

Changing biogeochemistry of the Southern Ocean and its ecosystem implications

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Supplementary information

1. Nutrient dynamics during winter cruises 2017 and 2019

1.1 Nutrient sample collection and analysis

Winter nutrient sampling was conducted aboard the R/V *SA Agulhas II* in 2017 (WC-17; 28 June – 13 July 2017) along WOCE line IO6 (Indian sector) and in 2019 (SCALE; 18 July – 12 August 2019) along WOCE line A12 (the GoodHope repeat hydrographic line; Atlantic sector) (Figure S1). Seawater was collected at regular depth intervals in 12-L Niskin bottles attached to a CTD rosette. Samples for the analysis of nitrate, nitrite, silicic acid and phosphate concentrations were decanted into replicate 50 mL HDPE tubes that were copiously rinsed prior to filling. Duplicate tubes were immediately frozen at -20°C for later measurement of nitrate and silicic acid, whilst nitrite and phosphate samples that were to be measured shipboard within a few hours were stored in the fridge. Duplicate samples of unfiltered seawater (~ 40 mL) were also collected at each depth between the surface and 500 m for the analysis of ammonium concentrations in 50 mL HDPE Nalgene bottles that had been stored (“aged”) with orthophthaldialdehyde working reagent (OPA-WR) prior to sample collection. The OPA-WR was decanted just prior to sample collection and bottles were rinsed three times with sample seawater prior to filling.

Phosphate and nitrite concentrations were analysed manually according to the methods described by Grasshoff et al. (1983), with absorbance measured using a Thermo Scientific Genesis 30 Visible spectrophotometer. Aliquots of a certified reference material (CRM; JAMSTEC) were analysed with each sample run to ensure data quality. Nitrate+nitrite and silicic acid were measured in the Marine Biogeochemistry Lab at the University of Cape Town (MBL-UCT) using a Lachat Quick-Chem flow injection autoanalyser (Wolters, 2002; Egan, 2008). Standards of varying concentration were run after every ten samples to monitor instrument performance and allow for correction of any drift, and a CRM was measured at the beginning and end of each run to ensure measurement accuracy. The precision of the nitrate+nitrite, silicic acid, phosphate, and nitrite measurements was $\pm 0.4 \mu\text{mol L}^{-1}$, $\pm 0.2 \mu\text{mol L}^{-1}$, $\pm 0.06 \mu\text{mol L}^{-1}$, and $\pm 0.05 \mu\text{mol L}^{-1}$, respectively, and the detection limit was $0.1 \mu\text{mol L}^{-1}$, $0.2 \mu\text{mol L}^{-1}$, $0.05 \mu\text{mol L}^{-1}$, and $0.05 \mu\text{mol L}^{-1}$, respectively.

Ammonium concentrations were measured shipboard via the fluorometric method of Holmes et al. (1999) using a UV module in a Turner Designs Trilogy Fluorometer 7500-000. Standards were made daily using Type-1 ultrapure Milli-Q water, and samples and standards were measured in duplicate. Precision was $\pm 0.01 \mu\text{mol L}^{-1}$ and the detection limit was $<0.02 \mu\text{mol L}^{-1}$. The matrix effect resulting from the calibration of seawater samples to Milli-Q standards was calculated according to the standard addition method (Saxberg and Kowalski, 1979). All samples were corrected for the matrix effect (Taylor et al., 2007), which was always $<10\%$ and typically $<5\%$.

Summer nutrient data for IO6 and A12 were downloaded from the WOCE Hydrographic Program data repository (weblink: <https://doi.org/10.21976/C6RP4Z>). No ammonium concentration data are available for the summer in the WOCE database. However, we collected triplicate samples of unfiltered seawater (~40 mL) from the underway system (~7 m intake depth) of the R/V *SA Agulhas II* every ~0.25 degrees of latitude during the 2018/2019 resupply voyage along WOCE line A12 between Cape Town and Antarctica (SANAE 58; 7 – 17 December 2018). These samples were measured shipboard as described above. Although not collected at the same time as the other summertime nutrient data shown in Figure 2, the SANAE 58 ammonium concentrations are included here to provide an indication of typical summertime conditions.

