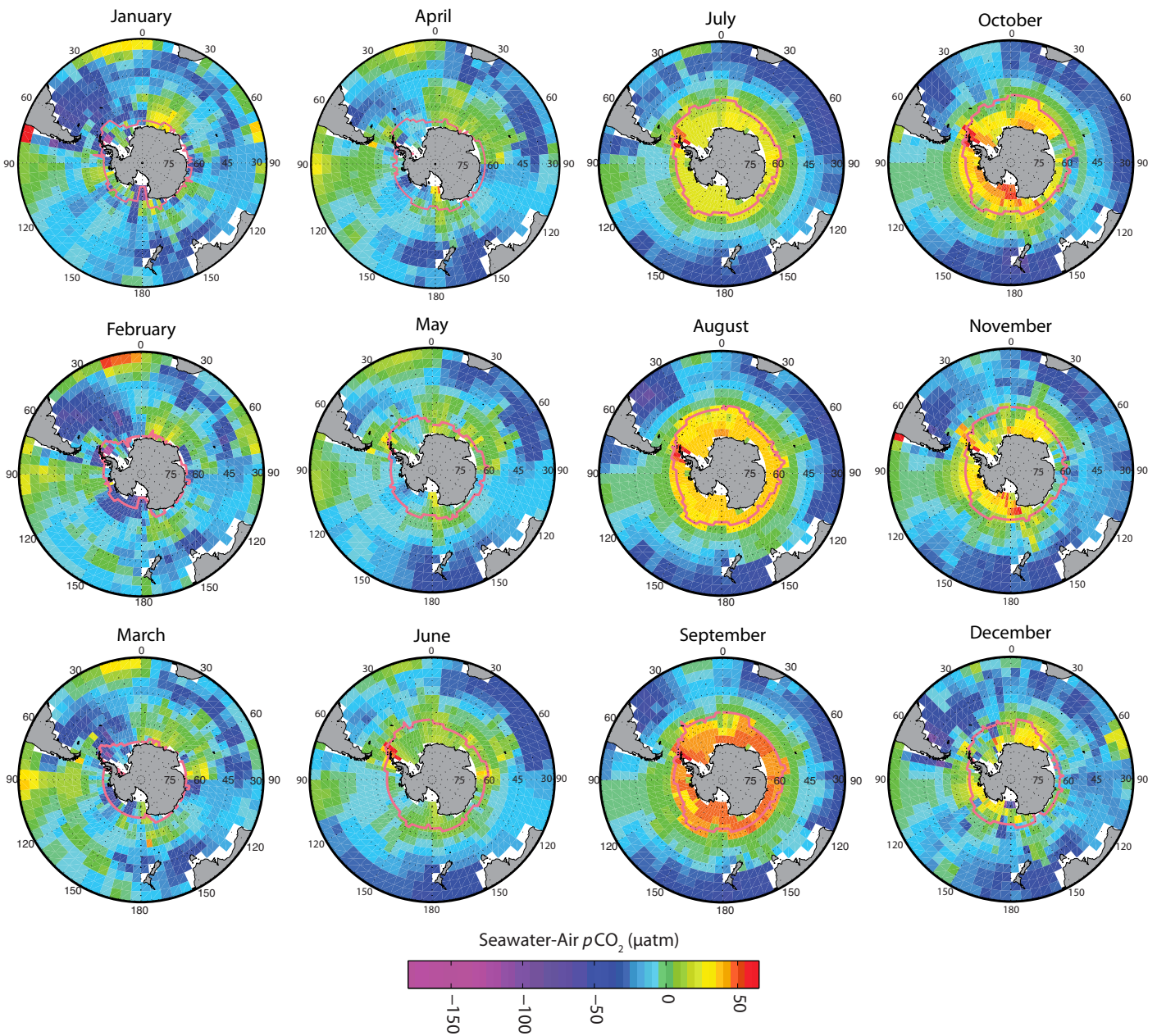


Figure 2. Monthly distribution maps for the climatological mean sea-air  $p\text{CO}_2$  difference ( $\mu\text{atm}$ ) for the reference year 2000. The pink curves indicate the approximate locations of the northern edges of ice fields, and hence define the seasonal ice zone. The high  $p\text{CO}_2$  values in the under-ice mixed layer are due to the upward mixing of high  $\text{CO}_2$  Upper Circumpolar Deep Water.

2000, observing that the summertime seawater  $p\text{CO}_2$  was lower than the atmospheric  $p\text{CO}_2$  ( $\Delta p\text{CO}_2 \sim -15 \mu\text{atm}$ ) due to photosynthesis, and the winter  $p\text{CO}_2$  was higher than the atmospheric ( $\Delta p\text{CO}_2 \sim +10 \mu\text{atm}$ ) due to the upwelling of high- $\text{CO}_2$  deep waters. Because the alkalinity was found to be similar, the biological effect on  $\text{CO}_2$  is due mostly to the production of organic carbon.

