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Seasonality of biological and physical controls on surface ocean CO₂ from hourly observations at the Southern Ocean Time Series site south of Australia

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Abstract The Subantarctic Zone (SAZ), which covers the northern half of the Southern Ocean between the Subtropical and Subantarctic Fronts, is important for air-sea CO₂ exchange, ventilation of the lower thermocline, and nutrient supply for global ocean productivity. Here we present the first high-resolution autonomous observations of mixed layer CO₂ partial pressure (pCO₂) and hydrographic properties covering a full annual cycle in the SAZ. The amplitude of the seasonal cycle in pCO₂ (~60 μatm), from near-atmospheric equilibrium in late winter to ~330 μatm in midsummer, results from opposing physical and biological drivers. Decomposing these contributions demonstrates that the biological control on pCO₂ (up to 100 μatm), is 4 times larger than the thermal component and driven by annual net community production of 2.45 ± 1.47 mol C m⁻² yr⁻¹. After the summer biological pCO₂ depletion, the return to near-atmospheric equilibrium proceeds slowly, driven in part by autumn entrainment into a deepening mixed layer and achieving full equilibration in late winter and early spring as respiration and advection complete the annual cycle. The shutdown of winter convection and associated mixed layer shoaling proceeds intermittently, appearing to frustrate the initiation of production. Horizontal processes, identified from salinity anomalies, are associated with biological pCO₂ signatures but with differing impacts in winter (when they reflect far-field variations in dissolved inorganic carbon and/or biomass) and summer (when they suggest promotion of local production by the relief of silicic acid or iron limitation). These results provide clarity on SAZ seasonal carbon cycling and demonstrate that the magnitude of the seasonal pCO₂ cycle is twice as large as that in the subarctic high-nutrient, low-chlorophyll waters, which can inform the selection of optimal global models in this region.

1. Introduction

The Southern Ocean is an important region for the global carbon cycle, exerting a major influence on the uptake of both natural [e.g., Metzl et al., 2006; Takahashi et al., 2009; Lenton et al., 2013] and anthropogenic carbon dioxide (CO₂) [e.g., Sabine et al., 2004; Khatiwala et al., 2013]. Present-day Southern Ocean carbon fluxes reflect both significant uptake of human-induced CO₂ emissions [Sabine et al., 2004] and spatial variations in the balance between uptake and outgassing of natural CO₂ [e.g., Takahashi et al., 2002; Lovenduski et al., 2009; Lenton et al., 2012]. Despite this importance to global climate, the Southern Ocean remains a region of considerable uncertainty with respect to its carbon budget [e.g., Gruber et al., 2009], due to both unresolved variability at the seasonal time scale and strong disagreement among simulated seasonal cycles in global carbon models [Lenton et al., 2013; Resplandy et al., 2014].

In the Subantarctic Zone (SAZ), between the Subtropical and Subantarctic Fronts (Figure 1) [e.g., Rintoul and Trull, 2001], the uptake of CO₂ is driven by biological and physical processes, both of which exhibit changes over seasonal and shorter time scales [e.g., Lenton et al., 2006; Resplandy et al., 2014]. Deep convective mixing in winter (to depths greater than 500 m) in the SAZ results in the formation of oxygen-rich Subantarctic Mode Water (SAMW), which makes a significant contribution to the uptake and storage of anthropogenic CO₂ [McNeil et al., 2001; Sabine et al., 2004; Sallée et al., 2012]. The equatorward spreading of SAMW supplies oxygen to ventilate the lower thermocline and delivers nutrients to fuel primary production in broad areas of the global ocean [e.g., Sarmiento et al., 2004].
Global Biogeochemical Cycles

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Figure 1. Maps of the study area showing (a) annual surface chlorophyll-a concentration and (b) annual sea surface temperature and the (climatological) locations of various Southern Ocean Fronts (following Orsi et al. [1995]): beginning in the north, the Subtropical Front (STF), the Subantarctic Front (SAF), the Polar Front (PF), and the Southern Antarctic Circumpolar Current (ACC) Front (SACCF). The location of the Southern Ocean Time Series (SOTS) station (46.8°S, 142°E) is indicated in both panels by the filled black square. The WOCE SR3 section is indicated by the open black squares in Figure 1a, and the location of the mooring during the (2012) drift period is shown by the black line in Figure 1b. The Subantarctic Zone (SAZ) is defined as the region between the STF and the SAF.

The Southern Ocean Time Series (SOTS) site (Figure 1) is located southwest of Tasmania, in the Indian/Australian sector of the SAZ, at a location that has been characterized as representative of a broader region of the SAZ between ∼90°E and 140°E [T. W. Trull et al., 2001]. The site is located between the eastward flowing Antarctic Circumpolar Current, concentrated along the Subantarctic Front (SAF) near 51°S, and the weaker westward flow of waters from the Tasman Sea to the north [Herraiz-Borreguero and Rintoul, 2011]. The environmental conditions at SOTS are temperate with seasonal mixed layer temperatures of ∼9°C in winter and ∼13°C in summer [Rintoul and Trull, 2001]. With respect to biogeochemical properties, this region of the SAZ is characterized by low to moderate chlorophyll (Figure 1a), relatively high nitrate and phosphate, and seasonal depletion of silicic acid [Lourey and Trull, 2001; Rintoul and Trull, 2001; T. Trull et al., 2001]. Low concentrations of dissolved iron [Bowie et al., 2009; Lannuzel et al., 2011] likely limit summertime phytoplankton production in this region [Sedwick et al., 1999]; but, nonetheless, the SAZ is one of the largest net sinks for atmospheric CO2 at the annual scale [Metzl et al., 1999; Lenton et al., 2013], attributed in large part to the summertime biological control on surface water CO2 concentrations [Metzl et al., 1999, 2006; McNeil and Tilbrook, 2009].

