The Changing Biological Carbon Pump of the South Atlantic Ocean

Louise Delaigue[1], Olivier Sulpis[2], Gert-Jan Reichart[3], and Matthew Paul Humphreys[4]

[1]NIOZ Royal Netherlands Institute for Sea Research
[2]CEREGE
[3]NIOZ
[4]Royal Netherlands Institute for Sea Research

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Abstract

Global marine anthropogenic CO2 inventories have traditionally emphasized the North Atlantic's role in the carbon cycle, while Southern hemisphere processes are less understood. The South Subtropical Convergence (SSTC) in the South Atlantic, a juncture of distinct nutrient-rich waters, offers a valuable study area for discerning the potential impacts of climate change on the ocean's biological carbon pump (Csoft). Using discrete observations from GLODAPv2.2022 and BGC-Argo at 40°S in the Atlantic Ocean, an increase in dissolved inorganic carbon (DIC) of +1.44 ± 0.11 µmol kg-1 yr-1 in surface waters was observed. While anthropogenic CO2 played a role, variations in the contribution of Csoft were observed. Discrepancies emerged in assessing Csoft based on the tracers employed: when using AOU, Csoft(AOU) recorded an increase of +0.20 ± 0.03 µmol kg-1 yr-1, whereas, using nitrate as the reference, Csoft(NO3) displayed an increase of +0.85 ± 0.07 µmol kg-1 yr-1. Nonetheless, our observations at 40°S indicate a significant intensification of Csoft, which, scaled to the entire ocean, represents an additional 23% to 35% of organic carbon degradation within the water column. Key processes such as water mass composition shifts, changes in oxygenation, remineralization in the Southern Ocean, and the challenges they pose in accurately representing the evolving Csoft are discussed. These findings highlight that while global studies primarily attribute DIC increase to anthropogenic CO2, observations at 40°S reveal an intensified biological carbon pump, showing that regional DIC changes are more complex than previously thought and challenging the dominance of anthropogenic sources in global DIC change.

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The Changing Biological Carbon Pump of the South Atlantic Ocean

L. Delaigue[1*], O. Sulpis[2,3], G-J Reichart[1,3] and M. P. Humphreys[1]

[1]Department of Ocean Systems (OCS), NIOZ Royal Netherlands Institute for Sea Research, PO Box 59, 1790 AB Den Burg (Texel), the Netherlands

[2]CEREGE, Aix Marseille Univ, CNRS, IRD, INRAE, Collège de France, Aix-en-Provence, France

[3]Department of Earth Sciences, Utrecht University, Utrecht, the Netherlands.

[*]Corresponding author: Louise Delaigue (louise.delaigue@nioz.nl)

Key Points:

- The South Subtropical Convergence (SSTC) at 40°S in the Atlantic Ocean shows an intensified biological carbon pump, amidst uncertainties.
- Uncertainties stem from local and far-field physical and biological changes impacting remineralization processes that are reflected at 40°S.
- Scaled to the entire ocean, this intensification marks an extra 23-35% of organic carbon degradation, challenging usual CO_2 inventory focus.

Abstract

Global marine anthropogenic CO_2 inventories have traditionally emphasized the North Atlantic's role in the carbon cycle, while Southern hemisphere processes are less understood. The South Subtropical Convergence (SSTC) in the South Atlantic, a juncture of distinct nutrient-rich waters, offers a valuable study area for discerning the potential impacts of climate change on the ocean's biological carbon pump (C_{soft}). Using discrete observations from GLODAPv2.2022 and BGC-Argo at 40°S in the Atlantic Ocean, an increase in dissolved inorganic carbon (DIC) of $+1.44 \pm 0.11$ µmol kg^{-1} yr^{-1} in surface waters was observed. While anthropogenic CO_2 played a role, variations in the contribution of C_{soft} were observed. Discrepancies emerged in assessing C_{soft} based on the tracers employed: when using AOU, $C_{soft(AOU)}$ recorded an increase of $+0.20 \pm 0.03$ µmol kg^{-1} yr^{-1}, whereas, using nitrate as the reference, $C_{soft(NO3)}$ displayed an increase of $+0.85 \pm 0.07$ µmol kg^{-1} yr^{-1}. Nonetheless, our observations at 40°S indicate a significant intensification of C_{soft}, which, scaled to the entire ocean, represents an additional 23% to 35% of organic carbon degradation within the water column. Key processes such as water mass composition shifts, changes in oxygenation, remineralization in the Southern Ocean, and the challenges they pose in accurately representing the evolving C_{soft} are discussed. These findings highlight that while global studies primarily attribute DIC increase to anthropogenic CO_2, observations at 40°S reveal an intensified biological carbon pump, showing that regional DIC changes are more complex than previously thought and challenging the dominance of anthropogenic sources in global DIC change.