In the seasonal ice zone (SIZ, south of  $\sim 60^\circ\text{S}$ , poleward of the “ice limit” curve in Figure 1 and poleward of the pink curves in Figure 2), the seawater in autumn has low  $p\text{CO}_2$  values because of biological utilization during the preceding season. As the sea ice field develops, a mixed layer of seawater forms under the ice field, and its  $\text{CO}_2$  and nutrient concentrations increase as deep waters are mixed into it as the seasons progress. As Figure 3 shows, the  $p\text{CO}_2$  in ice field waters is low ( $\sim 340 \mu\text{atm}$ ) soon after the formation of the ice in June (day 170), and it increases during the progressing winter season to about  $420 \mu\text{atm}$  in September (day 260). Although algae grow in the basal zone of sea ice, their photosynthetic utilization of  $\text{CO}_2$  is slow because of low light conditions due to winter darkness and ice-snow cover (Lizotte, 2001; Arrigo and Thomas, 2004), and it does not significantly reduce the large amount of  $\text{CO}_2$  dissolved in a thick under-ice mixed layer. From mid-July through September,  $p\text{CO}_2$  in the under-ice waters exceeds the atmospheric  $p\text{CO}_2$ , and therefore, the under-ice water  $\text{CO}_2$  is released to the air when the water is exposed to the air. In the early spring, as sea ice fields start to break up, the water in the marginal ice zone (MIZ) should be a  $\text{CO}_2$  source. When the winter sea ice thins

and melts away in the spring, phytoplankton blooms, fueled by high nutrient concentrations, reduce the  $p\text{CO}_2$  in water, and the water rapidly becomes a sink for atmospheric  $\text{CO}_2$ , as Bakker et al. (2008) observe in the Weddell Sea area. The transition from  $\text{CO}_2$  source to sink occurs as the ice fields retreat in the spring, sweeping across the  $15 \times 10^6 \text{ km}^2$  SIZ of the Southern Ocean.

The coastal waters reflect the properties of upwelled waters modified by complex shelf processes, and they regulate the transport of atmospheric  $\text{CO}_2$  into the deep and abyssal regimes (see Takahashi and Chipman, 2012, in this issue). In summer, the Ross and Weddell Seas and the coastal waters in the Amundsen and Bellingshausen Seas are strong  $\text{CO}_2$  sinks with  $p\text{CO}_2$  values as low as  $170 \mu\text{atm}$  ( $\sim 210 \mu\text{atm}$  below the air  $p\text{CO}_2$ ) due to intense photosynthesis, whereas they are a strong source during winter with  $p\text{CO}_2$  as high as  $425 \mu\text{atm}$

( $\sim 45 \mu\text{atm}$  above the present air  $p\text{CO}_2$ ) due to upwelling of high- $\text{CO}_2$  deep waters (Bakker et al., 1997, 2008; Bates et al., 1998; Rubin et al., 1998; Sweeney, 2003; Hales and Takahashi, 2004; Rubin, 2003; Arrigo and van Dijken, 2007).

#### Net Sea-Air $\text{CO}_2$ Flux from $\Delta p\text{CO}_2$

The net  $\text{CO}_2$  flux across the sea surface ( $F_{\text{sea-air}}$ ) may be estimated by Equation 1, in which the main drivers are wind speed and sea-air  $p\text{CO}_2$  difference ( $\Delta p\text{CO}_2$ ):

$$F_{\text{sea-air}} (\text{g C m}^{-2} \text{ month}^{-1}) = 0.585 \cdot K_o \cdot (\text{Sc})^{-1/2} \cdot (U_{10})^2 \cdot \Delta p\text{CO}_2, \quad (1)$$

where  $K_o$  is the solubility of  $\text{CO}_2$  in seawater ( $\text{mol CO}_2 \text{ liter}^{-1} \text{ atm}^{-1}$ ; Weiss, 1974),  $\text{Sc}$  is the Schmidt number (see Wanninkhof, 1992),  $U_{10}$  ( $\text{m sec}^{-1}$ ) is the wind speed at 10 m above the sea surface, and  $\Delta p\text{CO}_2$  is in  $\mu\text{atm}$ . The number 0.585 includes a unit conversion factor (changes from second to month, from liter to  $\text{m}^3$ ), the gas