Here we report the first full annual record of surface water CO2 partial pressure (pCO2) from an autonomous moored platform in the Southern Ocean. These high-frequency observations are used to partition seasonal changes in pCO2 in the SAZ into physical and biological drivers and to assess the impact of short-term (i.e., subseasonal) hydrographic events on the biological carbon pump. Observations in the SAZ are compared to annual cycles of pCO2 in high-nutrient, low-chlorophyll (HNLC) waters of the subarctic North Pacific, and important differences between the regions are identified. Given the appreciable role of the SAZ with respect to global biogeochemical cycling, this study, which identifies drivers of seasonal and shorter-term changes in the CO2 system, has implications for assessments of natural variability in carbon cycling and CO2 uptake in the broader global ocean.

2. Methods

2.1. Southern Ocean Time Series Observations

The Southern Ocean Time Series (SOTS) is part of the Australian Integrated Marine Observing System (IMOS), and consists of three deep ocean moorings [Schulz et al., 2012; Weeding and Trull, 2014] in the SAZ at near 46.8°E and 142°S (Figure 1). The SAZ mooring is a stiff subsurface wire and glass float design that collects sinking particles into time series sediment traps in the deep ocean and has no instruments above 800 m depth [T. Trull et al., 2001]. The Pulse mooring is an s-tether design with a small surface float that suspends a
Figure 2. Between 15 and 23 July 2012, the SOFS 2 and SOFS 3 mooring deployments overlapped. (a) pCO2 observations from both moorings over this period; (b) The pCO2 difference.

Hydrographic and atmospheric data from the SOTS moorings are publicly available via the IMOS Ocean Portal (http://imos.org.au).

Instruments attached to the surface buoy make ocean measurements of temperature, salinity, and pCO2 (and also dissolved oxygen, phytoplankton fluorescence, and particulate backscatter); the instruments record conditions at approximately 1 m depth. Additional temperature and pressure loggers attached along a 800 m length of wire below the SOFS float provide data for the estimation of mixed layer depth (from measurements at 10, 20, 29, 40, 55, 60, 65, 70, 75, 85, 100, 110, 120, 140, 160, 200, 240, 280, 320, 360, 400, 440, and 480 m depth). Three criteria were applied for mixed layer depth estimation: a threshold of 0.3 °C change from the surface temperature; a temperature gradient threshold of 0.005 °C m⁻¹; and the maximum vertical temperature gradient, with the shallowest depth chosen [Weeding and Trull, 2014]. The SOFS-2 mooring had temperature sensors extending to only 160 m depth, and, fortunately, mixed layer depths were shallower than this during this spring/summer/autumn period.

The Moored Autonomous pCO2 (MAPCO2) system measures the mole fraction of CO2 in surface seawater (at approximately 0.5 m below the sea surface) and marine boundary air (at approximately 1.5 m above the sea surface) every 3 h, using an automated equilibrator-based gas collection system and nondispersive infrared gas analyzer [Sutton et al., 2014]. These data, in addition to sample temperature, pressure and relative humidity, and sea surface temperature and salinity, are used to compute pCO2 [Weiss, 1974; Dickson et al., 2007]. Estimated uncertainty for MAPCO2 air and seawater pCO2 measurements is better than 2 µatm [Sutton et al., 2014]. The SOFS pCO2 data are archived at the Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/oceans/time_series_moorings.html).

We present results from three SOFS mooring deployments: SOFS2 from 24 November 2011 to 23 July 2012; SOFS 3 from 15 July 2012 to 2 January 2013; and SOFS 4 from 1 May 2013 to 14 October 2013. SOFS 2 data from the short overlapping period of 15–23 July 2012 are shown in Figure 2 and provide a useful reflection on pCO2 accuracy and precision, with a mean pCO2 difference between the two moorings of 0.74 µatm and standard deviation of 2 µatm. The analysis in this study is largely focused on the observations from 2012, with other data included to give a sense of the interannual variability in the hydrographic and CO2 system parameters at the SOTS site. From 24 September to 31 December 2012, the SOFS 3 the mooring broke free and drifted eastward (see Figure 1b) into waters with similar surface water properties. Results from this period of drift are discussed in section 3.1. Performance characteristics of the ASIMET system are available in Schulz et al. [2012] and for the mixed layer depth loggers in Weeding and Trull [2014].
Surface chlorophyll-a, was obtained from the NASA MODIS-Aqua satellite [Acker and Leptoukh, 2007]; 8 day values in the region bounded by 46–48° E and 141–143° S were used to construct a seasonal cycle of chlorophyll for the year 2012 at the SOTS site. Surface silicate was obtained from the CSIRO Atlas of Regional Seas in the same location (CARS) (www.cmar.csiro.au/cars) [Ridgway et al., 2002], which provides gridded fields of mean water properties and average (climatological) seasonal cycles generated from observations. Additional, discrete observations of total dissolved inorganic carbon (TCO₂) and total alkalinity (TA) were collected on the RV Southern Surveyor at the SOTS site predeployment and postdeployment in March 2010, August 2011, July 2012, and May 2013. These observations are presented along with observations from RV Aurora Australis voyages in the SAZ in March 1998 and January 2007 (Figure 3). Discrete TCO₂ and TA were determined by coulometric and (open cell) potentiometric titration, respectively, following standard procedures [Dickson et al., 2007] at the CSIRO Marine and Atmospheric Research Laboratory in Hobart. The precision and accuracy of the TCO₂ and TA measurements are on the order of ±3 μmol kg⁻¹.