Plain language summary

The South Atlantic Ocean at 40°S has experienced changes in dissolved inorganic carbon (DIC) levels over the years, affecting its carbon composition. This study running from 1972 to 2023 showcased an increase in DIC down to 2,000 meters deep. While anthropogenic CO_2 has traditionally been seen as the major contributor, the biological carbon pump's activity, influenced by various ocean processes, emerged as a significant driver. Specifically, factors such as photosynthesis, organic matter remineralization, sea ice movements, and freshwater influx from melting ice play pivotal roles in dictating oxygen and nitrate levels, both crucial components to predict the biological carbon pump's contribution to DIC. Our findings emphasize that this enhanced biological pump might contribute as much as human-made CO_2 to DIC in certain ocean regions. If unchecked, these changes could recalibrate ocean carbon budgets and predictions, with potential shifts in water mass compositions, demanding more vigilant future monitoring.

1 Introduction

The ocean has been acting as a sink for anthropogenic CO_2, absorbing an estimated 24% of anthropogenic CO_2 since the beginning of the industrial era, thus significantly mitigating climate change (Friedlingstein et al., 2023; Gruber et al., 2023). Part of this anthropogenic carbon remains in the form of dissolved inorganic carbon (DIC) and is transported into the ocean interior (Davila et al., 2022; Gruber et al., 2019; Khatiwala et al., 2009; Sabine & Tanhua, 2010; Sarmiento et al., 1992), and part of it is incorporated by marine organisms into organic matter or calcium carbonate (Heinze et al., 1991; Sarmiento et al., 1998; Volk & Hoffert, 1985).

The sequence of processes that store atmospheric carbon as biogenic matter at the surface ocean and sequester a small fraction of it in deep-sea sediments, where it can be stored permanently, is named the "biological pump" (Riebesell et al., 2009). While recent studies have focused on quantifying anthropogenic CO_2 uptake by the ocean at the air-sea interface, or its fate into the ocean interior as DIC, little is known about its effect on and removal by the biological carbon pump (BCP) over recent years, despite its importance for understanding future ocean carbon cycling. Biological processes in the upper ocean annually convert approximately 50-60 gigatons of dissolved inorganic carbon into organic matter (De La Rocha & Passow, 2014). Out of this amount, around 10% is transported out of the surface ocean in the form of organic carbon (De La Rocha & Passow, 2014). Through this natural and anthropogenic carbon export, the BCP lowers atmospheric CO_2 levels by ~200 ppm relative to a world without it (Henson et al., 2022). It is thus essential that we understand the drivers and variability of the BCP and its vulnerability to current anthropogenic changes to predict future climate. However, the complexity of ecosystem functioning and composition makes estimates of both present-day and future organic carbon export poorly constrained, in models and observations (Henson et al., 2022; Henson et al., 2012; Laufkötter et al., 2016; Marsay et al., 2015).

The oceanic distribution of DIC is mainly controlled by three pumps: the biological processes of photosynthesis, respiration, and remineralization(i.e. the soft-tissue pump, C_{soft}), the formation and dissolution of calcium carbonate (i.e. the carbonate pump, C_{carb}) and the uptake of natural and anthropogenic CO_2 (i.e. the solubility pump, C_{anth}; Gruber et al., 1996; Volk & Hoffert, 1985). While the solubility pump accounts for 30-40% of ocean carbon export flux to the deep ocean (Gruber et al., 2002; Toggweiler et al., 2003), the remaining portion is transported from the sunlit surface to the deep ocean as photosynthetically fixed organic carbon by the soft tissue