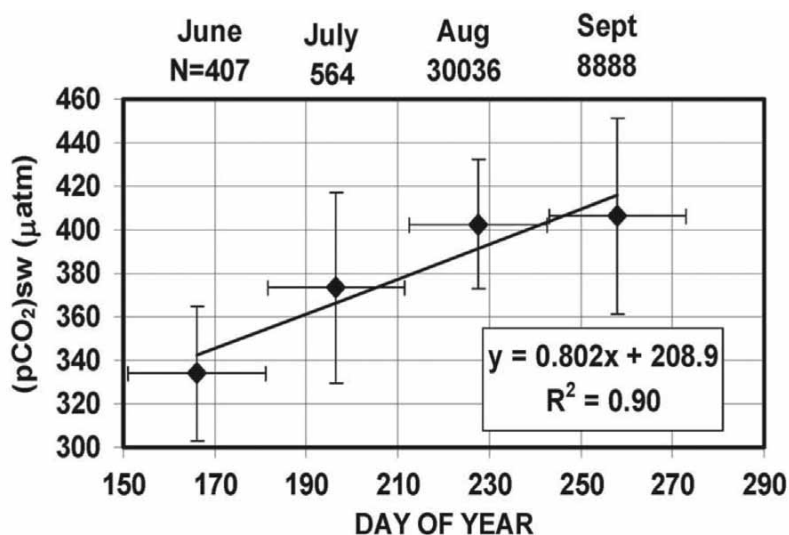


Figure 3. Seawater  $p\text{CO}_2$  observed in ice field waters with temperatures less than  $-1.75^\circ\text{C}$  in areas south of  $60^\circ\text{S}$  during June to September since 1998. The measurements were made possible by improvements in the intake port for the scientific water sampling line aboard RVIB *Nathaniel B. Palmer* that prevent ice clogging. The data obtained in different years are averaged for each month, and one standard deviation is shown. The  $p\text{CO}_2$  in under-ice water increases as the season progresses. From Takahashi et al. (2009)

transfer scaling factor of 0.26, and the reference Schmidt number of  $(660)^{1/2}$  at 20°C for seawater (Takahashi et al., 2009). Although  $K_o$  and  $Sc$  vary with temperature, the temperature effects cancel in the ratio, and  $K_o/(Sc)^{1/2}$  is nearly constant in the ocean temperature range. The  $0.26 (\pm 30\%)$  scaling factor for the gas transfer rate is determined using the bomb carbon-14 data with the Geophysical Fluid Dynamics Laboratory Ocean General Circulation Model (GFDL OGCM; Sweeney et al., 2007) specifically for the 1979–2005 NCEP-DOE AMIP-II Reanalysis six-hour wind data (Kanamitsu et al., 2002), which are used in this study. Several wind speed products are available for the global ocean, and they vary considerably. Hence, the estimated flux varies by about 20%, depending on the wind speed product used (Signorini and McClain, 2009).

### Climatological Mean Sea-Air CO<sub>2</sub> Flux

Figure 4 shows the meridional distribution of climatological mean CO<sub>2</sub> flux over the global ocean in the reference year 2000, which yields a net global ocean CO<sub>2</sub> uptake flux of  $1.6 \pm 0.7$  Pg C yr<sup>-1</sup>. Although the flux uncertainty from the error in  $\Delta pCO_2$  is relatively small (13%), the errors in the scaling factor for the gas transfer rate formula ( $\pm 30\%$ ) and the wind speed variability ( $\pm 20\%$ ) are major contributors to the flux uncertainty (Takahashi et al., 2009). The equatorial waters are the major CO<sub>2</sub> source of about 0.7 Pg C yr<sup>-1</sup>. This source is counteracted by the two major sinks: a 1.0 Pg C yr<sup>-1</sup> sink centered around 40°S in the Southern Hemisphere and a 0.7 Pg C yr<sup>-1</sup> sink centered around 40°N in the Northern Hemisphere. Thus, the Southern Ocean plays a significant

role in the global ocean CO<sub>2</sub> cycle.

Figure 5 shows the climatological mean distributions of CO<sub>2</sub> flux for February and August, and the annual average in the reference year 2000. During the austral summer (February), a belt of strong sink is centered around 45°S. This sink is especially robust in the Atlantic sector, perhaps due to intense mixing caused by rough topography and the confluence of warm subtropical and nutrient rich sub-Antarctic waters. Shallow mixed layers in this area (Dong et al., 2008) also enhance the effect of biological drawdown. Intense sink areas are also found in the Ross Sea gyre area, attributed primarily to biological drawdown of  $pCO_2$  fueled by abundant nutrients and sunlight. The zones south of about 50°S and north of about 40°S are neutral (green) or weak source areas (yellow), reflecting the small  $\Delta pCO_2$  that results from compensating effects of warming and increased biological CO<sub>2</sub> utilization.