2.2. Partitioning Changes in pCO₂ Across Physical and Biological Drivers

A linear relationship between salinity and alkalinity (n = 115, r² = 0.92, p < 0.001) was derived from observations at the SOTS site described above (Figure 3d) and used to compute hourly values of TA using the salinity data measured on the mooring. The relationship between TA and salinity is consistent with earlier observations from this region [Metzl et al., 1999] and is assumed to be seasonally invariant. The pCO₂ and TA data were then used to compute the seasonal cycles of TCO₂, pH (on the seawater scale), and aragonite saturation state (Ω), using the CO₂Sys program [Lewis and Wallace, 1998], with the equilibrium
The changes in mixed layer TCO₂ concentration are affected by the following: air-sea CO₂ exchange, vertical diffusion across the base of the mixed layer, entrainment of water from below the mixed layer, horizontal advection, and transfer between inorganic and organic carbon pools through the biological processes of photosynthesis and remineralization. In the SAZ, the mean wind-stress curl favors downwelling [e.g., T. Trull et al., 2001], and we thus ignore changes in mixed layer TCO₂ resulting from upwelling of CO₂-rich Circumpolar Deep Water, which have been shown to be important for surface CO₂ in waters south of the Polar Front [McNeil et al., 2001]. The SOTS site is located between the westward flowing inputs from the Tasman Sea, centered around 44°S [Herraiz-Borreguero and Rintoul, 2011], and the eastward flowing Antarctic Circumpolar Current, concentrated along the Subantarctic Front (SAF) near 51°S (Figure 1b) [Rintoul and Trull, 2001]. At the SOTS site, the surface flow is typically westward, with speeds generally less than 20 cm s⁻¹. East-west horizontal gradients in mixed layer pCO₂ in this region are small [Metzl et al., 1999; Takahashi et al., 2012], thus, for the moment, the impact of horizontal advection is ignored; this choice will be evaluated in more detail below. Our upper ocean (<400 m) observations suggest a conservative relationship between TA and salinity (Figure 2d), and we thus assume that carbonate mineral formation is negligible at the SOTS site. Changes in mixed layer TCO₂ are therefore attributed to combination of air-sea CO₂ exchange (ΔTCO₂bio), vertical entrainment and diffusion (ΔTCO₂ert), and biological processes (ΔTCO₂bio). The gas exchange, and vertical entrainment and diffusion terms can be estimated directly from observations, allowing the biological component of changes in mixed layer TCO₂ to be estimated by difference:

\[
\Delta TCO_{2}^{\text{bio}} = \Delta TCO_{2}^{\text{obs}} - \Delta TCO_{2}^{\text{gas}} - \Delta TCO_{2}^{\text{ert}}.
\]

By using this residual method to partition observed changes in TCO₂ without explicitly determining the impact of horizontal advection, these lateral processes are included in the resulting ΔTCO₂bio term.

The contribution from gas exchange was computed from the air-sea CO₂ fluxes, described above, and mixed layer depth (see Figure 4e). Entrainment was computed assuming that only periods of deepening introduce subsurface waters into the mixed layer [e.g., Shadwick et al., 2011]. Vertical diffusion was computed following Weeding and Trull [2014], using a constant eddy diffusivity of 0.33 x 10⁻⁴ m² s⁻¹ [Law et al., 2003]. We applied a constant subsurface TCO₂ concentration of 2125 ± 10 μmol kg⁻¹, representative of SAMW, and the upper limit on the observed concentrations at the SOTS site over all seasons between 100 and 400 m depth (see Figure 3c). We used a linear gradient (over 50 m) between the subsurface and mixed layer value; observed profiles of TCO₂ from the SOTS site indicate that gradients occur over roughly this depth range directly below the mixed layer in all seasons (Figure 3c).

Using a similar approach as described for TCO₂, with the additional inclusion of temperature effects, the seasonal changes in pCO₂ were attributed to physical and biological drivers:

\[
\Delta pCO_{2}^{\text{obs}} = \Delta pCO_{2}^{\text{temp}} + \Delta pCO_{2}^{\text{gas}} + \Delta pCO_{2}^{\text{ert}} + \Delta pCO_{2}^{\text{bio}}.
\]

with superscripts of ΔpCO₂ corresponding to variations resulting from the changes in temperature (temp) and changes in TCO₂ (gas, vert, and bio). Each term in equation (3) was computed by assuming that the
process acted on the carbonate system individually; the changes in TCO$_2$ (and temperature) were considered in turn, while other variables were held constant [e.g., Shadwick et al., 2011; Jiang et al., 2013]. The difference in pCO$_2$ between the original (observed) and modified conditions were then computed. To explore the impact of advective changes on TCO$_2$, and consequently pCO$_2$, anomalies in salinity and ΔpCO$_2^{bio}$ were used. The salinity anomalies were defined as deviations greater than 0.05 from the annual mean (2012) salinity; the ΔpCO$_2^{bio}$ anomalies were defined as deviations greater than 10 μatm from a (polynomial) model fit to the (computed) seasonal cycle.