1.2 Derived variables

N^* is a quasi-conservative tracer used to track the changes in dissolved inorganic nitrogen (DIN) relative to phosphate, thereby providing information as to whether fixed nitrogen is being added to or lost from an ecosystem relative to phosphorus (Gruber and Sarmiento, 1997). N^* was originally defined as $N^* (\mu\text{mol L}^{-1}) = [\text{NO}_3^-] - 16 \times [\text{PO}_4^{3-}]$. Here, we further derive $N^*_{\text{DIN}} = [\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+] - 16 \times [\text{PO}_4^{3-}]$ where DIN is the sum of nitrate, nitrite and ammonium, and 16 is the average stoichiometric N:P ratio observed during the autotrophic production and heterotrophic remineralisation of organic matter (Redfield et al., 1963; Anderson and Sarmiento, 1994).

The tracer Si^* was initially developed to track SAMW from its formation region into the lower latitude ocean (Sarmiento et al., 2004). It is also an indicator of the nutrient status of diatoms. Si^* leverages the general observation that under favourable conditions, diatoms consume silicic acid and nitrate in a ratio of ~1:1 (Hutchins and Bruland, 1998; Takeda, 1998; Ragueneau et al., 2000), but that under conditions of limitation (e.g. of low iron), the ratio of silicic acid-to-nitrate uptake changes (e.g. Franck et al., 2000; Brzezinski et al., 2003). Si^* was computed from measurements of nitrate and silicic acid concentrations following Sarmiento et al. (2004) as $\text{Si}^* (\mu\text{mol L}^{-1}) = [\text{Si}(\text{OH})_4] - [\text{NO}_3^-]$.

1.3 Hydrography

Southern Ocean frontal positions were identified from 1/4° climatological sea surface temperature (SST) data from WOA13 (<https://www.nodc.noaa.gov/OC5/woa13/woa13data.html>). The Sub-Tropical Front (STF), Sub-Antarctic Front (SAF) and Polar Front (PF) were identified with SSTs of 11.5°C, 4°C and 2.5°C respectively (Deacon, 1982; Orsi et al., 1995). Water masses were identified using potential temperature, absolute salinity and potential density anomalies calculated from temperature and salinity data measured by the CTD during each cruise according to the criteria outlined by Whitworth and Nowlin (1987), Park et al. (1993), Orsi et al. (1995), and Belkin and Gordon (1996).