During the austral winter (August), wind intensifies and water cools, causing the sink zone centered around 40°S to intensify. The gas transfer rate is increased as a square function of wind speed (Equation 1), and the cooling reduces surface water  $pCO_2$ , although these effects are partially compensated by the increased  $pCO_2$  of upwelling of deep waters. The neutral zone (green) south of the sink zone expands, perhaps due to the increase in deepwater upwelling. In the sea ice zone south of about 55°S, the sea-air CO<sub>2</sub> flux is computed assuming that a layer of solid ice blocks gas exchange and that sea-air gas exchange takes place only through open water areas in ice fields. For the open water areas, the CO<sub>2</sub> flux is computed using Equation 1, in

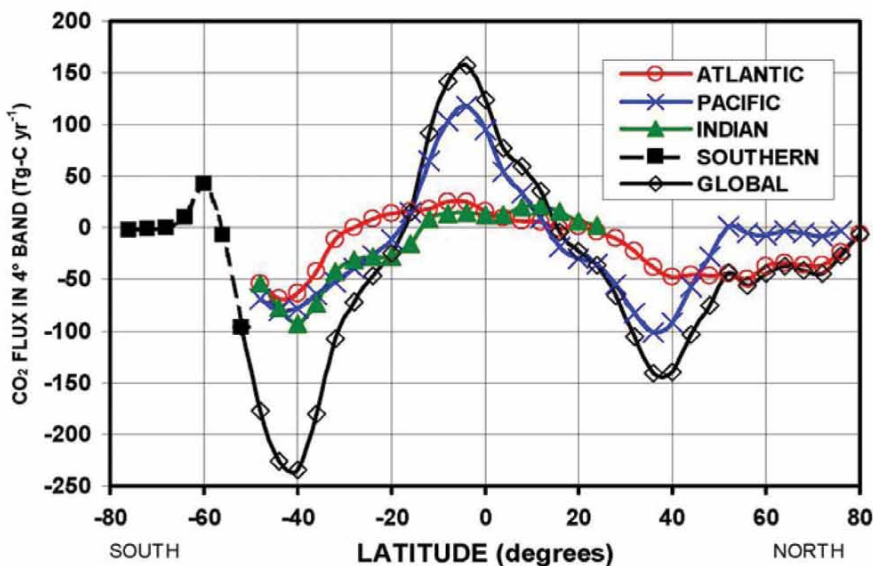


Figure 4. Climatological mean sea-air CO<sub>2</sub> flux in 4° zonal bands in the four major ocean basins in the reference year 2000. The flux values are expressed in Tg C yr<sup>-1</sup> (Tg = teragrams = 10<sup>12</sup> grams = million tons) for each 4°-wide zonal band across each ocean basin. This plot gives a total global air-to-sea flux of 1.6 Pg C yr<sup>-1</sup>. The wind speed data are from the 1979–2005 NCEP-DOE AMIP-II Reanalysis, and the gas transfer coefficient is computed using Equation 1. From Takahashi et al. (2009)



which the  $\Delta p\text{CO}_2$  is represented by ice field measurements shown in Figure 3. In June, the  $\Delta p\text{CO}_2$  in under-ice waters is negative, reflecting the low  $p\text{CO}_2$  conditions produced by the biological pump during the preceding months. Hence, when water is exposed to the air, it acts as a sink for atmospheric  $\text{CO}_2$ , and as the season progresses, it becomes a source by July. For the ice field surrounding the continent, the NCEP/DOE 2 Reanalysis (2005) ice cover data are regridded to our  $4^\circ \times 5^\circ$  grid and averaged for each month. When the ice cover is less than 10% in a  $4^\circ \times 5^\circ$  box area, it is assumed to be all water. Between 10% and 90%, the flux is computed proportional to the water area. Because ice fields have leads and polynyas due to dynamic motion of sea ice, we assume the fields to be 10% open water even though the satellite data report 100% ice cover (Worby et al., 2008). The strong  $\text{CO}_2$  source zone centered around  $60^\circ\text{S}$  (yellow-orange) reflects the ice field edge zone in late winter months, when a large area of seawater with positive  $\Delta p\text{CO}_2$  values is exposed to the air, allowing gas exchange. Although the seasonal ice zone exhibits large seasonal changes in physical, biological, and chemical conditions, this zone appears to make a small contribution in terms of annual sea-air  $\text{CO}_2$  flux to the global sea-air  $\text{CO}_2$  budget.