pump (Riebesell et al., 2009; Schlunegger et al., 2019). To quantify the rate of soft tissue and carbonate pump changes, one could monitor particulate organic and inorganic carbon sinking fluxes through time, but sediment trap data are sparse and associated with large uncertainties (Buesseler et al., 2007). Monitoring changes in DIC is also complicated because C_{soft}, $C_{carb,}$ and C_{anth} cannot be readily distinguished from the DIC analyses themselves. Instead, one can unravel the different components of the carbon pump and changes therein by combining multiple proxies, such as the apparent oxygen utilization (AOU; the difference between the saturation oxygen concentration, [$O_{2,sat}$] and the observed oxygen concentration, [O_2]), or release rates of organic-matter degradation byproducts, i.e., NO_3, PO_4 or alkalinity. For the carbonate pump, calcification and dissolution can be tracked in seawater by measuring dissolved calcium or alkalinity changes (Chen, 1978; Feely et al., 2004). Carbon sequestration by the soft tissue pump can be estimated from nutrient and oxygen observations, taking advantage of the constant stoichiometric ratios of carbon, nutrients, and oxygen in marine organic matter in the open ocean, also known as the Redfield Ratio (Ito & Follows, 2005; Redfield, 1958). Using the latter, these variables are converted back to carbon units in the natural components of DIC (C_{carb}, and C_{soft}) as well as anthropogenic CO_2 (C_{anth}), allowing for the disentanglement of changes in each DIC component.

Although global evaluations of the oceanic CO_2 inventory have often highlighted the North Atlantic Ocean as the primary region of interest for anthropogenic CO_2 subduction, with a storage estimated at 23% of global ocean anthropogenic CO_2 (Khatiwala et al., 2013; Sabine et al., 2004), the importance of southern hemisphere processes, such as the formation of Antarctic Intermediate Water (AAIW), has recently gained attention (Groeskamp et al., 2016; Landschützer et al., 2015). The South Subtropical Convergence (SSTC), an intersection point of low-macronutrient subtropical gyre waters and high-macronutrient Antarctic Circumpolar Current waters, is a significant biogeochemical feature of the South Atlantic Ocean (Browning et al., 2014). This convergence zone results in strong downwelling and pronounced surface gradients in salinity and temperature, leading to distinct water column stratification with shallow mixing in a thermally homogeneous surface layer, increasing light availability and productivity (Browning et al., 2014). Such stratification can impact the marine carbon cycle by potentially inhibiting the transport of heat, oxygen, and carbon dioxide deeper into the ocean (Li et al., 2020).

Simultaneously, the Southern Ocean is known for its high macronutrient supply, primarily from the upwelling of nutrient-rich deep waters (Moore et al., 2001; Tagliabue et al., 2014).These waters provide nitrate that fuels primary production. As organic matter produced in the Southern Ocean sinks to the SSTC region, it undergoes remineralization, converting back into inorganic nutrients. Nitrate concentrations can thus indicate the extent of remineralization in an area (Moore et al., 2001; Tagliabue et al., 2014), with higher concentrations suggesting more organic matter has been remineralized. This enhanced remineralization, fueled by the increased nitrate supply from Southern Ocean waters, may then contribute to a stronger soft tissue pump and carbon export to deeper waters (Boyd & Trull, 2007; Sarmiento, 2006)

Although not historically prominent, anticipated changes in the BCP are emerging due to specific climatic and oceanographic drivers. Behrenfeld et al. (2006) reported alterations in ocean productivity linked to climate change, with increased stratification in some regions affecting

primary production. Polovina et al. (2008) identified the expansion of subtropical gyres and associated shifts in phytoplankton communities in the Pacific. Furthermore, Orr et al. (2005) demonstrated that escalating CO_2 concentrations lead to ocean acidification, challenging marine calcifying organisms crucial for carbon sequestration. Considering these documented changes in diverse oceanic regions and the critical nature of the SSTC around 40°S in the Atlantic Ocean, it is plausible that similar dynamics will impact the BCP in this region.

In this study, we aim to quantify changes in the biological carbon pump at 40°S in the Atlantic Ocean. We leverage data from the GEOTRACES 40°S cruise, the first zonal expedition at this latitude in the South Atlantic to measure DIC. We join up all the other GLODAPv2.2022 cruises going perpendicularly and recent autonomous marine observations from the BGC-Argo array into a single analysis. This time series of marine carbonate chemistry measurements is used to calculate the rates of change in key variables and used to disentangle changes in the natural components of DIC (carbonate pump, C_{carb} and soft tissue pump, C_{soft}) from anthropogenic CO_2 (C_{anth}). We examine the underlying reasons for the divergence in BCP estimations, probing into the shifts in water mass composition within formation areas and delving into the effects of diminished oxygenation and heightened remineralization in the Southern Ocean. BCP estimates are then aligned with global carbon budgets, highlighting potential gaps in our understanding of the biological carbon pump's inclusion in these estimates.

