Quantifying Anthropogenic Carbon Inventory Changes in the Pacific Sector of the Southern Ocean

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Abstract

The Southern Ocean plays a major role in mediating the uptake, transport, and long-term storage of anthropogenic carbon dioxide (CO₂) into the deep ocean. Examining the magnitude and spatial distribution of this oceanic carbon uptake is critical to understanding how the earth's carbon system will react to continued increases in this greenhouse gas. Here, we use the extended multiple linear regression technique to quantify the total and anthropogenic change in dissolved inorganic carbon (DIC) along the S04P and P16S CLIVAR/U.S. Global Ocean Carbon and Repeat Hydrography Program lines south of 67°S in the Pacific sector of the Southern Ocean between 1992 and 2011 using discrete bottle measurements from repeat occupations. Along the S04P section, which is located in the seasonal sea ice zone south of the Antarctic Circumpolar Current in the Pacific, the anthropogenic component of the DIC increase from 1992 to 2011 is mostly found in the Antarctic Surface Water (AASW, upper 100 m), while the increase in DIC below the mixed layer in the Circumpolar Deep Water can be primarily attributed to either a slowdown in circulation or decreased ventilation of deeper, high CO₂ waters. In the AASW we calculate an anthropogenic increase in DIC of 12–18 $\mu\text{mol kg}^{-1}$ and an average storage rate of anthropogenic CO₂ of $0.10 \pm 0.02 \text{ mol m}^{-2} \text{ yr}^{-1}$ for this region compared to a global average of $0.5 \pm 0.2 \text{ mol m}^{-2} \text{ yr}^{-1}$. In surface waters this anthropogenic CO₂ uptake results in an average pH decrease of $0.0022 \pm 0.0004 \text{ pH units yr}^{-1}$, a $0.47 \pm 0.10 \% \text{ yr}^{-1}$ decrease in the saturation state of aragonite ($\Omega_{\text{Aragonite}}$) and a $2.0 \pm 0.7 \text{ m yr}^{-1}$ shoaling of the aragonite saturation horizons (calculated for the $\Omega_{\text{Aragonite}}=1.3$ contour).

Introduction

Since the beginning of the industrial era, atmospheric concentrations of carbon dioxide (CO₂) have risen from approximately 280 ppm to over 400 ppm due to fossil fuel burning, cement production, and land-use changes by humans (Rhein et al., 2013; Tans, 2009). This atmospheric increase accounts for only 44% of the total anthropogenic carbon (C_{Anth}) that has been released because the terrestrial biosphere and the surface ocean absorb the remaining 56% (Le Quéré et al., 2014). The surface ocean currently absorbs about one quarter of the total C_{Anth} (Keeling et al., 1996; Le Quéré et al., 2014; Rhein et al., 2013; Sabine and Feely, 2007; Sabine et al., 2004d; Sarmiento and Gruber, 2002; Sarmiento, 1992; Siegenthaler and Sarmiento, 1993); however, this uptake is not spatially uniform and varies based on ocean circulation, solubility differences, air-sea exchange, and water-mass properties. The Southern Ocean, in particular, plays a key role in the oceanic uptake of C_{Anth} and, as a result, has gained increased interest in recent years. Studies have shown that the Southern Ocean (south of 50°S) accounts for approximately 30–40% of the global oceanic C_{Anth} uptake (Khatiwala et al., 2009; Sabine and Feely, 2007), while its waters store only about 9% of the global ocean's C_{Anth} (Sabine et al., 2004a). This difference between uptake and storage is accounted for by large-scale northward transport of C_{Anth}-enriched surface waters out of the Southern Ocean and into the interior of the subtropical oceans (Caldeira, 2000; Gruber, 1998; Hoppema et al., 2001; Sabine et al., 1999).

The ability of the Southern Ocean to continue to take up C_{Anth} is dependent on factors like mixed-layer depth, surface currents, wind stress, subduction rates, and eddy fluxes that may be sensitive to changes in climate (Ito et al., 2010; Sallée et al., 2012). Researchers often use model projections to analyze these potential changes, but the Southern Ocean is a location where models and observations tend to deviate considerably and detailed comparisons are necessary to bridge this gap (Hoppema et al., 2001; Khatiwala et al., 2013; Lo Monaco, 2005; Russell et al., 2006; Takahashi et al., 2012). Because the Southern Ocean is known to play a large role in global C_{Anth} uptake, continued measurement-based and modeling studies of this region are necessary to further our understanding of the global oceanic carbon sink.

While it is possible to measure dissolved inorganic carbon concentrations (DIC) in the ocean, it is not possible to measure C_{Anth} directly. The fractional change in the amount of dissolved inorganic carbon in the oceans from preindustrial times to present is less than 1% and decadal changes are even less. Several approaches have been developed to calculate C_{Anth} inventories: data-based back-calculation methods such as C^* , ΔC^* , multiple linear regression (MLR), and $\delta^{13}\text{C}$ (Brewer, 1978; Chen and Millero, 1979; Chen, 1994; Goyet et al., 1999; Gruber et al., 1996; Gruber, 1998; Lee et al., 2003; Lo Monaco, 2005; Pérez et al., 2002; Quay et al., 1992; Sabine et al., 2004b, 1999, 2002; Touratier et al., 2007; Wallace, 1995), tracer-based approaches (Hall et al., 2004, 2002; Waugh et al., 2004), and model-based estimates (Ito et al., 2010; Khatiwala et al., 2013; McNeil et al., 2003; Orr, 2004; Pardo et al., 2014). Some approaches have also been developed to quantify C_{Anth} inventory changes on decadal time scales (Friis et al., 2005; Peng et al., 1998; Quay et al., 2003; Tanhua et al., 2007; Wanninkhof et al., 2010). A review of many of these methods can be found in Sabine and Tanhua (2010). While these methods show good agreement in many oceanic regions, the estimation of C_{Anth} storage in the Pacific Sector of the Southern Ocean has proven to be more challenging because high-quality carbon observations in this region are limited. Chen (1994, 1987, 1982) reports on the distribution of C_{Anth} in this region using the DIC- measurement-based back-calculation technique and the only DIC-measurement-based decadal C_{Anth} inventory change calculation in this region to date is from Sabine et al. (2008) which reports C_{Anth} inventory changes along 150°W on the meridional P16S hydrographic line between 1991/92 (WOCE Hydrographic Program/JGOFS) and 2005 (CLIVAR).

The ongoing CLIVAR/U.S. Global Ocean Carbon and Repeat Hydrography Program aims to help fill in the gaps in the ocean carbon puzzle by reoccupying 19 hydrographic lines from the earlier WOCE/JGOFS survey on decadal timescales (<http://ushydro.ucsd.edu/>). Here we present results from a subset of Southern Pacific Ocean WOCE/JGOFS and CLIVAR/U.S. Global Ocean Carbon and Repeat Hydrography Program cruises and calculate changes in the carbon system between 1992 and 2011 based on these observations.