On the annual mean, the zone centered around  $40^\circ\text{S}$  (magenta-blue; sea surface temperature [SST] between  $10^\circ\text{C}$  and  $15^\circ\text{C}$ ) stands out as a prominent sink for the global sea-air carbon budget. To investigate Southern Ocean  $\text{CO}_2$  uptake and its relationship to the Southern Annular Mode (SAM), Lovenduski et al. (2007) used the forward Parallel Ocean Program Ocean GCM coupled with a

biogeochemical-ecological model. They found strong  $\text{CO}_2$  sink zones centered around  $40^\circ\text{S}$ , and they determined that the sink in the Atlantic and the western Indian Ocean sectors were most intense and the southeastern Pacific less so. Their model results for the distribution and magnitude of the  $\text{CO}_2$  sink/source in the contemporary ocean (see their Figure 3a) are in good agreement with our results in the “Annual” panel in Figure 5. The Ocean GCM results obtained by Lenton and Matear (2007) also exhibit a strong

$\text{CO}_2$  sink zone around  $40^\circ\text{S}$ . However, the distribution patterns are somewhat different from our results: the sink zone is strongest in the Pacific and Indian Ocean sectors, while it is much weaker in the Atlantic sector.

### CHANGE OF THE SOUTHERN OCEAN $\text{CO}_2$ SINK/SOURCE

Whether the  $\text{CO}_2$  sink intensity in the Southern Ocean has changed in recent decades in response to increasing atmospheric loading of  $\text{CO}_2$  and

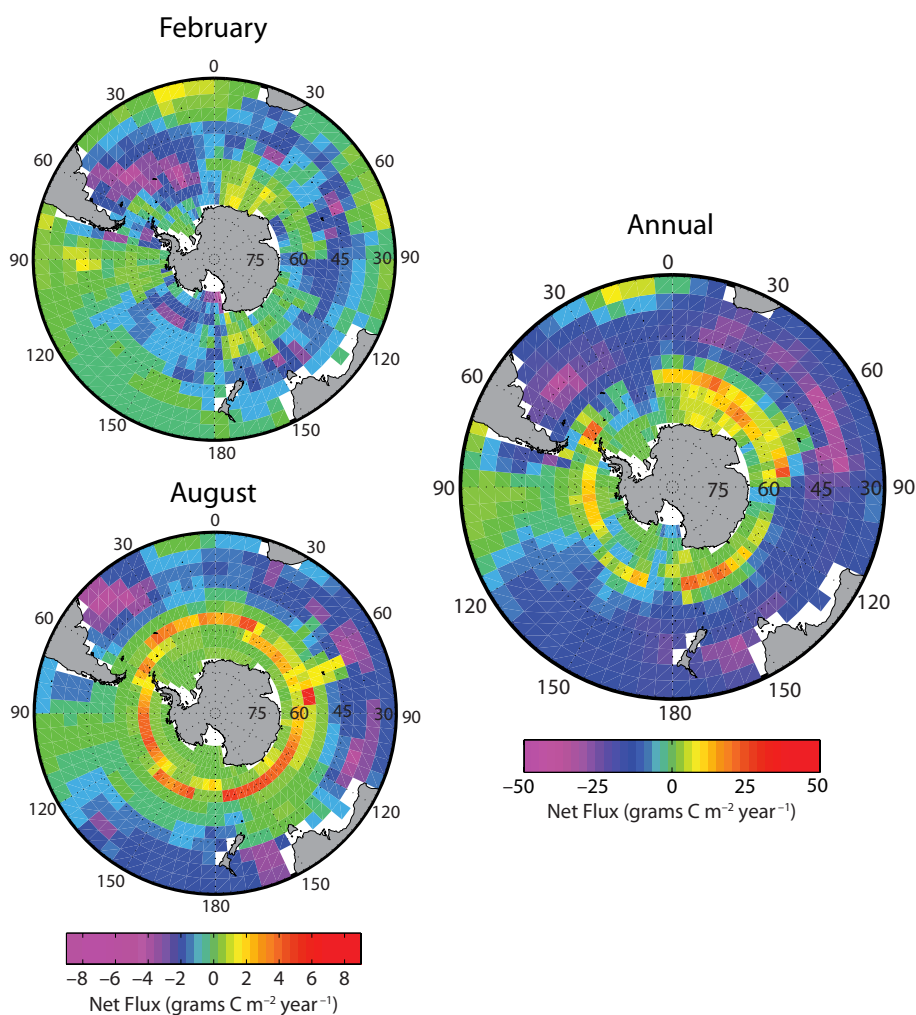


Figure 5. Distribution of climatological mean sea-air  $\text{CO}_2$  flux in the reference year 2000 for February and August, along with the annual mean. See text for the assumptions used for estimating the flux in the sea ice fields. The source zone is indicated with yellow and orange, the sink zone with blue and magenta, and the neutral (small flux) zone with green.