2 Materials and Methods

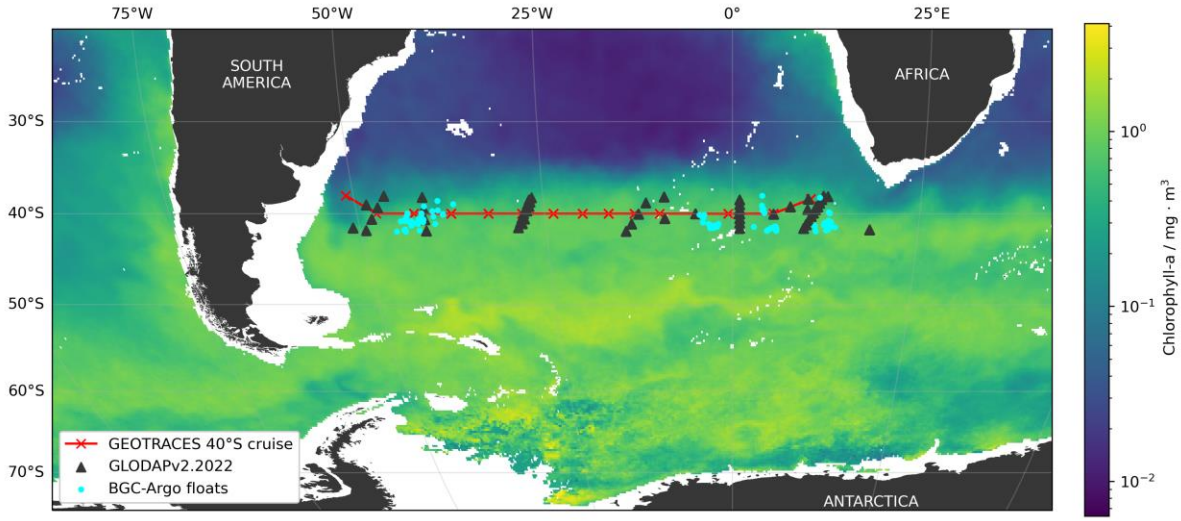

Figure 1. Map of the study region in the South Atlantic Ocean. Red line with crosses show the trajectory of the longitudinal GEOTRACES 40°S cruise. Black triangles show the location of GLODAPv2.2022 cruises. Red dots show BGC-Argo float data. Color scale shows Chl-a concentration (log-scale; Chl-a data downloaded from CMEMS following Sauzède et al. (2016)).

2.1 Discrete measurements from GLODAPv2.2022

Data from 11 cruises along latitude 40°S in the Atlantic Ocean were extracted from the Global Ocean Data Analysis Project version 2 (GLODAPv2.2022; Lauvset et al. (2022), Fig. 1; see Table 1 in supplementary information) and analyzed. From these, only the GEOTRACES 40°S cruise occupied the entire latitudinal transect (Expocode #740H20111224, 2011, RRS James

Cook; cruise #4095 in GLODAPv2.2022) while the rest either covered it partially, or crossed it latitudinally. Only stations with a bottom depth beyond 1000 m were considered, as to remove data falling on the continental shelf and/or slope. Rather than using original cruise data, the analysis benefited from the GLODAPv2.2022 applied adjustment of properties, making the analysis internally consistent. Hydrographic parameters included temperature (T), salinity (S_P), dissolved oxygen ([O_2]) , dissolved inorganic carbon (DIC), total alkalinity (A_T) and nitrate (NO_3^-). Only data with a quality control deemed "Good" (Flag = 2) were used. This analysis considered the full depth of the water column, with an emphasis on the central and intermediate waters during the discussion as most change has been observed in these waters (Piñango et al., 2022).