Study region

All stations used for this study are part of the S04P and P16S hydrographic lines (see Fig. 1 for map of stations). The stations are located south

of the Polar Front of the Antarctic Circumpolar Current (ACC) within the Seasonal Sea Ice Zone (SSIZ) and span the entire width of the Pacific sector of the Southern Ocean. The SSIZ is defined as the area south of 62°S that experiences a seasonal cycle of sea ice coverage and melt (Popp et al., 1999). The zonal S04P line along 67°S was occupied in austral fall of 1992 and 2011, and the meridional P16S line along 150°W was occupied in austral fall 2005 and partially again in austral fall 2011.

The SSIZ is located within the Polar Zone (PZ) south of the eastward flowing ACC and is a region where the surface layer, Antarctic Surface Water (AASW), is extremely cold ($\theta < -1.8^{\circ}\text{C}$) and relatively fresh ($S < 33.4$) due to heat loss to the atmosphere and the addition of freshwater from melting seasonal sea ice. In the austral summer months the upper ~50 m of the AASW layer warms due to seasonal heating and caps the waters beneath (Dong et al., 2008). The prevailing winds in this region are Westerlies, which export AASW water northward via Ekman transport. Low-oxygen Circumpolar Deep Waters (CDW) flow southward and to the surface to replace this exported AASW by means of Ekman pumping, creating what is known as the diabatic Deacon cell (Callahan, 1972; Speer et al., 2000). As this cool and relatively fresh AASW flows north across the ACC it meets warmer, less dense surface waters and joins the Subantarctic Mode Water (Speer et al., 2000). A portion subducts in the Drake Passage region along the $\gamma^n \approx 27.2 \text{ kg m}^{-3}$ neutral density contour, forming Antarctic Intermediate Water (AAIW; Naveira Garabato et al., 2009), which is the subsurface salinity minimum throughout much of the world's ocean basins (e.g. Talley et al., 2011). The remainder of the water column in the SSIZ is filled with upwelling CDW and the very dense bottom layers contain Antarctic Bottom Waters (AABW; Orsi et al., 1999). See Fig. 2 for a schematic of the zonally-averaged circulation.

The S04P 2011 and P16S 2011 potential temperature (θ), salinity, and DIC sections shown in Fig. 3 reflect the large-scale circulation in the Pacific sector of the SSIZ. Refer to the WOCE Atlas Volumes 1 and 2 for sections of the earlier S04P 1992 and P16S 2005 occupations (Orsi and Whitworth, 2005; Talley, 2007). The cool and fresh cap of AASW formed by freshwater release from the melting of seasonal sea ice and cooling by strong westerly winds covers the surface of the entire S04P and P16S transects. The S04P transect is divided into two major regimes an approximately 150°W. The region to the east of 150°W is dominated by the eastward-flowing ACC which dips southward close to the Antarctic continent and then back northward as it follows the shelf in the Bellingshausen Sea. In the clockwise Ross Gyre to the west of 150°W the eastward-flowing ACC dominates the northern edge of the gyre, while a westward return flow prevails closer to the continental shelf. This circulation is also clearly discernable in dynamic height and the transport streamfunction (Orsi et al., 1995). In both regimes a relatively warm (~2°C) and low-oxygen core of Upper Circumpolar Deep Water (UCDW) fills the upper 200–500 m of the water column, and below that lies Lower Circumpolar Deep Water (LCDW), which is marked by a salinity maximum (Callahan, 1972). The warm UCDW core is less defined in the Ross Gyre to the west, which is instead filled mostly by LCDW.

West of 172°E, where the S04P line turns southwest and moves up the continental slope toward Cape Adare, is a region of AABW formation characterized by cool, relatively fresh, and extremely dense ($\gamma^n > 28.27 \text{ kg m}^{-3}$) water flowing down the shelf to the bottom of the basin (Swift and Orsi, 2012). AABW formation is seasonal and sporadic, and therefore the relatively small volumes of AABW produced are quickly mixed with LCDW. This mixing process makes the dividing line between AABW and LCDW difficult to define in this region, although the presence of AABW can be confirmed by the decrease in salinity near the ocean floor (Orsi et al., 1999).

The P16S portion of this transect is situated in the eastern portion of the Ross Gyre and shows the same general water mass features as the S04P line. Moving southward along P16S toward the Antarctic continent the AASW layer thickens due to increased convective cooling. Only stations between 67°S and 71°S were used for this study due to the limited poleward sampling in the 2005 occupation.

Data analysis

Analytical methods

As part of the continuing CLIVAR/U.S. Global Ocean Carbon and Repeat Hydrography Program, high-quality carbon system, oxygen, nutrient, tracer, and other hydrographic observations were made along the S04P and P16S lines in the Pacific basin of the Southern Ocean in February–April 2011 (Swift and Orsi, 2011). Here we will use observations made during the WOCE/JGOFS program along S04P during the same season in 1992 (Beaupre et al., 2005) and along P16S from austral fall of 2005 as part of the CLIVAR/U.S. Global Ocean Carbon and Repeat Hydrography Program (Sloyan and Swift, 2009) to look for decadal changes in water-mass properties.

For all three occupations used for this study, DIC measurements were made using the coulometric titration method (Chipman et al., 1997; DOE, 1994; Feely et al., 2009b; Johnson et al., 1987, 1985, 1993; Sabine et al., 2012). Total alkalinity (TA) measurements were made in 2005 and 2011 using an open-cell, two-stage, potentiometric titration procedure (Dickson et al., 2003, 2007; Feely et al., 2009b). During the 1992 S04P occupation, total alkalinity was not measured directly, however water column $p\text{CO}_2$ (partial pressure of CO_2) measurements were made at 4°C using a fully-automated equilibrator-gas chromatograph system (Chipman et al., 1997, 1993). Certified reference materials (CRMs) were used to assure the quality of the shipboard measurements (Dickson et al., 2003; Dickson, 2010, 1990a). See Table 1 for a summary of carbon measurements used for this study. All data are available online from the CLIVAR and Carbon Hydrographic Data Office (<http://cchdo.ucsd.edu>) and from the Carbon Dioxide Information Analysis Center (<http://cdiac.ornl.gov/oceans/>).

Crossover analysis

To check the measurement consistency between data sets we performed a crossover analysis of the 2011 measurements with measurements from earlier occupations in the same locations using the MATLAB 2nd QC toolbox developed by Tanhua (2010). The MATLAB 2nd QC toolbox references the GLODAP

(Key et al., 2004; Sabine et al., 2004c) and CARINA (Key et al., 2010; Tanhua et al., 2010) databases to objectively assess differences in deep-water values (depths 1500–3000 m) along σ_4 density surfaces where properties are not expected to change over the 19-year study period. This comparison was performed for all carbon system parameters as well as all other physical and chemical parameters used in this analysis. No significant differences were found in deep waters between occupations and therefore no corrections were made to the data sets (see Supplementary Material).