climate change is an important question. This issue has been addressed actively in recent GCM studies. Le Quéré et al. (2007) inverted the atmospheric CO<sub>2</sub> concentration data from 12 stations located south of 30°S to obtain sea-air CO<sub>2</sub> flux, and observed that the Southern Ocean CO<sub>2</sub> sink weakened during 1981–2004. They attributed this weakening to the increase in upwelling of deep waters caused by stronger winds during this period. Le Quéré et al. (2010) used a forward Ocean GCM coupled with a marine biogeochemistry model to investigate the contributions of temperature, atmospheric CO<sub>2</sub>, wind regimes, and heat-water flux to the sea-air CO<sub>2</sub> flux using three different wind products. They found that regional differences in the annual rates for sea-air *p*CO<sub>2</sub> change developed only when the model was driven using both increasing atmospheric CO<sub>2</sub> and changing climate. Their model study yielded a mean decadal rate of Δ*p*CO<sub>2</sub> change of about 20 μatm decade<sup>-1</sup>, which is about 4 μatm decade<sup>-1</sup> faster than the mean atmospheric CO<sub>2</sub> increase rate of about 16 μatm decade<sup>-1</sup> for their study period of 1981–2007. Lenton and Matear (2007) and Lovenduski et al. (2007) used Biogeochemistry-Ocean GCMs to explore the relationship between the SAM and changes in the Southern Ocean CO<sub>2</sub> flux. These investigators found that the southward shift and the intensification of zonal winds that occurred during the positive trend of SAM for the past several decades caused an increase in deepwater upwelling, which in turn increased surface water *p*CO<sub>2</sub> and decreased CO<sub>2</sub> sink intensity. The magnitudes of changes estimated by these model studies are broadly in agreement.