Uncertainties associated with each of the terms in equation (2) were estimated and are summarized in Table 1. The pCO$_2$ uncertainty is associated with the measurement by the MAPCO2 system (see section 2.1). The uncertainty associated with TA concentrations was estimated from the residuals of the linear fit to the relationship between observed TA and salinity (Figure 3d). There is a relatively large uncertainty associated with TCO$_2$ resulting from the CO$_2$ system computations with TA and pCO$_2$ as input variables; the corresponding uncertainty associated with computed pH and Ω are 0.01 and 0.1, respectively. The uncertainty associated with TCO$_2$ concentration of the subsurface SAMW (for the vertical entrainment and diffusion terms) results from the seasonal variability observed in profiles at the SOTS site (Figure 2c). We applied a 30% uncertainty to the air-sea CO$_2$ flux term, largely due to the uncertainty in the parameterization of the gas transfer velocity (equation (1)), [see Naegler et al., 2006; Watson et al., 2009]. To estimate the uncertainty associated with the mixed layer depth, determined on the basis of temperature observations.
Table 1. Uncertainty Associated With Terms Used in the Estimate of Annual NCP, Computed From $\Delta TCO_{2}^{bio}$, See Equation (2)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncertainty</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pCO_2$ (μatm)</td>
<td>2</td>
<td>From MAPCO2 system measurement</td>
</tr>
<tr>
<td>$TA$ (μmol kg$^{-1}$)</td>
<td>5</td>
<td>From fit to discrete observations of $TA$ and salinity (Figure 2d)</td>
</tr>
<tr>
<td>$TCO_2$ (μmol kg$^{-1}$)</td>
<td>11</td>
<td>From CO2 system computations (with $TA$ and $pCO_2$)</td>
</tr>
<tr>
<td>$TCO_2^{SMW}$ (μmol kg$^{-1}$)</td>
<td>10</td>
<td>From range of subsurface $TCO_2$ observations (Figure 2c)</td>
</tr>
<tr>
<td>$F$ (mmol C m$^{-2}$ d$^{-1}$)</td>
<td>2</td>
<td>From gas transfer parameterization</td>
</tr>
<tr>
<td>MLD (m)</td>
<td>22</td>
<td>Difference between values based on temperature and density</td>
</tr>
<tr>
<td>NCP (mmol C m$^{-2}$ yr$^{-1}$)</td>
<td>1.5 (~ 60%)</td>
<td>Propagation of above: $\sqrt{\sum (errors^2)}$</td>
</tr>
</tbody>
</table>

(see section 2.1), we computed mixed layer depth for the profiles at the SOTS site (Figure 3) using both temperature and density criteria. We found that the mean difference in mixed layer depth between the methods was less than 15%; we therefore assume a 15% uncertainty on our mixed layer depth computations using hourly temperature observations. These errors were propagated through the computation of $\Delta TCO_{2}^{bio}$ and the corresponding (annual) estimate of NCP (Table 1).

3. Results and Discussion

3.1. Seasonal Cycles

Atmospheric and hydrographic observations between 2010 and 2012 reveal expected annual evolutions of surface water properties [e.g., Rintoul and Trull, 2001; T. Trull et al., 2001]: a seasonal temperature cycle with a magnitude of 4°C (from a minimum of $\sim$8.5°C to a maximum of $\sim$12.5°C); mixed layer depths increasing from a seasonal minimum of $\sim$50 m to $\geq$400 m in the winter and spring; relatively constant salinity; and strong winds throughout the year (Figure 4). Observations from the three deployments reveal modest interannual variability in hydrographic properties, with similar seasonal cycles of temperature and salinity in 2011, 2012, and 2013. During the period when the mooring drifted eastward (see Figure 1b), surface water properties were consistent with observations at the SOTS site immediately before the drift period, and with observations from the same time of year in 2011 (Figure 4). We therefore treat the drift period as part of the 2012 annual record.

Short-term departures from mean salinity and temperature (Figures 4b and 4c) are observed in all years, lasting from days to several weeks. Unlike temperature and salinity, the seasonal evolution of mixed layer depth indicates significant interannual variability, with respect to the onset of deep mixing in autumn and shoaling in spring (Figure 4d). The impact of high-frequency hydrographic variability and the timing of seasonal changes in mixed layer depth on the carbon system is discussed in more detail below.

The magnitude of the seasonal cycle in surface water $pCO_2$ is on the order of 60 μatm, from a minimum of $\sim$330 μatm in the summer, to near-atmospheric equilibrium ($\sim$390 μatm) in spring (September, see Figure 5a). In contrast, atmospheric $pCO_2$ varied by less than 5%. Almost all this variability was driven by total atmospheric pressure, and the atmospheric CO$_2$ mole fraction exhibits a very small seasonal variation, remaining nearly constant at a mean annual value of 390 ppm in 2012, with minimum and maximum values of 387.5 ppm and 391 ppm, respectively (Figure 5a). These values and associated weak seasonality are consistent with observations at the Cape Grim Remote Atmospheric Baseline station in northwestern Tasmania, where the annual average atmospheric CO$_2$ in 2012 was 390.0 ± 1.2 ppm (data available online at http://www.csiro.au/greenhouse-gases/).

The magnitude of the seasonal cycle of surface water $pCO_2$ and the degree of winter disequilibrium with the atmosphere ($\sim$ ±5 μatm) are consistent with earlier observations in the SAZ [Metzl et al., 1999; Takahashi et al., 2009]. The SOTS $pCO_2$ observations presented here indicate very similar seasonality to earlier observations, with concentrations approximately 40 μatm higher in 2012 relative to the observations (largely from the early 1990s) compiled by Metzl et al. [1999]. This is broadly consistent with the increase in atmospheric CO$_2$ over this period ($\sim$36 μatm between 1992 and 2012), suggesting that surface waters in the SAZ are tracking the global ocean average response [e.g., Takahashi et al., 2009]. Furthermore, observations from the SOTS site have a similar seasonality to the gridded data from Takahashi et al. [2012], which indicate
near-atmospheric equilibrium of the surface waters from a brief period in winter and seasonal range of roughly 30 μatm, with small zonal and larger north-south gradients.