Preliminary DIC change estimate

To assess measured changes in DIC, we performed a direct subtraction of gridded measured DIC values as a function of location. This subtraction, shown in Fig. 4(a), gives patchy results in the upper water column where seasonal and interannual variability, large-scale movement of water masses, and isopycnal heave play large roles in controlling DIC. The $\sim 45 \mu\text{mol kg}^{-1}$ DIC change observed in the upper 200 m of S04P near 140°W , for example, is much larger than the expected anthropogenic change and is likely the result of a slight lateral movement of the front between the Ross Gyre and the ACC Loop Gyre between the 1992 and 2011 occupations, which can be observed in the temperature and salinity data as well. Also, the DIC change observed from the surface down to the ocean floor between 80°W and the Antarctic Peninsula in the easternmost part of the S04P transect is likely an artifact of a latitudinal difference in location of the stations between the 1992 and 2011 S04P occupations.

AOU Changes

When examining changes in DIC it is also important to estimate Apparent Oxygen Utilization (AOU) changes. AOU is a function of the amount of respiration and decay of organic matter that has occurred in a parcel of water since it last was in contact with the atmosphere. At the surface, where the measured oxygen values are approximately equal to saturation values, the AOU is zero. As the surface water mixes downward into the ocean interior it loses contact with the atmosphere, AOU increases as oxygen is consumed during respiration by marine organisms, and DIC also increases due to the release of CO_2 during these respiration processes. As a result, AOU generally correlates well with water-mass age and increases with depth to a maximum around 300–1000 m and then begins to decrease slightly in LCDW and AABW, which have been more recently ventilated than the overlying UCDW. Figure 4(b) shows a plot of the measured change in AOU along the S04P and P16S lines. At the surface, where waters are saturated with respect to oxygen during all occupations, the measured AOU change is small. At 50 to 500 m depth, we observe changes in AOU between occupations of up to $70 \mu\text{mol/kg}$ along S04P, and above $100 \mu\text{mol/kg}$ along P16S. Like the direct subtraction of DIC values shown in Fig. 4(a), the direct subtraction of AOU values is not corrected for changes in the location of fronts and isopycnal heave. Changes in observed AOU over time can be an indication that there has either been a change in the flux of organic matter into a water mass or a change in circulation which also has implications for the observed change in carbon.

eMLR method

In an attempt to remove seasonal and interannual biases, changes in the location of major fronts, and isopycnal heave, and to calculate a more realistic change in DIC, we used a variation of the extended multiple linear regression (eMLR) method developed by Friis et al. (2005). We employed the eMLR method along five neutral density (γ^n) layers, similar to the eMLR_{dens} method used by Wanninkhof et al. (2010). We chose the five neutral γ^n layers to represent the major water masses that occupy this region (Table 2).

The eMLR and the previously developed MLR methods are empirical approaches that rely on the robust correlation of changes in DIC with changes in other physical and chemical parameters throughout a large section of the ocean, and account for seasonal and interannual variability between data sets. The eMLR method minimizes the errors introduced by independent variables to the ΔC_{Anth} calculation as compared to the previously developed MLR method (Friis et al., 2005; Wallace, 1995). The measured DIC data for each occupation are fit independently using a MLR to a series of independent predictor variables; in this case, potential temperature (θ), salinity (S), neutral density (γ^n), silicate (Si), and phosphate (P). The same set of predictor variables is fit separately to each of the five density layers for both occupations, resulting in 10 independent sets of MLR coefficients per hydrographic line. The change (or difference) in the resultant MLR coefficients between the two occupations is then used in conjunction with the hydrographic data from the most recent occupation to calculate ΔC_{Total} , the change in DIC between the two cruises. Equations (1) through (3) illustrate the eMLR fit method:

$$DIC_{t2} = A + B(S_{t2}) + C(\theta_{t2}) + D(\gamma_{n,t2}) + E(P_{t2}) + F(Si_{t2}) \quad [1]$$

$$DIC_{t1} = a + b(S_{t1}) + c(\theta_{t1}) + d(\gamma_{n,t1}) + e(P_{t1}) + f(Si_{t1}) \quad [2]$$

$$\Delta C_{\text{Total}} = (A - a) + (B - b)(S_{t2}) + (C - c)(\theta_{t2}) + (D - d)(\gamma_{n,t2}) + (E - e)(P_{t2}) + (F - f)(Si_{t2}) \quad [3]$$

The coefficients of the MLR fits for DIC are shown in Table 3. The standard errors in ΔC_{Total} associated with the fits range from ± 0.6 to $\pm 3.6 \mu\text{mol kg}^{-1}$. Errors in the individual measurements used for the fits are inherently canceled out by the subtraction of the MLR fit coefficients. Plots of MLR-predicted versus measured DIC are shown in the Supplemental Material along with maps of the residuals of the fits. Note that stations located west of 172°E were not used for the eMLR fit because this is a region where short-timescale processes such as surface freezing, nonlinear mixing, and air-sea gas exchange act to drive AABW formation (Jacobs et al., 1970; Orsi et al., 1999). As a result, the entire water column acts like a deep mixed layer in this region and the eMLR method cannot be applied. In addition, we did not use data from south of 71°S along the P16S line because this was the southernmost extent of the 2005 dataset.

Mixed layer calculation

In the seasonally affected mixed layer where the eMLR method produces the largest errors we used the known atmospheric change in $p\text{CO}_2$ (GLOBALVIEW-CO₂, 2013) between the two occupations to estimate a change in DIC using CO2SYS (Lewis and Wallace, 1998; van Heuven et al., 2011). This method assumes that despite the large seasonal and spatial variations in surface $p\text{CO}_2$, the average surface $p\text{CO}_2$ south of the Polar Front (PF) of the ACC

has increased proportionally to the average atmospheric increase ($\sim 1.8 \mu\text{atm yr}^{-1}$) during the study period (Takahashi et al., 2009; Yoshikawa-Inoue and Ishii, 2005). This assumption that the surface ocean mixed layer is in equilibrium or, at least, a constant disequilibrium with the atmosphere during all occupations, which could cause a 5-10% overestimation in ΔC_{Anth} (Hall et al., 2004). We calculated the mixed layer depth to be on average ~ 50 m using the potential density and potential temperature gradients as described by Dong et al. (2008). To calculate the mixed layer ΔC_{Total} we calculate the pre- ΔC_{Anth} DIC using CO2SYS (Lewis and Wallace, 1998; van Heuven et al., 2011) using the most recently measured TA and surface $p\text{CO}_2$ values minus the atmospheric $p\text{CO}_2$ increase during that time period as shown in Eq. (4). We use constants of Lueker et al. (2000) and Dickson (1990) for all CO2SYS calculations in this study. In Eq. (5), we subtract the pre- ΔC_{Anth} DIC value from the measured DIC of the most recent occupation and the difference is the ΔC_{Total} for the mixed layer. We then combine the ΔC_{Total} calculated using the eMLR method (for depths > 50 m) and the ΔC_{Total} calculated in the mixed layer (for depths < 50 m) using the atmospheric change to obtain a full water column ΔC_{Total} . One assumption that is inherent to the eMLR method is that TA has not changed between the two occupations, and as TA was not measured directly on the 1991-1992 occupations we cannot check the validity of this assumption.