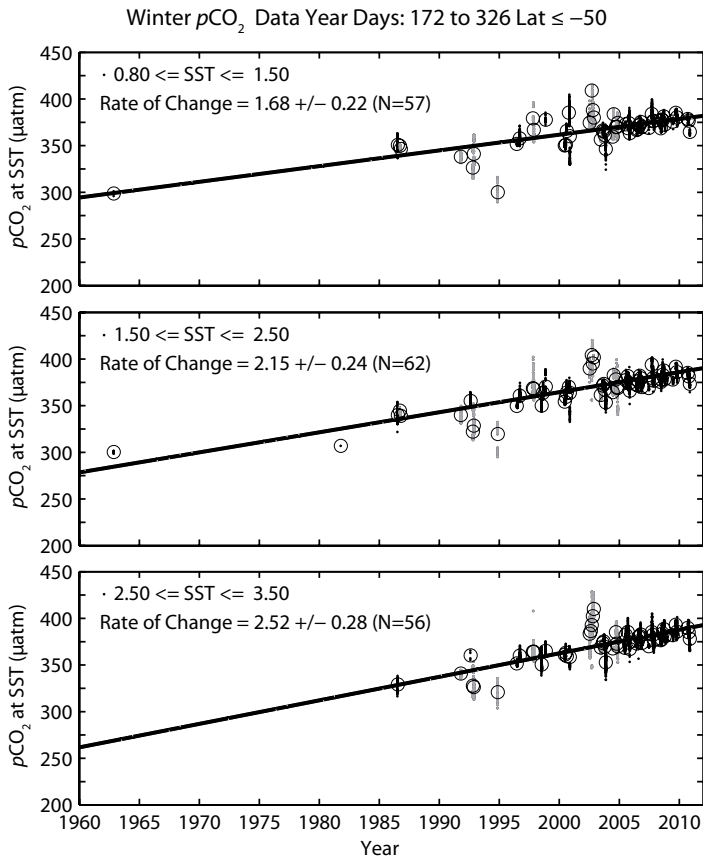
### Circumpolar Open Water Zone

To document how the primary driving force of CO<sub>2</sub> uptake over the Southern Ocean has changed in recent decades, we analyzed the wintertime data for surface water *p*CO<sub>2</sub> in the open ocean water zone, which includes the AAIW formation areas. Because biological activities are minimal and the vertical mixing of water is expected to be maximal during the winter months, the trend in winter surface water *p*CO<sub>2</sub> should indicate the trends in vertical mixing and possibly meridional transport rate. Furthermore, the time trend must be evaluated based on the *p*CO<sub>2</sub> time-series values of a similar water mass or type. We have chosen wintertime SST as the indicator, and divided the data into five temperature zones between 0.8°C and 5.5°C. Figure 6 shows the time plots and data locations, and Table 1 summarizes the results of linear regression analysis for *p*CO<sub>2</sub> and SST in each zone. The *p*CO<sub>2</sub> rates that are corrected for changes in SST are also listed. While the rates for the coldest and warmest zones (0.80°–1.5°C and 4.5°–5.5°C, respectively) are similar to the atmospheric rate, the middle three zones (1.5°–4.5°C, about 50°–55°S) have significantly faster rates (23.9 ± 3.8 μatm decade<sup>-1</sup>) than the atmospheric rate of about 16 μatm decade<sup>-1</sup>, indicating that the ocean CO<sub>2</sub> uptake is weakening. The faster increase in seawater *p*CO<sub>2</sub> compared to atmospheric *p*CO<sub>2</sub> means that this zone, which had been a sink for atmospheric CO<sub>2</sub> since the beginning of our measurements in the 1960s, changed to a source some time after 2005. In 1960, the atmospheric *p*CO<sub>2</sub> was about 310 μatm (CO<sub>2</sub> concentration in dry air of 316 ppm corrected

for the barometric pressure and water vapor), whereas the seawater *p*CO<sub>2</sub> was between 275 and 300 μatm, 10 to 35 μatm below the atmospheric. In contrast, the atmospheric *p*CO<sub>2</sub> was about 377 μatm (385 ppm CO<sub>2</sub> in dry air) in 2010, and the seawater *p*CO<sub>2</sub> was 375 to 385 μatm, equal or slightly greater than the atmospheric value.

Importantly, this temperature zone corresponds to the formation region for the AAIW, and the observed high rate of *p*CO<sub>2</sub> increase suggests a reduction of the CO<sub>2</sub> sink intensity for AAIW due to an increase in upwelling of CO<sub>2</sub>-rich deep waters. Although the validity of the eddy mixing parameterizations used in the ocean model studies has been questioned by Böning et al. (2008) and Downs et al. (2011), Le Quéré et al.'s (2010) estimate of 20 μatm decade<sup>-1</sup> (when the model results are sampled at the same location and time as the observations) is consistent with our observations.

Changes in the intense CO<sub>2</sub> sink zone centered around 40°S are clearly important for projecting future global ocean CO<sub>2</sub> uptake. However, presently available *p*CO<sub>2</sub> data are not extensive enough to address this issue reliably. For example, Metzl (2009) investigated changes in the intense CO<sub>2</sub> sink zone in the southern Indian Ocean and reported a 1991–2007 mean winter rate of increase ranging between 36 ± 4 and 47 ± 10 μatm decade<sup>-1</sup> (corrected for SST change) in the southern half of the sink zone between 40°S and 55°S; this indicates a weakening of the sink intensity due to much faster rates of oceanic *p*CO<sub>2</sub> increase than the atmospheric rate of 16 μatm decade<sup>-1</sup>. On the other hand, a much lower rate of 6 μatm yr<sup>-1</sup> was



Surface  $p\text{CO}_2$  Winter (Day 172-326) 1981-2010

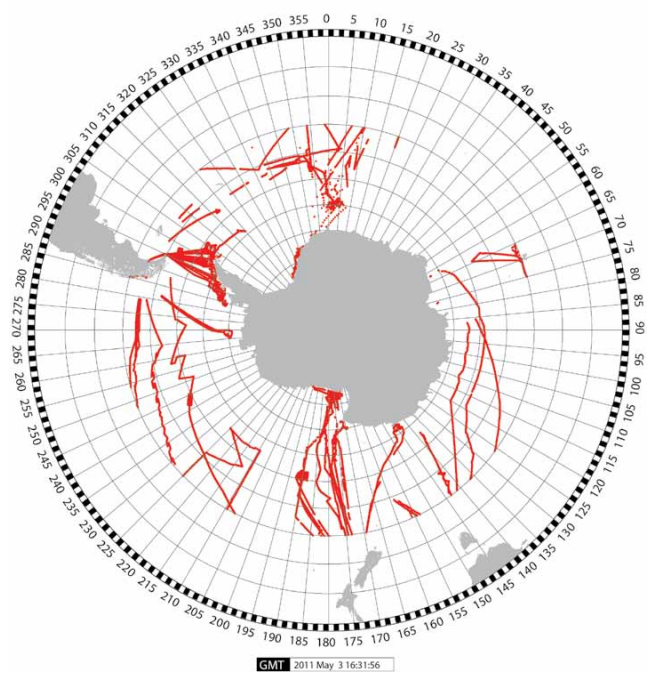


Figure 6. Sample locations and the time trend of surface water  $p\text{CO}_2$  data during the winter months (year days 172–326). The mean rate of change is shown with the heavy black linear regression line and the values in the unit of  $\mu\text{atm yr}^{-1}$ . The data collected during the El Niño and non-El Niño periods are shown, respectively, with gray and black dots. The open circles are monthly means, used for linear regression calculations. The data are available at CDIAC. From Takahashi et al. (2011)