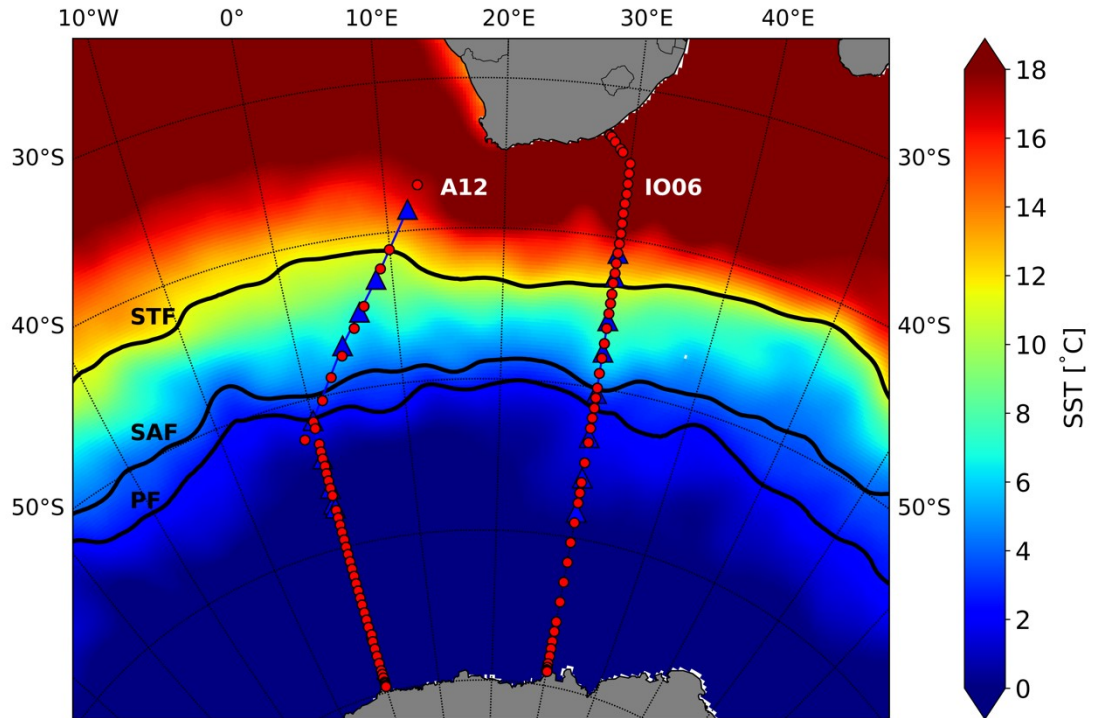


Figure S1: Map showing the cruise tracks (A12 and IO6) for which nutrient data are presented here, overlaid on annual SST climatology (1955-2012; averaged annually; WOA13). The red circles show the position of summertime CTD casts (WOCE Hydrographic Program) and the blue triangles denote the positions of CTD casts conducted on cruises in winter 2017 (WC-17 along IO6) and 2019 (SCALE along A12). The southernmost CTD casts on the winter cruises were conducted at the northern edge of the sea ice. The average positions of the major Southern Ocean fronts, identified according to the criteria of Deacon (1982) and Orsi et al. (1995), are shown by the black lines (STF: Sub-Tropical Front; SAF: Sub-Antarctic Front; PF: Polar Front).

2. Nutrient dynamics in Marguerite Bay 2013 – 2016

2.1 Seawater sampling and analysis

Water column sampling was conducted between November 2013 and March 2016 in Ryder Bay, northern Marguerite Bay at the west Antarctic Peninsula (WAP) (Figure S2), within the framework of the Rothera Time Series (RaTS) program of the British Antarctic Survey (Meredith et al., 2004; Clarke et al., 2008; Venables et al., 2013). Sampling and oceanographic monitoring were conducted approximately twice-weekly during the austral spring/summer growing seasons of 2013/14, 2014/15 and 2015/16, and approximately weekly during the intervening winter periods. Water column samples were collected over the deepest point (~520 m) in Ryder Bay from a 12 ft rigid-hulled inflatable boat (RIB) using Niskin bottles deployed with a hand-cranked winch. Samples were taken for the determination of macronutrient (nitrate, nitrite, phosphate, silicic acid) and chlorophyll *a* concentrations, and stored in acid-clean HDPE containers in the dark, for processing on return to the laboratory. Data shown here are from 15 m water depth, being the long-term average depth of the CTD fluorescence maximum.

On return to the laboratory at Rothera Research Station, samples for analysis of macronutrient concentrations were filtered through Acrodisc PF syringe filters with 0.2 μm supor membranes, snap-frozen at -80°C , and then stored at -20°C in acid-cleaned HDPE Nalgene bottles. Prior to analysis, samples were thawed for 48 hours to ensure complete redissolution of secondary silicate precipitates to silicic acid. Samples were analysed for nitrate+nitrite, nitrite, phosphate and silicic acid using a

Technicon AAI segmented flow auto-analysis system calibrated to elemental standards at Plymouth Marine Laboratory, UK. Raw sample data were corrected to ambient ocean salinity and pH (Woodward and Rees, 2001). Samples were assayed in duplicate or triplicate and standard deviation was generally better than $\pm 0.2 \mu\text{mol L}^{-1}$ for nitrate+nitrite, $\pm 0.01 \mu\text{mol L}^{-1}$ for nitrite, $\pm 0.02 \mu\text{mol L}^{-1}$ for phosphate and $\pm 0.6 \mu\text{mol L}^{-1}$ for silicic acid. Instrument performance was assessed using CRMs from General Environmental Technos Co. / KANSO Ltd. (Japan).

Samples for the determination of ammonium concentration were analysed within four hours of sample collection using orthophthaldialdehyde (OPA) and fluorometry (Holmes et al., 1999; Clarke et al., 2008). Samples were assayed in triplicate, calibration was by standard addition at four concentrations, and the detection limit was $0.01 \mu\text{mol L}^{-1}$.

Samples for chlorophyll *a* analysis were obtained by gravity filtration onto 47 mm diameter nucleopore filters with $0.2 \mu\text{m}$ pore size. Chlorophyll *a* was extracted using chloroform and methanol (Wood, 1985), and measured by fluorometry using a Turner AU-10 fluorometer before and after acidification with 0.1 N HCl. Extraction and fluorometry took place in the dark and the fluorometer was calibrated frequently to a chlorophyll *a* standard, *Anacystis nidulans* (Sigma).