$$DIC_{\text{Pre-}\Delta C_{\text{Anth}}} = \text{CO2SYS} \left\{ TA_{\text{Measured 2011}}, [p\text{CO}_{2\text{CO2SYS 2011}} - (1.8 \mu\text{atm yr}^{-1} \times \text{yrs})], \text{measured } T, S, \text{Pressure} \right\}$$

[4]

$$\Delta C_{\text{Total for surface}} = DIC_{\text{Measured 2011}} - DIC_{\text{Pre-}\Delta C_{\text{Anth}}} \quad [5]$$

Results

DIC changes

The results of the total carbon change (ΔC_{Total}) eMLR are shown in Fig. 5a. The ΔC_{Total} ranges from 2–18 $\mu\text{mol kg}^{-1}$ along the S04P line between 1992 and 2011 and extends from the surface down to a depth of 1000 m in the Ross Gyre in the west and down to around 2200m in the ACC Loop Gyre in the east. The ΔC_{Total} signal roughly follows isopycnals, which are deeper in the ACC Loop Gyre in the east than in the Ross Gyre in the west. The estimated DIC change corresponding to the measured atmospheric change in the mixed layer along S04P between 1992 and 2011 is 12–18 $\mu\text{mol kg}^{-1}$. Similarly, the ΔC_{Total} in the mixed layer along the P16S line corresponding to the measured atmospheric change between 2005 and 2011 is 3–5 $\mu\text{mol kg}^{-1}$. Measurable changes in ΔC_{Total} extend from the surface down to 450 m along P16S between 2005 and 2011, with deeper penetration in the southernmost stations, again due to deepening isopycnals towards the south. The small changes observed in the AABW and ‘new’ AABW layers will be addressed in the discussion.

AOU change correction

The eMLR method is sensitive to changes in AOU due to the dependence of DIC concentrations on organic matter respiration (Sabine et al., 2008; Wanninkhof et al., 2010). In order to calculate the portion of the ΔC_{Total} that can be associated with a change in AOU, ΔC_{AOU} , we use a method similar to Sabine et al. (2008) and fit AOU separately from DIC using a second set of MLRs and the

same set of five predictor variables between 50 m and the seafloor. Note that oxygen was purposely not used for the initial DIC MLR fits so that AOU could be used to evaluate the contribution of circulation and remineralization changes. The ΔAOU is obtained in the same way as the $\Delta\text{C}_{\text{Total}}$: by taking the difference between AOU MLR fit coefficients for two occupations, and multiplying by the measured data for the most recent occupation. The fitted coefficients for the AOU MLR fits are shown in Table 4. The standard errors associated with the AOU MLR fits range from ± 0.01 to $\pm 8.5 \mu\text{mol kg}^{-1} \text{O}_2$. Because the surface water is saturated with respect to oxygen, the surface ΔAOU was set to zero and the ΔAOU values for the mixed layer were linearly interpolated between the surface and the eMLR fit result at 50 m.

Carbon is released and oxygen consumed at a known stoichiometric ratio during the decay of organic matter, which has been empirically calculated as $117 \text{ CO}_2 : -170 \text{ O}_2$ (Anderson and Sarmiento, 1994). We obtained the $\Delta\text{C}_{\text{AOU}}$ by multiplying the ΔAOU from the eMLR result by $117/170$ as shown in Eq. (6). We then subtract this $\Delta\text{C}_{\text{AOU}}$ from the $\Delta\text{C}_{\text{Total}}$ to obtain the anthropogenic portion, $\Delta\text{C}_{\text{Anth}}$, as shown in Eq. (7) (Sabine et al., 2008).

$$\Delta\text{C}_{\text{AOU}} = \Delta\text{AOU} * \left(\frac{117}{170}\right) \quad [6]$$

$$\Delta\text{C}_{\text{Anth}} = \Delta\text{C}_{\text{Total}} - \Delta\text{C}_{\text{AOU}} \quad [7]$$

The $\Delta\text{C}_{\text{AOU}}$ is shown in Fig. 5b and is on the order of ~ 0 – $10 \mu\text{mol kg}^{-1}$ along S04P between 1992 and 2011 in CDW at depths of 150 to 2200 m. The $\Delta\text{C}_{\text{AOU}}$ along P16S is 0 – $5 \mu\text{mol kg}^{-1}$ at depths between 150 and 400 m. The $\Delta\text{C}_{\text{AOU}}$ signal roughly follows isopycnals and therefore it is much more prominent in the ACC Loop Gyre in the eastern half of the S04P transect and is less prominent in the Ross Gyre to the west and along the P16S transect.

The changes in AOU obtained from the eMLR fit account for approximately 0 – $10 \mu\text{mol kg}^{-1}$ of the $\Delta\text{C}_{\text{Total}}$ between 1992 and 2011 at intermediate depths and up to 75% of the column inventory of $\Delta\text{C}_{\text{Total}}$, and imply that these waters have experienced an increase in respiration either due to an increase in the flux of organic matter or a slowdown in circulation. This AOU increase is greatest in the ACC Loop Gyre in the eastern half of the section (east of 150°W), and less in the Ross Gyre in the western half of the section (west of 150°W). Using these data we are unable to draw a conclusion about the driver behind this AOU change; however, other studies have suggested that changing climate and circulation changes could act to change water mass ages in this region. For example, Waugh et al. (2013) used CFC-12 data along P16S to show an increased apparent age of polar CDW. Matear et al. (2000) also both observed and modeled a subsurface decrease in oxygen concentrations (increased AOU) around 350 m depth in the Southern Ocean and have attributed the decrease to a reduction in convective ventilation owing to shallower winter mixed layers and southward shifted Westerlies.

Another explanation for this measured increase in AOU between occupations comes from possible errors inherent in the assumptions that are made to calculate AOU. To calculate AOU, we assume that the water parcel was in equilibrium with the atmosphere and was at 100% saturation with respect to oxygen before it subducted. In the Southern Ocean in particular, this assumption

is not always correct, and researchers have shown that undersaturation in AAIW is common and can vary over time (Russell and Dickson, 2003). An undersaturation during water mass formation due to blockage by sea ice or a short residence time at the surface would result in falsely large AOU calculations. Any overestimations in AOU for either the earlier or later occupation would result in errors in ΔC_{AOU} , and, in turn, an error in ΔC_{Anth} . The eMLR method decreases the uncertainty due to possible undersaturation/disequilibrium when we take a difference between occupations because we are assuming constant conditions at the surface. For example, if waters in this region were undersaturated with respect to oxygen during the same times and to the same extent each year, then this error in our assumption of saturation would cancel out.