Surface TA, computed as a function of salinity (see section 2, Figure 3d), indicates relatively constant values throughout the year, while the seasonality of TCO$_2$ indicates minimum concentrations of roughly 2060 μmol kg$^{-1}$ in summer (coincident with annual minimum pCO$_2$), and maximum concentrations of greater than 2100 μmol kg$^{-1}$ (coincident with maximum pCO$_2$), in spring. The annual evolution of both pH and aragonite saturation state (Ω) mirrors the seasonality in pCO$_2$ with annual maxima in winter and minima in spring (Figures 5d and 5e); the magnitude of the seasonal cycles in pH and Ω are roughly 0.06 and 0.34, respectively. The annual mean surface ocean pH at the SOTS site (8.07), is lower than the (zonally averaged) Southern Hemisphere high-latitude surface water mean (~8.13, based on GLODAP data; [Key et al., 2004]), while the annual mean Ω (2.18) is somewhat higher than this mean value (~1.87) throughout the year.

### 3.2. Physical and Biological Controls of the CO$_2$ System

The thermal component of seasonal changes in pCO$_2$ ranges from a maximum of ΔpCO$_2$$_{temp}$ = 30 μatm between late November and April, to a minimum of ΔpCO$_2$$_{temp}$ = −30 μatm in July (Figure 6a). This seasonal change in pCO$_2$, driven by changes in surface temperature, is less than half the magnitude of the thermal component observed in the North Pacific and North Atlantic [e.g., Takahashi et al., 2002] at similar latitudes, and due to the small amplitude seasonal temperature cycle in the SAZ (Figure 4b). Air-sea CO$_2$ fluxes ranged from 1 to 20 mmol C m$^{-2}$ d$^{-1}$, with the largest fluxes observed between January and June, coincident with the largest air-sea CO$_2$ disequilibrium. The impact of this oceanic CO$_2$ uptake on surface pCO$_2$ was modest: 0.5 < ΔpCO$_2$$_{gas}$ ≤ 6 μatm.
Figure 6. Partitioning across physical and biological controls on the CO₂ system at the SOTS station in 2012: (a) the temperature component of seasonal changes in pCO₂; (b) the combined influence of vertical entrainment and diffusion, and air-sea gas exchange on pCO₂; (c) the biological component of seasonal changes in pCO₂ (in green), with the polynomial fit to the seasonal cycle of ΔpCO₂.bio in yellow, the seasonal cycle in surface silicate (from the CARS Atlas) shown by the bold grey line, and the thin grey line indicating silicate concentrations equal to 1 μmol kg⁻¹; (d) the physical (temperature, vertical entrainment and diffusion, and gas exchange, shown in red) and biological (in green) contributions to seasonal changes in pH; and (e) as in Figure 6d but for Ω. The bold black lines represent daily averages of the data in all panels.

The supply of TCO₂-rich subsurface waters to the mixed layer by deep winter mixing plays an important role in controlling surface pCO₂ [Metzl et al., 1999]. The seasonal observations presented here allow a high-frequency quantification of this vertical supply and the corresponding impact on surface pCO₂. We find that short-term (based on hourly observations) increases in pCO₂ of greater than 100 μatm, result from entrainment of subsurface waters (Figure 6b). By contrast, we find the contributions from vertical diffusion to be negligible (<2 μatm) throughout the year. However, given that entrainment is computed only during periods of mixed layer deepening, many of the hourly observations (during periods of mixed layer shoaling) return a null value; using a daily average, the ΔpCO₂.entr is between 5 and 30 μatm. The TCO₂ gradients between the surface and the water column below the mixed layer are largest in summer and early autumn, when mixed layer depths are less than 200 m (Figure 3c); the (daily) impact of entrainment (ΔpCO₂.entr = 20 to 30 μatm) is therefore dominant in these seasons because the volume of water through which the entrained signal is diluted is not that large. By contrast, in winter, when mixing extends to greater than 400 m, the gradient in TCO₂ between the surface and below the mixed layer is smaller (Figure 3c), and given the large volume of water in the mixed layer, the impact of entrainment (ΔpCO₂.entr ~10 μatm) is smaller than that observed in autumn. Thus, while the vertical supply of TCO₂-rich waters is important in controlling seasonal changes in surface pCO₂, the (maximum) magnitude of this process is similar to the thermal component. Furthermore, while these observations reinforce earlier studies which attribute the winter near atmospheric equilibrium of pCO₂ in the SAZ to deep mixing [Metzl et al., 1999, 2006], our annual observations allow this
to be refined, identifying the period of autumn mixing, to depths less than 200 m as dominant over very
deep winter mixing, with respect to subsurface contributions to surface pCO_2.

The biological component of seasonal changes in pCO_2 was estimated by difference after each of the
physical drivers described above were quantified (Figure 6c). Our observations indicate a biologically driven
decrease in pCO_2 over the productive season from December through June (described in more detail below)
that ranged from ΔpCO_2biol = −120 to −20 μatm. Outside of the productive season (July to November),
respiration or remineralization of organic matter increases pCO_2 by up to 40 μatm, with a corresponding
increase of −10 μmol kg⁻¹ in ΔTCO_2biol (not shown). The required pool of particulate and/or dissolved
organic matter required to close the annual cycle by respiration, as suggested by our analysis, is on the order
of 10−20 μmol kg⁻¹. Suspended particulate organic carbon (POC) concentrations of 4 ± 3 μmol kg⁻¹ at the
end of the summer period, representing less than half of this requirement have been reported [Lourey and
Trull, 2001]. A late summer increase in dissolved organic carbon (DOC) on the order of 15−25 μmol kg⁻¹,
which must later be mixed away or respired, has also been observed at the SOTS site (T. W. Trull and D.
Davies, RV Aurora Australis Voyage AA9706, unpublished data, March 1998). Thus, there may be sufficient
POC and/or DOC to fuel the estimated winter respiration in the region. This finding differs from earlier mod-
eling studies that suggest a dominance of vertical supply in restoring winter nutrient concentrations at the
SOTS site [Wang et al., 2001]. However, because our estimated ΔpCO_2biol includes potential contributions from
horizontal advection (see section 2), the winter return to atmospheric equilibrium is likely due to a
combination of respiration and horizontal inputs.