2.2 Autonomous data from BGC-Argo floats

Float data were downloaded from the Argo Global Data Assembly Centre (AOML) for a 8-year period (2015 – 2023). Only months matching GLODAPv2.2022 were kept (i.e. October, November, December, January, February and March). Selected floats all fell within a defined geographical area matching GLODAPv2.2022 (38°S to 42°S, 15°W to 50°E, Fig. 1). All selected float profiles included temperature (*T*), practical salinity (S_P), dissolved oxygen ([O_2]), pH on the total scale (pH_T) and nitrate (NO_3^-) (i.e. 9 floats, 73 profiles; see Table 2 in supplementary information). All BGC-Argo profiles used here were downloaded as Delayed Mode files which are designed for scientific exploitation and represent the highest quality of data to possibly extract climate-related trends (Bittig et al., 2019). Only adjusted data that were flagged as "Good" (QC=1) were used in this study, except for T and S_P, for which estimated values (QC=8) were used when adjusted data was missing. Each float profile was treated as the equivalent of a GLODAPv2.2022 cruise in the analysis.

2.3 Derived variables

For all BGC-Argo profiles, A_T was calculated using Python SciPy nonlinear least-square fitting (v.1.9.3; Virtanen et al., 2020), with T, S_P and depth as input parameters. More information can be found in the supplementary information, along with a comparison to Lee et al. (2006) A_T estimates (supp. info., Figs. B1, B2 and B3).

Neutral density surfaces (γ^n) were calculated from T, S_P, pressure, latitude and longitude using the EOS-80 Legacy toolbox for MATLAB® (MathWorks®, USA). Absolute salinity (S_A) and potential temperature (θ) were calculated from T, S_P, and pressure using the Gibbs-SeaWater Oceanographic Toolbox for MATLAB® (MathWorks®, USA). Apparent oxygen utilization (AOU) was calculated from θ, S_A and [O_2] using the combined fit coefficients from Garcia and Gordon (1992). These calculations were carried out for all datasets without above variables either already measured or calculated.

The Mixed Layer Depth (MLD) for each station during the GEOTRACES 40°S cruise was determined using a density criterion, with density calculated from T, S_P, and pressure data according to the Python implementation of the Gibbs SeaWater (GSW) Oceanographic Toolbox of TEOS-10 (v. 3.6.16; McDougall and Barker (2011)). The MLD was defined as the depth at which the water's density increases by 0.03 kg m^{-3} compared to the surface. Then, the mean

MLD and mean neutral density across all stations for that cruise was calculated, resulting in a MLD of 54m ($\gamma^n \approx 25.8$).2.4 Marine carbonate system parameters

Depending on available variables, remaining marine carbonate parameters were calculated from any pair of DIC, A_T, pH_T using PyCO2SYS v1.8.1 (Humphreys et al., 2022), and with the carbonic acid dissociation constants from Sulpis et al. (2020), bisulfate dissociation constant from Dickson (1990), the total boron:chlorinity from Uppström (1974) and the hydrogen fluoride dissociation constant from Dickson and Riley (1979). When available, phosphate and silicate were included in the carbonate system calculations but their inclusion did not affect the results significantly as their concentrations are relatively low in the open ocean. Calculated parameters include pH on the total scale (pH_T) and the seawater partial pressure of CO_2 (pCO_2) for GLODAPv2.2022 data, and DIC and pCO_2 for BGC-Argo data.

2.5 Interpolations

For each year, all variable data were clustered and interpolated vertically to γ^n levels using Piecewise Cubic Hermite Interpolating Polynomial (PCHIP) fits to observations (Fritsch & Carlson, 1980; Humphreys et al., 2016). Briefly, the PCHIP method uses monotonic cubic splines to find the value of new points. This allows for comparability between all cruises across the transect as averaging on isopycnals mimics real oceanic mixing processes occurring primarily along isopycnals, or, more precisely, along neutral density surfaces. Data were not extrapolated beyond the measured observational γ^n levels.