Anthropogenic carbon changes

After correcting ΔC_{Total} for ΔC_{AOU} using Eq. (7), the 19-year ΔC_{Anth} shown in Fig. 5c ranges from ~ 2 to $18 \mu\text{mol kg}^{-1}$ along the S04P transect. The ΔC_{Anth} is mostly isolated to the AASW layer, and penetrates to a depth of 100–150 m along the entirety of the S04P transect. There is a ~ 2 – $4 \mu\text{mol kg}^{-1}$ increase in C_{Anth} observed in the youngest AABW and a ~ 2 – $4 \mu\text{mol kg}^{-1}$ decrease observed in several stations between 3000 and 4000 m in the Ross Gyre. These ~ 2 – $4 \mu\text{mol kg}^{-1}$ changes are close to the detection limit of ΔC_{Anth} for these density layers, which is 3.4 and 3.6 for layers 4 and 5, respectively. The detection limit of ΔC_{Anth} varies between each density layer and between P16S and S04P, but can be calculated using the standard errors in the eMLR fits in Tables 3 and 4. Along P16S, the six-year ΔC_{Anth} signal is ~ 2 – $8 \mu\text{mol kg}^{-1}$ in the AASW layer and we also observe a $\sim 4 \mu\text{mol kg}^{-1}$ ΔC_{Anth} around 3400 m in two of the southernmost stations.

Discussion

Anthropogenic carbon storage rates

In order to compare the results of this study with other similar studies we integrate each component of the carbon change over depth and calculate annual rates of change across each hydrographic transect. Figure 6 shows rates of column inventory change of ΔC_{Total} , ΔC_{AOU} , and ΔC_{Anth} along each transect based on the column inventory of Figs. 5a, b, and c. We calculate a storage rate of C_{Anth} of $0.10 \pm 0.02 \text{ mol m}^{-2} \text{ yr}^{-1}$ along S04P and $0.16 \pm 0.03 \text{ mol m}^{-2} \text{ yr}^{-1}$ along P16S. The thickness of the AASW layer is relatively uniform across the S04P transect and, as a result, the C_{Anth} storage rate is longitudinally uniform as well. The C_{Anth} storage rate along the P16S transect, however, increases southward from $0.09 \pm 0.03 \text{ mol m}^{-2} \text{ yr}^{-1}$ at the S04P/P16S crossover point at 67°S to a maximum of $0.34 \pm 0.03 \text{ mol m}^{-2} \text{ yr}^{-1}$ at 71°S as the AASW thickens southward, consistent with the findings of Chen (1994, 1987, 1982). Along S04P, AOU changes account for $\sim 65\%$ of the ΔC_{Total} between 1992 and 2011 and account for $\sim 20\%$ of the ΔC_{Total} between 2005 and 2011 along P16S. Because most of the carbon change in the UCDW layer can be associated with a change in AOU, the column-integrated ΔC_{Total} and ΔC_{AOU} are larger in the eastern half of the S04P transect where the UCDW layer is thicker than in the western half. The C_{Anth} storage rates calculated independently from S04P and P16S agree at the crossover point, but the AOU-related carbon change rate—and therefore the total

carbon change rate—do not agree within their uncertainties. This disagreement is an indication that the processes acting to change AOU may not be uniform in time between 1992 and 2011 in this region.

The average storage rate of C_{Anth} calculated in this study of $0.10 \pm 0.02 \text{ mol C m}^{-2} \text{ yr}^{-1}$ is consistent with the previous storage rate of $0.1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ obtained by Sabine et al. (2008) using the eMLR method between 1992 and 2005 at the crossover point for S04P and P16S at $67^\circ\text{S } 150^\circ\text{W}$. Table 5 shows the C_{Anth} storage rate calculated in this study compared with results from other regions of the ocean. The storage rates measured in this study region south of the PF are relatively small ($0.10 \pm 0.02 \text{ mol C m}^{-2} \text{ yr}^{-1}$) compared to the global average storage rate of $0.5\text{--}0.55 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Khaliwala et al., 2009; Sabine et al., 2008). Storage rates are relatively low south of the PF due to ongoing wind-driven northward export of C_{Anth} -rich surface waters from south to north across the PF of the ACC and the constant upwelling of older waters. In addition, strong summertime surface stratification and winter sea ice coverage prevent mixing of C_{Anth} past the depth of the mixed layer on the timescale of this study. These C_{Anth} -rich surface waters move north across the ACC where they meet less-dense waters and subduct along the $\gamma^n \approx 27.2 \text{ kg m}^{-3}$ neutral density isopycnal to form AAIW, facilitating northward subsurface advection of C_{Anth} . Storage rates increase to $0.75 \text{ mol C m}^{-2} \text{ yr}^{-1}$ moving equatorward into the Pacific Ocean (Sabine et al., 2008) where waters are experiencing both diffusion of C_{Anth} from above and advection of C_{Anth} into the region from the south at depth.

The results of this study are also consistent with results from a recent total C_{Anth} inventory, $[C_{\text{ant}}]$, calculated by Pardo et al. (2014) using the ζ_T^0 method. This approach, which calculates total C_{Anth} changes from preindustrial to present, showed that along the S04P line, the overall C_{Anth} inventory from preindustrial time to 1994 is $\sim 5\text{--}7 \mu\text{mol kg}^{-1}$ in both CDW and AABW (Pardo et al., 2014). If we extrapolate this inventory to our study, a DIC increase of less than $1 \mu\text{mol kg}^{-1}$ would be expected in both CDW and AABW for the period between 1992 and 2011. We consider our results to be in agreement with Pardo et al. because we were unable to detect a significant ΔC_{Anth} signal in CDW during our study period and we detected only a small ($\sim 3 \mu\text{mol kg}^{-1}$) change in AABW in a few of the westernmost stations where we find the most recently formed AABW (Swift and Orsi, 2012). Anthropogenic carbon storage is undetectable in CDW throughout this study period likely due to seasonal sea ice coverage and strong surface stratification. In addition, the C_{Anth} storage rate is small in AABW over this study period. It is possible that AABW does not absorb a significant amount of anthropogenic CO_2 before it sinks to depth and/or that AABW is formed in such small quantities that it quickly mixes with LCDW and the anthropogenic signal is diluted below the detection limit of the eMLR method (Poisson and Chen, 1987).

Changes in surface water pH and aragonite saturation state

It has been estimated that the average surface ocean pH has dropped by about 0.11 pH units since the beginning of industrialization, which equates to approximately a 30% increase in the hydrogen ion concentration and acidity, and

a 16% decrease in the saturation state of aragonite ($\Omega_{\text{Aragonite}}$; Feely et al., 2012, 2009a; Orr, 2011; Orr et al., 2005). This acidification reduces the ocean's ability to store additional carbon, and also has significant negative impacts on the growth of calcifying organisms and on the livelihood of many other organisms that depend on them (Bednaršek et al., 2014, 2012; Doney et al., 2009; Feely et al., 2004). The ΔC_{Anth} results from this study can be used in conjunction with measured alkalinity data to calculate pH and $\Omega_{\text{Aragonite}}$ changes using CO2SYS (Lewis and Wallace, 1998; van Heuven et al., 2011). The estimated anthropogenic pH and $\Omega_{\text{Aragonite}}$ changes are shown in Fig. 7.