Derived variables N^* and N^*_{DIN} are defined for Marguerite Bay data as for the winter cruises detailed above (Section 1.2).

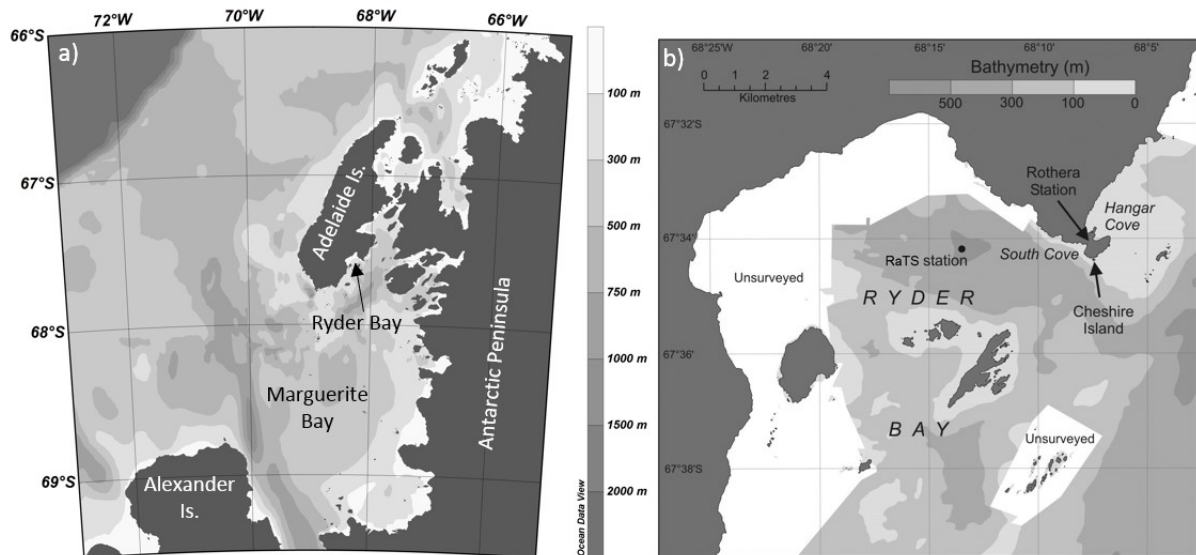


Figure S2: Maps showing a) the position of Marguerite Bay and Ryder Bay adjacent to the WAP, and b) the RaTS sampling station in Ryder Bay.

3. Contribution of biological and solubility pump processes to the Southern Ocean carbon sink

3.1 Estimation of the drivers of seasonal changes in $p\text{CO}_2$

We attempt to compare the relative contributions of the biological and solubility pumps to total CO_2 uptake for three latitudinal bands of the Southern Ocean in 2002-2007 and 2012-2017 using the Surface Ocean CO_2 Atlas (SOCAT) version 2019 (Bakker et al., 2016). The drivers of seasonal changes in $p\text{CO}_2$ were estimated by the approach described in Takahashi et al. (2014), based on the seasonal amplitudes of the parameters (i.e. the difference between winter and summer averaged values). The Revelle factors used were 11, 14 and 15, and those of alkalinity were -11, -14 and -15 for the latitudinal bands of 30-45°S, 45-60°S and south of 60°S, respectively. Total alkalinity (A_T) was estimated from sea surface salinity by the regression of Lee et al. (2006) and DIC was estimated through CO2SYS v2.1 (Lewis and Wallace, 1998; Pierrot et al., 2006), using input parameters $p\text{CO}_2$, A_T , temperature and salinity. We used the constants K1 and K2 proposed by Goyet and Poisson (1989) and the sulphate and borate constants

proposed by Dickson (1990) and Uppström (1974), respectively. The combined influence of the seasonal drivers is consistent with the calculated seasonal variation in $p\text{CO}_2$, with an average error of around 10%. Whilst it remains a challenge to separate clearly the effects of the solubility and biological pumps, this approach indicates the relative importance of the different processes influencing $p\text{CO}_2$ over the seasonal cycle, and allows us to conclude that the biological and solubility pumps are most likely to account for a similar proportion of circumpolar CO_2 uptake. This conclusion is in agreement with previous studies showing that biological and physical forcings of Southern Ocean $p\text{CO}_2$ are of the same order of magnitude (Hauck et al., 2015; Merlivat et al., 2015; Bushinsky et al., 2019).

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