Because the ΔpCO_2biol term is computed using hourly observations of changes in mixed layer depth (to
quantify the physical drivers), which can be significant in the SAZ (Figure 4e), we resolve variations in the
biological component that are likely too rapid to be representative of in situ processes. High-frequency obser-
vations of mixed layer depth are not often used in mixed layer mass balance approaches to
partition changes in TCO_2 and pCO_2 since monthly or seasonal observations are more readily available,
resulting in relatively smoothly varying, or climatological, annual cycles of mixed layer depth and drivers of
changes in mixed layer TCO_2 and pCO_2 [e.g., Gruber et al., 1998; Shadwick et al., 2011; Brix et al., 2013; Jiang
et al., 2013]. The impact of these high-frequency variations remains evident in the daily average of ΔpCO_2biol,
which is pulled away from the zero line in response to rapid increases in autotrophy in the first half of the
year (Figure 6c), and which we consider to be representative of processes occurring in the surface layer. The
impact of hydrographic changes acting on time scales of days to weeks on ΔpCO_2biol will be explored in more
detail (section 3.4).

The combined physical (temperature, vertical entrainment and diffusion, and gas exchange) and biological
controls on seasonal changes in pH and Ω are similar to those described above for pCO_2 (Figures 6d
and 6e). Warming (from November to July), vertical supply of TCO_2-rich water, oceanic CO_2 uptake, and
respiration all act to decrease pH. During the productive season, biologically driven increases in pH are of
equal magnitude to the (combined) physically driven decreases. From July to December, cooling (which
increases pH) and a reduced supply of water from below allow heterotrophic decreases in pH to outweigh
the physically driven increases. The seasonality in Ω is somewhat different than that of pH due to the
opposing effect of temperature; warming from December to July results in modest increases in Ω, such
that the biological control on the seasonal cycle is larger than the physical control throughout the year.
Understanding the subtle differences in the seasonality of physical and biological drivers on pH and Ω is
important to predicting the evolution of high-latitude systems to anthropogenic change [Shadwick et al.,
2013]. In the SAZ south of Australia, the southward extension of the (warm) East Australian Current [e.g., Cai
et al., 2005; Ridgway, 2007] will amplify the effects of ocean CO_2 uptake on pH while partially countering
the associated decrease in Ω.

3.3. Net Community Production and Initiation of Springtime Production

The annual cycle of ΔpCO_2biol indicates a clear delineation between the autotrophic season, when
production exceeds respiration (ΔpCO_2biol < 0), and the heterotrophic season, when respiration dominates
(ΔpCO_2biol > 0, Figure 6c). From the seasonal evolution of ΔTCO_2biol (not shown), we estimate an annual net
community production (NCP, the imbalance between net primary production and heterotrophic respiration)
of 2.45 ± 1.47 mol C m⁻² yr⁻¹ (∼29 g C m⁻² yr⁻¹), at the SOTS site. The export fluxes of particulate organic
carbon at 1000 m, 2000 m, and 3900 m, at this location between August 2011 and July 2012 were 1.9,
1.6, and 1.1 g C m⁻² yr⁻¹, respectively (S. Bray, personal communication, 2014) and consistent with earlier
Interestingly, their observations, as well as the 2011 event was associated with decreased TA and decreased the beginning of the heterotrophic period in mid-July (event E4 in Figure 7). In this case the freshening increase in net autotrophic conditions and the onset of the spring bloom. Additionally, the initial October decrease in TA (see Figure 5b). This event (E3 in Figure 7) is associated with a modest decrease in observed ΔpCO₂, corresponding to a dampening of the net heterotrophic signal and a positive ΔpCO₂ anomaly, that persisted for less than 10 days.

In late 2012 we observe a decrease in pCO₂ (and ΔpCO₂bio < 0), near the beginning of October, coincident with a short-term shoaling of the mixed layer from greater than 400 m to roughly 100 m (Figure 4e). This period of shoaling is followed by an episode of deep mixing, to roughly 400 m, a coincident increase in pCO₂ to near-atmospheric equilibrium, and values of ΔpCO₂bio > 0. When stratification is achieved in early November, we see a sustained decrease in pCO₂ and a maintenance of ΔpCO₂bio < 0, indicating net autotrophic conditions and the onset of the spring bloom. Additionally, the initial October decrease in pCO₂, as well as the sustained decrease in November are broadly consistent with increases in surface chlorophyll concentration, inferred from the 8 day MODIS satellite data (Figure 5c). Our observations indicate a reversal in the sign of the heat flux that corresponds to the onset of prolonged stratification in November, supporting the notion that the shutdown of convection may serve as an indicator of bloom initiation [Taylor and Ferrari, 2011]. The 2013 data indicate that the mixed layer remained quite deep (~200 m) in early October, and corresponding pCO₂ values near-atmospheric equilibrium suggest that the initiation of net production may have been delayed until the onset of stratification (i.e., a view consistent with the concept of a critical stratification depth; [Sverdrup, 1953]).