Anthropogenic carbon uptake along S04P has decreased surface water pH by 0.042 ± 0.007 pH units between 1992 and 2011 and by 0.014 ± 0.006 pH units along P16S between 2005 and 2011. We calculate an overall rate of anthropogenic pH decrease in surface waters of 0.0022 ± 0.0004 pH units yr^{-1} and 0.0024 ± 0.0009 pH units yr^{-1} along S04P and P16S, respectively. We calculate an anthropogenic decrease in the surface water $\Omega_{\text{Aragonite}}$ of 0.47 ± 0.10 % yr^{-1} along S04P and 0.50 ± 0.20 % yr^{-1} along P16S, resulting in an average shoaling of the saturation horizons (using $\Omega_{\text{Aragonite}}=1.3$ horizon) of 2.0 ± 0.7 m yr^{-1} throughout the study region. A summary of these results as well as results from previous surface water pH and $\Omega_{\text{Aragonite}}$ studies is shown in Table 6. It is important to note that while anthropogenic pH and $\Omega_{\text{Aragonite}}$ changes are only detected in the mixed layer in this region, C_{Anth} penetrates much deeper in areas north of the PF and pH and $\Omega_{\text{Aragonite}}$ changes are observed at deeper depths in those regions.

Revelle factors are generally lower in the tropics and subtropics (currently ~ 9) and increase poleward (currently ~ 15) making high-latitude surface waters more sensitive to changes in DIC. Hence when one estimates the $\Delta p\text{CO}_2$, ΔpH , or $\Delta \Omega_{\text{Aragonite}}$ resulting from a particular amount of uptake of C_{Anth} it will be higher for high-latitude waters than for the tropics and subtropics. Surface water anthropogenic pH and $\Omega_{\text{Aragonite}}$ changes in our study region are among the highest measured globally and the rates are comparable to those observed in other high-latitude surface waters. For example, Midorikawa et al. (2012) measured a pH decrease of 0.0020 ± 0.0003 pH units yr^{-1} in the PZ of the Southern Ocean and Takahashi et al. (2014) calculated a decrease of 0.0015 ± 0.0008 pH units yr^{-1} in the PZ of the Drake Passage. In the Iceland and Irminger Seas, researchers have measured a pH decrease of 0.0023 ± 0.0003 (Olafsson et al., 2009) and 0.0026 ± 0.0006 pH units yr^{-1} (Bates et al., 2014), respectively, compared to a decrease of 0.0022 ± 0.0004 pH units yr^{-1} for the S04P line. Tropical and subtropical regions are experiencing pH decreases on the order of 0.0017 pH units yr^{-1} and $\Omega_{\text{Aragonite}}$ saturation horizon shoaling of 1 ± 0.6 m yr^{-1} (Bates et al., 2014; Byrne et al., 2010; Dore et al., 2009; Feely et al., 2012; González-Dávila et al., 2010; Ishii et al., 2011; Midorikawa et al., 2010; Takahashi et al., 2014; Waters et al., 2011), indicating that polar surface waters are acidifying more quickly than tropical and subtropical waters.

Conclusions

Over the period of 1992 to 2011, south of the Polar Front (PF) in the Pacific Sector of the Southern Ocean, measurable anthropogenic CO_2 storage is

isolated to the mixed layer and to the most recently formed Antarctic Bottom Water (AABW). Anthropogenic carbon (C_{Anth}) storage rates in this region are small compared to storage rates north of the Antarctic Circumpolar Current (ACC) because of the large-scale transport of C_{Anth} -rich surface waters northward across the ACC where they subduct to form Antarctic Intermediate Water (AAIW). Regions north of the PF have higher storage rates because they are experiencing both uptake of C_{Anth} from the atmosphere and addition of C_{Anth} via advective transport within the AAIW layer at depth. Although C_{Anth} storage rates are low in this region, the Southern Ocean is responsible for a large portion of the global C_{Anth} storage beneath the thermocline.

We observe an increase in Apparent Oxygen Utilization (AOU) in Circumpolar Deep Water (CDW) over the study period, which may indicate a recent change in circulation in the Pacific sector of the Southern Ocean. This change in circulation may impact the ability of this region to take up C_{Anth} in the future.

In addition, the surface waters in this region are acidifying at a faster rate than the tropical and subtropical oceans due to the higher sensitivity of polar waters to C_{Anth} . As a result, the surface water saturation state of aragonite ($\Omega_{\text{Aragonite}}$) is decreasing more quickly in this region and these waters will likely become undersaturated sooner than the warmer subtropical and tropical waters to the north.

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Figure Captions

Figure 1. Map of S04P and P16S stations occupied from westernmost to easternmost during February–April 2011.

Figure 2. A depiction of the large-scale Southern Ocean circulation processes occurring in the study region. Thick red arrows indicate the mean flow of the Antarctic Slope Current and the Antarctic Circumpolar Current (ACC), orange arrows indicate water mass circulation, yellow arrows indicate the direction of the prevailing winds, and transparent red lines indicate the locations of the S04P and P16S hydrographic lines relative to these features. (Adapted from National Research Council 2011)

Figure 3. (a) Potential temperature (Θ), (b) Salinity, and (c) DIC (Dissolved Inorganic Carbon) measured in 2011 along the S04P (left) and P16S (right) transects. Thick black contours correspond to constant neutral density and the thick black vertical line denotes the crossover point between S04P and P16S.

Figure 4. (a) Measured DIC change along the S04P (left) and P16S (right) transects highlighting seasonal and interannual variability in surface waters and movement of water masses, (b) Apparent Oxygen Utilization (AOU) change measured along S04P (left) and P16S (right). Thick black contours correspond to constant neutral density and the thick vertical black line denotes the crossover point between S04P and P16S.

Figure 5. (a) ΔC_{Total} , total carbon change calculated from eMLR using Eqs. (3)–(5), (b) ΔC_{AOU} , carbon change due to AOU changes calculated from eMLR using Eq. (6), (c) ΔC_{Anth} , anthropogenic carbon change calculated from the difference between (a) and (b) using Eq. (7) along S04P (2011–1992) (left) and P16S (2011–2005) (right). Thick black contours correspond to neutral density layers used for the MLR fits and the thick black vertical line denotes the crossover point between S04P and P16S.

Figure 6. S04P (left) and P16S (right) annual column inventory changes of ΔC_{Total} (blue line), ΔC_{AOU} (green line), and ΔC_{Anth} (red line).