Table 1. The mean decadal rate of change for wintertime surface water  $p\text{CO}_2$  and sea surface temperature (SST) in five temperature zones. The second column shows the mean rate of  $p\text{CO}_2$  change as observed in Figure 6, and the SST change in the third column is estimated using the temperature data obtained concurrently with the  $p\text{CO}_2$  data. The fourth column shows the  $p\text{CO}_2$  change corrected for the SST change using 4.23%  $p\text{CO}_2$  change per  $^{\circ}\text{C}$ .

| SST Range ( $^{\circ}\text{C}$ ) | $p\text{CO}_2$ Change $\mu\text{atm decade}^{-1}$ (1986–2010) | SST Change $^{\circ}\text{C decade}^{-1}$ (1986–2010) | $p\text{CO}_2$ Change corrected for SST $\mu\text{atm decade}^{-1}$ | No. of Months | Data Counts |
|----------------------------------|---|---|---|---------------|-------------|
| 0.80–1.50                        | $16.8 \pm 2.9$  | $-0.031 \pm 0.021$                                    | $17.3 \pm 3.2$  | 56            | 4,668       |
| 1.50–2.50                        | $23.8 \pm 3.0$  | $+0.020 \pm 0.028$                                    | $23.5 \pm 3.4$  | 61            | 9,326       |
| 2.50–3.50                        | $25.2 \pm 2.8$  | $+0.13 \pm 0.038$                                     | $23.3 \pm 3.4$  | 56            | 12,473      |
| 3.50–4.50                        | $24.3 \pm 4.2$  | $-0.045 \pm 0.036$                                    | $24.9 \pm 4.7$  | 59            | 19,163      |
| 4.50–5.50                        | $16.7 \pm 2.8$  | $+0.031 \pm 0.034$                                    | $16.2 \pm 3.3$  | 59            | 24,114      |
| -----                            | -----   | -----   | -----   | -----         | -----       |
| 0.80–5.50                        | $21.4 \pm 4.2$  | $0.02 \pm 0.03$                                       | $21.0 \pm 3.4$  | 288           | 69,744      |
| 1.50–4.50                        | $24.4 \pm 3.3$  | $0.04 \pm 0.09$                                       | $23.9 \pm 3.8$  | 176           | 40,962      |

observed in the northern half between 35°S and 40°S, suggesting an increase in sink intensity. More observations are needed to document the change in this important sink zone.

## CONCLUSION

The global ocean is currently absorbing annually about 2 Pg C yr<sup>-1</sup> of CO<sub>2</sub> from the air, and it plays a significant role in the uptake and long-term storage of anthropogenic CO<sub>2</sub> that is emitted to the atmosphere, affecting Earth's climate. The climatological mean sea-air flux is estimated by the observed sea-air pCO<sub>2</sub> difference and the gas transfer rate parameterized as a function of (wind speed)<sup>2</sup>. A Southern Ocean zone between 30°S and 50°S is found to be a major sink for atmospheric CO<sub>2</sub>, taking up 1.0 Pg C yr<sup>-1</sup>. Thus, the Southern Ocean is a major ocean sink for atmospheric CO<sub>2</sub>. This paper discusses how this CO<sub>2</sub> sink is changing in response to recent climate change.

We investigated the multidecadal mean trends for surface water pCO<sub>2</sub> and temperature (0.8°–5.5°C) during winter in the formation region for AAIW. The wintertime waters were chosen because of minimal winter biological activity in order to avoid large biologically induced variability in seawater pCO<sub>2</sub>, and because of the maximal vertical mixing. The pCO<sub>2</sub> in the waters between 1.5°C and 4.5°C has increased at a rate of 23.9 ± 3.8 μatm decade<sup>-1</sup>, which is faster than the rate of atmospheric pCO<sub>2</sub> increase of about 16 μatm decade<sup>-1</sup>. This suggests weakening CO<sub>2</sub> sink intensity for AAIW, which transports water to depths of about 900 m. The rate of change in the intense CO<sub>2</sub> sink zone centered at about 40°S is clearly important,

but it cannot be determined reliably due to limited observations. The observed distribution and the mean rate of change in surface water pCO<sub>2</sub> of the Southern Ocean are generally in agreement with the results of the Biogeochemistry-Ocean GCM studies.

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