3.4. Salinity and ΔpCO₂bio Anomalies

The resolution of hydrographic and pCO₂ observations at the SOTS site allow detailed examination of high-frequency events, lasting between several days and several weeks. We defined salinity and ΔpCO₂bio anomalies (see section 2, Figures 7a and 7b) and here explore the relationship between the two, effectively allowing the impact of grouping horizontal advection and biology together in the partitioning of changes in pCO₂ to be evaluated.

We observed events, i.e., coincident salinity and ΔpCO₂bio anomalies, falling into three broad categories:

1. fresh with weakening of the biological pump;
2. saline with strengthening of the biological pump; and
3. fresh with strengthening of the biological pump (Figure 7c). The majority of events fall into the first category, where surface waters are fresher than the annual mean salinity, and the biological pump is weakened, reflected by a positive ΔpCO₂bio anomaly. These events were observed throughout the year, in both the autotrophic and heterotrophic periods (Figure 6a). For example, at the end of January (at the height of the autotrophic season), when surface pCO₂ is near the annual minimum (Figure 5a), we observed a freshening of the surface waters, associated with a positive ΔpCO₂bio anomaly, indicating a weakening of the biological pump. This freshening event was also associated with a decrease in TA and an increase in observed pCO₂ from the seasonal minimum (~330 μatm) to ~370 μatm over a period roughly 10 days (event E1, in Figure 7). Another event in this first category (freshening and weakening of the biological pump) was observed near the beginning of the heterotrophic period in mid-July (event E4 in Figure 7). In this case the freshening event was associated with decreased TA and decreased pCO₂, corresponding to a dampening of the net heterotrophic signal and a positive ΔpCO₂bio anomaly, that persisted for less than 10 days.

In the second most common class of events, surface waters are more saline than the annual mean, and the biological pump is strengthened. These events were also observed throughout the year, regardless of the net autotrophic or heterotrophic status of the surface waters. We observed a relatively long-lived saline anomaly, from early June through early July (in the autotrophic period), with a coincident enhancement of TA (see Figure 5b). This event (E3 in Figure 7) is associated with a modest decrease in observed pCO₂, smaller
Figure 7. The impact of the advection of high- and low-salinity waters on the biologically driven changes in surface $p$CO$_2$: (a) $\Delta$pCO$_{2}^{\text{bio}}$ anomalies with the auto/heterotrophic period indicated by the green/blue shading; (b) salinity anomalies; and (c) the relationship between $\Delta$pCO$_{2}^{\text{bio}}$ anomalies and salinity anomalies, with the autotrophic (black circles) and heterotrophic (black squares) periods of the season indicated. Five events (E1 to E5, described in section 3.4) are indicated above Figure 7a and are plotted according to the text color with circles (autotrophic period) or squares (heterotrophic period) in Figure 7c).

than what might be expected from the roughly 20 $\mu$mol kg$^{-1}$ increase in TA and a strengthening of the biological pump (a negative $\Delta$pCO$_{2}^{\text{bio}}$), particularly at the beginning of the event, when the largest change in salinity is observed. A shorter event of the same type was observed toward the end of the heterotrophic period, over roughly 10 days in mid-October (event E5 in Figure 7), in which the positive salinity anomaly was associated with a strengthening of the biological pump (a negative $\Delta$pCO$_{2}^{\text{bio}}$ anomaly), an increase in TA, and decrease in surface pCO$_2$ (see Figures 5a and 5b).

Previous studies in the SAZ have shown that biomass is higher in the north and starts earlier in the season; the waters in the northern region, closer to the Subtropical Front (STF), are also more saline (and warmer, Figure 1b; [Bowie et al., 2011]). Thus, the saline events likely reflect the input of water from the north, which bring biomass, either as particles or their imprint on the surface TCO$_2$ field, enhancing autotrophy during the productive season and fuelling additional heterotrophy outside of the productive period. The fresh events, which are likely the result of inputs of water from the south do not supply “additional” biomass and thus weaken the biological pump in both the productive and heterotrophic periods. Another parallel view of these processes is that the fresh/salty, weaker/stronger biological pump events reflect the influence of the far-field surface TCO$_2$; a maximum (surface) concentration gradient of 30 $\mu$mol kg$^{-1}$ in TCO$_2$ is required to produce the $\Delta$pCO$_{2}^{\text{bio}}$ anomaly of 60 $\mu$atm (i.e., $\pm 30$ $\mu$atm). Based on TCO$_2$ observations from the WOCE SR3 section (see Figure 1), mixed layer TCO$_2$ varies from 2085 $\mu$mol kg$^{-1}$ at 46$^\circ$S to 2100 $\mu$mol kg$^{-1}$ at 48.5$^\circ$S, indicating that north-south gradients (with surface TCO$_2$ increasing southward) large enough to explain the $\Delta$pCO$_{2}^{\text{bio}}$ anomalies are present over a relatively small spatial range in the SAZ. The duration of the events may also suggest the influence of eddies in changing surface properties; mesoscale motions in the region are common [e.g., Weeding and Trull, 2014] and north-south gradients in surface
temperature (see Figure 1b) and salinity are large enough to explain the observed salinity anomalies at the SOTS site [e.g., Lourey and Trull, 2001].