Figure 7. (a) Anthropogenic pH change and (b) anthropogenic aragonite saturation state ($\Omega_{\text{Aragonite}}$) change along S04P (2011–1992, 19 years) and P16S (2011–2005, 6 years). A neutral density contour (27.75 kg m^{-3}) is overlaid in thick black contours and the crossover point between S04P and P16S is shown with a vertical black line.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1. A summary of carbon and oxygen measurements used in this study

Year	Parameter	Number	Uncertainty	Method
1992	DIC	1119	$\pm 1.8 \mu\text{mol kg}^{-1}$	Coulometric titration
1992	pCO ₂	1112	$\pm 0.12 \%$ (ppm)	Equilibrator-infrared gas analyzer
1992	Oxygen	2329	$\pm 0.5 \mu\text{mol kg}^{-1}$	Automated titration
2005	DIC	257	$\pm 2.0 \mu\text{mol kg}^{-1}$	Coulometric titration
2005	TA	257	$\pm 1.1 \mu\text{mol kg}^{-1}$	HCl titration
2005	Oxygen	309	$\pm 0.5 \mu\text{mol kg}^{-1}$	Automated titration
2011	DIC	2439	$\pm 1.9 \mu\text{mol kg}^{-1}$	Coulometric titration
2011	TA	2420	$\pm 1.0 \mu\text{mol kg}^{-1}$	HCl titration
2011	Oxygen	3762	$\pm 0.5 \mu\text{mol kg}^{-1}$	Automated titration

Table 2

Table 2. Neutral density (γ^n) surfaces	
Water Mass	γ^n (kg m ⁻³)
AASW	< 27.75
UCDW	27.75 - 28.15
LCDW	28.15 - 28.27
AABW	28.27 - 28.3
'New' AABW	> 28.3

Table 3. DIC MLR fit coefficients

MLR fit equation: $DIC = a + b (S) + c (\Theta) + d (\gamma^n) + e (P) + f (Si)$								
Cruise								std. error
γ^n layer	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>n</i> ^a	$\mu\text{mol kg}^{-1}$
S04P 2011								
Layer 1	−311.41	−1.64	115.87	0.54	27.17	−55.15	174	3.4
Layer 2	790.14	−1.49	79.70	0.44	57.17	−52.24	1247	2.3
Layer 3	−5101.86	11.00	157.30	0.32	−12.24	66.83	664	1.6
Layer 4	4271.66	−93.40	389.67	0.25	−6.93	−549.41	206	1.3
Layer 5	−650.82	−34.75	254.71	0.16	−14.55	−208.99	135	1.3
S04P 1992								
Layer 1	−390.66	−1.93	106.09	0.67	44.05	−42.16	219	3.5
Layer 2	545.18	−1.42	101.21	0.51	53.75	−70.19	928	2.7
Layer 3	−6630.17	−6.96	281.25	0.31	5.20	−32.51	475	2.0
Layer 4	−2301.19	119.49	−367.44	0.20	−37.87	613.74	162	1.5
Layer 5	−1420.92	−75.96	414.96	0.24	23.36	−381.65	220	1.7
P16S 2011								
Layer 1	12681.98	132.22	−2778.47	0.15	15.20	3049.38	17	3.6
Layer 2	2165.41	7.66	16.37	0.52	29.49	−21.43	129	3.3
Layer 3	−27224.26	−190.12	1614.65	0.10	−27.46	−936.03	90	1.7
Layer 4	149098.00	2457.97	−14272.66	−0.87	−110.17	12322.56	18	0.6
Layer 5	64633.17	701.28	−4721.91	0.14	24.79	3582.65	47	1.8
P16S 2005								
Layer 1	1493.39	6.52	−244.94	0.44	91.90	320.12	25	2.6
Layer 2	1454.31	0.87	69.45	0.55	42.44	−62.59	98	1.6
Layer 3	−596.36	23.57	5.48	0.37	−12.32	93.46	65	0.6
Layer 4	−6176.18	−198.98	1095.73	0.26	−5.81	−1045.97	19	0.7
Layer 5	12970.37	−70.97	−80.95	0.58	−13.37	−280.73	53	0.6

^a where *n* is the number of observations in each fit

Layer 1: $\gamma^n \leq 27.75 \text{ kg m}^{-3}$

Layer 2: $27.75 \text{ kg m}^{-3} < \gamma^n \leq 28.15 \text{ kg m}^{-3}$

Layer 3: $28.15 \text{ kg m}^{-3} < \gamma^n \leq 28.27 \text{ kg m}^{-3}$

Layer 4: $28.27 \text{ kg m}^{-3} < \gamma^n \leq 28.3 \text{ kg m}^{-3}$

Layer 5: $\gamma^n > 28.3 \text{ kg m}^{-3}$

Table 4. AOU MLR fit coefficients

MLR fit equation: $AOU = a + b(S) + c(\Theta) + d(\gamma^n) + e(P) + f(Si)$								
Cruise								std. error
γ^n layer	a	b	c	d	e	f	n^a	$\mu\text{mol kg}^{-1}$
S04P 2011								
Layer 1	-3363.09	-16.82	419.59	0.70	49.25	-398.91	174	8.5
Layer 2	-2401.05	-9.79	230.29	0.42	97.37	-202.61	1247	2.5
Layer 3	-6230.21	-8.50	277.32	0.29	8.53	-117.18	664	0.8
Layer 4	-4144.54	-5.26	211.94	0.16	2.49	-109.62	206	0.5
Layer 5	-6322.14	20.25	142.94	0.12	1.18	52.18	135	0.5
S04P 1992								
Layer 1	-1706.38	0.52	160.01	1.54	50.31	-140.37	219	6.0
Layer 2	-3284.89	-7.39	244.52	0.36	94.57	-188.51	928	2.7
Layer 3	-3338.19	-7.97	188.85	0.18	29.57	-112.08	475	0.6
Layer 4	1275.05	51.18	-178.53	0.20	8.12	176.91	162	0.4
Layer 5	-536.625	38.97	-75.88	0.16	7.52	115.29	220	0.3
P16S 2011								
Layer 1	-338.46	47.47	-800.04	0.07	20.41	1000.95	17	1.3
Layer 2	-228.63	7.09	112.51	0.56	77.12	-134.02	129	2.9
Layer 3	12261.66	135.14	-851.14	0.12	1.87	614.29	90	0.3
Layer 4	6959.95	58.97	-354.93	0.19	7.29	192.46	18	0.1
Layer 5	15196.00	258.30	-1480.67	0.20	9.12	1281.43	47	0.1
P16S 2005								
Layer 1	211.66	15.98	-372.04	0.48	132.84	443.40	25	6.9
Layer 2	-4180.85	-3.89	174.72	-0.11	77.84	-67.37	98	2.7
Layer 3	-475.93	28.12	-65.68	-0.10	2.12	102.40	65	0.1
Layer 4	1334.04	73.86	-274.10	0.20	-3.15	292.91	19	0.0
Layer 5	-2005.29	-1.58	125.71	0.23	-2.19	-79.48	53	0.1

