Marine Chemistry 174 (2015) 147–160

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Quantifying anthropogenic carbon inventory changes in the Pacific sector of the Southern Ocean

Nancy L. Williams [a,b,*], Richard A. Feely [b], Christopher L. Sabine [b], Andrew G. Dickson [c], James H. Swift [c], Lynne D. Talley [c], Joellen L. Russell [d]

[a] School of Oceanography, University of Washington, Box 357940, Seattle, WA 98195-7940, USA
[b] Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, 7600 Sand Point Way NE, Seattle, WA 98115-6349, USA
[c] Scripps Institution of Oceanography, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA
[d] Department of Geosciences, University of Arizona, 1040 E 4th Street, Tucson, AZ 85721, USA

ARTICLE INFO

Article history:
Received 29 November 2014
Received in revised form 17 June 2015
Accepted 18 June 2015
Available online 21 June 2015

Keywords:
Carbon dioxide
Dissolved inorganic carbon
Anthropogenic carbon
pH
Carbonate chemistry
Ocean acidification
Apparent oxygen utilization
Hydrography
Southern ocean
Decadal change

ABSTRACT

The Southern Ocean plays a major role in mediating the uptake, transport, and long-term storage of anthropogenic carbon dioxide (CO_2) 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 CO_2 waters. In the AASW we calculate an anthropogenic increase in DIC of 12–18 μmol kg^{-1} and an average storage rate of anthropogenic CO_2 of 0.10 ± 0.02 mol m^{-2} yr^{-1} for this region compared to a global average of 0.5 ± 0.2 mol m^{-2} yr^{-1}. In surface waters this anthropogenic CO_2 uptake results in an average pH decrease of 0.0022 ± 0.0004 pH units yr^{-1}, a 0.47 ± 0.10% yr^{-1} decrease in the saturation state of aragonite ($\Omega_{Aragonite}$) and a 2.0 ± 0.7 m yr^{-1} shoaling of the aragonite saturation horizons (calculated for the $\Omega_{Aragonite} = 1.3$ contour).

1. Introduction

Since the beginning of the industrial era, atmospheric concentrations of carbon dioxide (CO_2) 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 and Duffy, 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; Rusell

* Corresponding author at: School of Oceanography, University of Washington, Box 357940, Seattle, WA 98195-7940, USA.
E-mail addresses: Nancy.Williams@oregonstate.edu (N.L. Williams), Richard.A.Feely@noaa.gov (R.A. Feely), Chris.Sabine@noaa.gov (C.L. Sabine), adickson@ucsd.edu (A.G. Dickson), jswift@ucsd.edu (J.H. Swift), ltalley@ucsd.edu (L.D. Talley), jrussell@email.arizona.edu (J.L. Russell).

http://dx.doi.org/10.1016/j.marchem.2015.06.015
0304-4203/

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 $\delta^{13}C$ (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., 1999, 2002, 2004b; Touratier et al., 2007; Wallace, 1995), tracer-based approaches (Hall et al., 2002, 2004; 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 (1982, 1987, 1994) 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.

2. 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 ($\theta < -1.8$ °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 $\gamma^n \approx 27.2$ 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 ($\gamma^n > 28.27$ 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

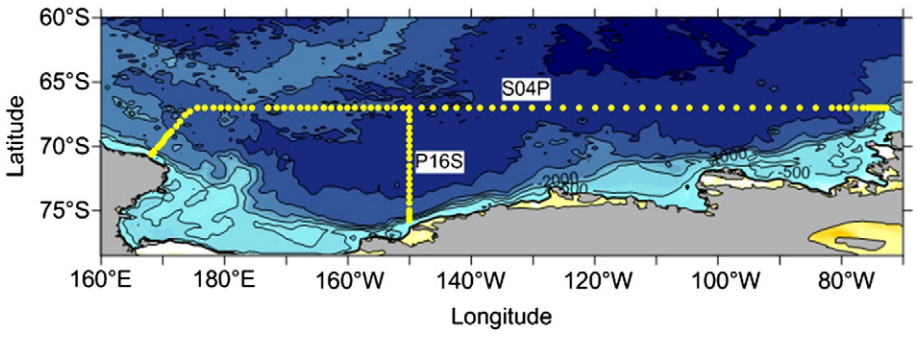

Fig. 1. Map of S04P and P16S stations occupied from westernmost to easternmost during February–April 2011.