The third class of events, characterized by surface waters fresher than the annual mean, and a strengthening of the biological pump, are only observed in the summer season, and under net autotrophic conditions (Figure 7). The origin of these events is unknown, but the relief of either silicic acid or iron limitation is a possible explanation. The SAZ region undergoes seasonal depletion of silicic acid when nitrate remains available; based on the 2007 SAZ-Sense study [Bowie et al., 2011] and climatological concentrations from CARs (see section 2; Ridgway et al., 2002), silicic acid is limiting well before the end of the autotrophic period (<1 μmol kg⁻¹, Figure 6c). Given that these fresh anomalies likely originate in the south, they may also supply silica to the extent that they bring macronutrient rich water northward across the Subantarctic Front [Rintoul and Trull, 2001]. We observe short-term (on the order of 10 days) freshening events associated with negative ΔpCO₂bio anomalies only in late March and early April (event E2, for example, in Figure 7), consistent with the onset of silica limitation and suggesting a stimulation of biological production associated with pulses of fresh water. Relief of iron limitation by aerosol inputs, potentially associated with freshening by wet deposition, is also a possibility given that surface iron enrichments have been observed in spring and summer [Sedwick et al., 1997, 2008; Lannuzel et al., 2011].

3.5. Comparison With Other High-Latitude Observations

Time series observations of physical and biogeochemical variables at the seasonal and subseasonal time scale have done much to resolve uncertainties in carbon cycling at a few important study sites (e.g., Bermuda, Hawaii; Bates et al., 1995; Karl and Lukas, 1996), though the majority of these efforts have been restricted to the Northern Hemisphere [Bates et al., 2014]. An exception is the routine sampling of waters at the STF east of New Zealand (Munida Station, Currie et al., 2009), which provides a unique subantarctic parallel to our observations at the SOTS site.

The (median) annual amplitude of pCO₂ at the Munida Station (between 1998 and 2009) is on the order of 30 μatm [Brix et al., 2013], which is roughly half the magnitude of that observed at the SOTS site. This discrepancy may be due in part to the sparser (bimonthly) temporal resolution of the Munida pCO₂ observations; the January 2012 pCO₂ minima we observed at the SOTS site was short-lived (Figure 5a), and followed by a rapid increase of roughly 50 μatm, associated with a freshening event (E1, described in the previous section) lasting less than 2 weeks, a feature that would not necessarily have been captured with bimonthly sampling. Daily rates of summer NCP at the Munida station, based on observations of pCO₂ and TA and a one-dimensional model for mixed layer TCO₂, are roughly 20 mmol C m⁻² d⁻¹ (based on a drawdown of ∼33 μmol kg⁻¹ over 90 days of summer and an average mixed layer depth of ∼55 m; Brix et al., 2013). From the computed annual cycle of ΔTCO₂bio (see equation (2)), similar daily rates of NCP (∼20 mmol C m⁻² d⁻¹) from mid-October to the end of the year at the SOTS site are estimated from a 30 μmol kg⁻¹ decrease in TCO₂bio over 2.5 months. Our analysis indicates that the productive season in the SAZ proceeds slowly from its initiation in mid-October, coincident with mixed layer shoaling (see section 3.3), to its cessation in late June (Figure 6c). Observations at both the Munida Station and the SOTS site indicate that biological carbon uptake exerts a dominant control on surface water pCO₂ and correspondingly on the uptake of atmospheric CO₂ in these regions of the SAZ.

The SAZ is characterized by high-nutrient, low-chlorophyll (HNLC) conditions, which extend, broadly speaking, in a zonally homogeneous ring around the globe. These HNLC surface waters are not associated with an annual phytoplankton bloom, a phenomenon which occurs annually in the North Atlantic Ocean [e.g., Siegel et al., 2002]. Daily rates of primary production in the North Atlantic (at 47°N, a similar northern latitude to the SOTS site), based on both the ¹⁴C assimilation method and observations of TCO₂, of 84 to 107 mmol C m⁻² d⁻¹ over a 12 day period have been reported [Chipman et al., 1993]. These observations are comparable to the rapid decreases in pCO₂, from >400 to ∼250 μatm, and TCO₂ (from 2060 to 1980 μmol kg⁻¹) observed over 2 weeks in the Scotian Shelf region of the northwestern Atlantic [Shadwick et al., 2010, 2011]. By contrast, the seasonal decrease in pCO₂ of roughly 60 μatm (and daily rates of NCP smaller by a factor of 4 to 5) at the SOTS site occurs over a period of several months in the absence of rapid increases in biomass observed annually at similar latitudes in the North Atlantic.

Parallels are routinely drawn between the seasonally silicate-depleted HNLC waters of the subarctic North Pacific [e.g., Wong and Matear, 1999] and the SAZ, often as a result of a lack of observations from the latter system [e.g., Banse, 1996]. The annual cycle of pCO₂ from Ocean Station Papa (OSP, 50.12°N, 144.83°W;
4. Conclusion

Autonomous, high-resolution measurements of surface water pCO₂ at an open ocean site in the Subantarctic Zone, covering a full annual cycle allowed seasonality in the physical and biological controls on the surface CO₂ system to be resolved. The biological control on pCO₂ during the productive season was up to 4 times larger than the thermal control. Entrainment of subsurface waters was dominant in early autumn in mixed layers of ~200 m, with the return to near-atmospheric equilibrium occurring in late winter and early spring due to heterotrophic increases in pCO₂. Physics and biology contributed equally to seasonal changes in pH, while biological processes dominated changes in carbonate saturation state.

Changes in surface salinity acting on seasonal to interannual timescales influenced pCO₂ throughout the year via the meridional advection of waters with different TCO₂ signatures. This region of the SAZ acts as a net annual sink for atmospheric CO₂ largely due to the summer time biology (that persists over several months), a small seasonal warming, and a relatively slow return to near equilibrium with the atmosphere that is achieved shortly before the onset of production in the subsequent season. These perspectives and the high-resolution observations of the CO₂ system will be useful in improving Southern Ocean carbon cycle models, which currently display a wide range of seasonal cycles.

References