^a where n is the number of observations in each fit

Layer 1: $\gamma^n \leq 27.75 \text{ kg m}^{-3}$

Layer 2: $27.75 \text{ kg m}^{-3} < \gamma^n \leq 28.15 \text{ kg m}^{-3}$

Layer 3: $28.15 \text{ kg m}^{-3} < \gamma^n \leq 28.27 \text{ kg m}^{-3}$

Layer 4: $28.27 \text{ kg m}^{-3} < \gamma^n \leq 28.3 \text{ kg m}^{-3}$

Layer 5: $\gamma^n > 28.3 \text{ kg m}^{-3}$

Table 5

Table 5. Anthropogenic Carbon Storage Rate Comparison

Region	Storage Rate (mol m ⁻² yr ⁻¹)	Method	Study	Study Period
67°S Pacific	0.10 ± 0.02	eMLR	this study	1992–2011
60°S–71°S Pacific	0.10	eMLR	Sabine et al., 2008	1992–2005
20°N–50°S Pacific	0.6 ± 0.1	eMLR	Sabine et al., 2008	1991–2006
N. of 50°S in S. Pacific	0.9 ± 0.3	MLR	Peng et al., 2003	1974–1996
N.E. Pacific	1.3 ± 0.5	MLR	Peng et al., 2003	1973–1991
4°S–30°N Pacific	0.5 ± 0.2	ΔnC_T^{CAL}	Murata et al., 2009	1993–2005
~160°E, ~45°N Pacific	0.4 ± 0.1	DIC corrected with ΔC^*	Wakita et al., 2010	1992–2008
20°S–20°N Pacific	0.3 ± 0.1	eMLR	Sabine et al., 2008	1991–2006
110°W in S. Pacific	0.46 ± 0.2	eMLR	Waters et al., 2011	1994–2008
32°S Pacific	0.72 ± 0.2	eMLR	Waters et al., 2011	1992–2010
32°S Pacific	0.79 ± 0.2	TTD	Waters et al., 2011	1992–2010
North of 20°N Pacific	0.4 ± 0.2	eMLR	Sabine et al., 2008	1994–2004
45°S–65°S Pacific	0.4 ± 0.2	CFC MLR	Matear and McNeil, 2003	1968–1996
S. Pacific	1.0 ± 0.4	ΔnC_T^{CAL}	Murata et al., 2007	2003–1992
20°S Indian	1.0 ± 0.1	ΔnC_T^{CAL}	Murata et al., 2010	1995–2004
20°S–10°S Indian	0.10	DIC _n	Peng et al., 1998	1978–1995
10°S–5°N Indian	0.70	DIC _n	Peng et al., 1998	1978–1995
30°S Atlantic	0.6 ± 0.1	ΔnC_T^{CAL}	Murata et al., 2008	1992–2003
Atlantic	0.5 ± 0.3	eMLR	Peng and Wanninkhof, 2010	1973–1994
40°N–65°N Atlantic	2.2 ± 0.7	eMLR	Friis et al., 2005	1981–1997
20°N–40°N Atlantic	1.2 ± 0.3	eMLR	Tanhua et al., 2007	1981–2004
Nordic Seas	0.9 ± 0.2	eMLR	Olsen et al., 2006	1981–2003
Atlantic	0.53 ± 0.05	eMLR _{dens}	Wanninkhof et al., 2010	1989–2005
North Atlantic	0.60	$\delta^{13}C$ MLR	Quay et al. 2007	1981–2003
Global Average	0.55	DGOM	Sabine et al., 2008	preindustrial to 2005

Table 6

Table 6: Comparison of pH changes and Aragonite Saturation changes in surface waters

Region	pH Change (pH units yr ⁻¹)	$\Omega_{\text{Aragonite}}$ Shoaling (m yr ⁻¹)	$\Omega_{\text{Aragonite}}$ Change (% yr ⁻¹)	Study	Study Period
Pacific Southern Ocean (S4P)	-0.0022 ± 0.0004	2.0 ± 0.7 ($\Omega=1.3$)	-0.47 ± 0.10	this study	1992–2011
Pacific Southern Ocean (P16S)	-0.0024 ± 0.0009	2.0 ± 0.8 ($\Omega=1.3$)	-0.50 ± 0.20	this study	1995–2011
Polar Zone Southern Ocean	-0.0020 ± 0.0003			Midorikawa et al, 2012	1963–2003
Drake (PZ)	-0.0015 ± 0.0008		-0.46 ± 0.4	Takahashi et al., 2014	2002–2012
Drake (SAZ)	-0.0023 ± 0.0007		-0.69 ± 0.4	Takahashi et al., 2014	2002–2012
S.W. Pacific (Munida)	-0.0013 ± 0.0003		-0.43 ± 0.13	Bates et al., 2014	1998–2012
S. Pacific		1.9 ± 0.8 ($\Omega=1.0$)	-0.35 ± 0.05	Feely et al., 2012	1991–2005
S. Pacific	-0.0016			Waters et al., 2011	1994–2008
N.W. Pacific	-0.0015 ± 0.005			Midorikawa et al., 2010	1983–2007
N.W. Pacific	-0.002		-0.34	Ishii et al., 2011	1994–2008
N. Pacific	-0.0017			Byrne et al., 2010	1991–2006
N. Pacific		1 ± 0.6 ($\Omega=1.0$)	-0.34 ± 0.04	Feely et al., 2012	1994–2004
N. Pacific (ALOHA)	-0.0018 ± 0.0001		-0.28	Dore et al., 2009	1988–2007
N. Pacific (HOT)	-0.0016 ± 0.0001		-0.28 ± 0.04	Bates et al., 2014	1988–2012
N. Pacific (HOT)	-0.0018 ± 0.0001		-0.27 ± 0.03	Takahashi et al., 2014	1988–2009
Iceland Sea	-0.0023 ± 0.0003	4 ($\Omega=1.0$)	-0.48 ± 0.07	Olafsson et al., 2009	1985–2008
Irminger Sea	-0.0026 ± 0.0006		-0.40 ± 0.20	Bates et al., 2014	1983–2012
N. Atlantic (BATS)	-0.0017 ± 0.0001		-0.26 ± 0.02	Bates et al., 2014	1983–2012
N. Atlantic (BATS)	-0.0018 ± 0.0002		-0.34 ± 0.03	Takahashi et al., 2014	1983–2010
N. Atlantic (ESTOC)	-0.0018 ± 0.0002		-0.34 ± 0.07	Bates et al., 2014	1995–2012
N. Atlantic (ESTOC)	-0.0017 ± 0.0001		-0.36	González-Dávila et al., 2010	1995–2004
N. Atlantic (ESTOC)	-0.0020 ± 0.0004		-0.29 ± 0.06	Takahashi et al., 2014	1996–2010
Caribbean (CARIACO)	-0.0025 ± 0.0004		-0.18 ± 0.08	Bates et al., 2014	1995–2012
E. Equatorial Indian	-0.0016 ± 0.0001		-0.25 ± 0.01	Xue et al., 2014	1962–2012