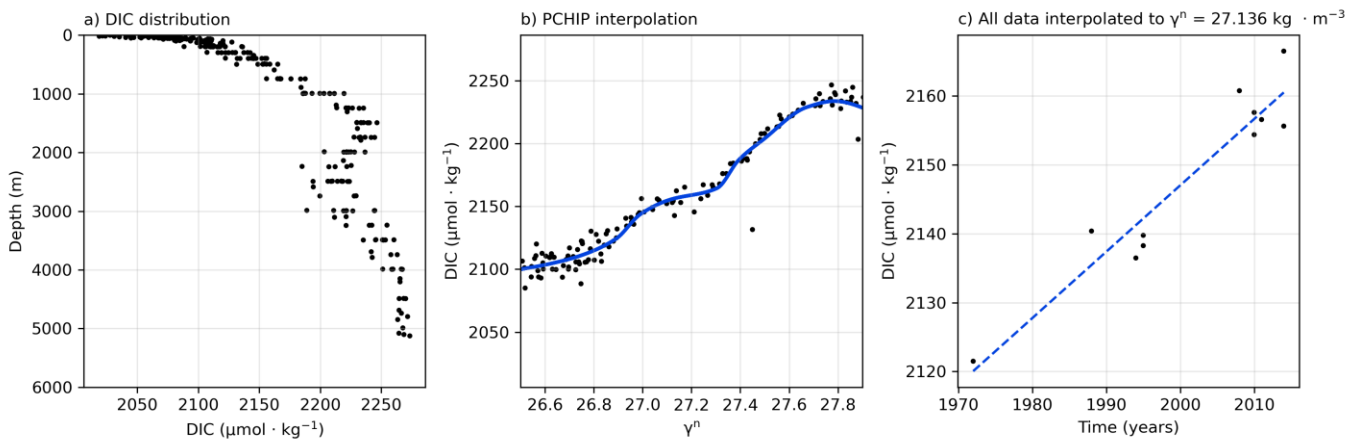

Figure 2. Analysis routine for each cruise and float profile, here showing for GEOTRACES 40°S longitudinal cruise: a) the vertical distribution of DIC; b) the PCHIP interpolation for DIC along neutral density levels; and c) the linear regression at a given neutral density level.

2.6 Rates of change

For each variable, ordinary least square regressions were used to determine their rate of change at each γ^n level. All rates of change are reported as $\frac{dX}{dt} \pm U$, where X is the variable and U is the associated uncertainty. Regressions were achieved using Python library SciPy v.1.9.3 (Virtanen et al., 2020). All rates of change were calculated with the same time range for all variables, that is from 1972 to 2023, except for silicate for which only GLODAPv2.2022 data is available up to 2014.

2.7 CO_2 components

Three pumps contribute to the distribution of DIC: photosynthesis, respiration and remineralization(C_{soft}), the formation and dissolution of calcium carbonate (C_{carb}) and the uptake of natural and anthropogenic CO_2 (C_{anth}; Gruber et al., 1996; Volk & Hoffert, 1985. Thus, DIC changes can be described as:

$$\Delta T_C = \Delta C_{soft} + \Delta C_{carb} + \Delta C_{sol} \quad (1).$$

Biological activity is responsible for converting dissolved inorganic nutrients to particulate organic matter. These particles are transported down the water column through gravitational settling and active transport by marine organisms. During their settling to deeper waters, carbon and nutrients are returned to their dissolved, inorganic forms through remineralization while taking up O_2 and thus increasing AOU (Redfield, 1963). This process drives the soft tissue pump, which is defined as:

$$\Delta C_{soft(AOU)} = -R_{C/O_2} \cdot \Delta AOU \quad (2a),$$

$$\Delta C_{soft(NO3)} = R_{C/NO_3^-} \cdot \Delta NO_3^- \quad (2b),$$

where $\boldsymbol{R_{C/X}}$ is the increase in $\boldsymbol{C}$ as a fraction of X variable consumption during remineralization. In this study, we used the ratio from Anderson and Sarmiento (1994) as follows:

$$\underset{1:16:117:170}{\mathrm{P:N:C:}-O_2} \quad (3),$$

Thus, R_{C/O_2} and R_{C/NO_3^-} can be assumed to be a constant value of -0.688 ± 0.092 and 7.31± 0.092 respectively (Anderson & Sarmiento, 1994).

The formation and dissolution of $CaCO_3$ makes up the carbonate pump, where an increase in $\boldsymbol{C}$ is coupled with an increase in A_T of double the magnitude (Wolf-Gladrow et al., 2007):

$$\Delta C_{carb} = 0.5 \cdot (\Delta A_T - R_{N/O_2} \cdot \Delta NO_3^-) \quad (4),$$

where $\boldsymbol{R_{N/O_2}}$ is a ratio of -0.0941 ± 0.0081 (Anderson & Sarmiento, 1994).

The remaining term, namely the solubility pump, relies on the uptake of anthropogenic CO_2 ($\Delta \boldsymbol{C_{anth}}$) and the CO_2 air-sea disequilibrium ($\Delta \boldsymbol{C_{diseq}}$) at the time the water lost contact with the atmosphere (Gruber et al., 1996). Assuming $\Delta \boldsymbol{C_{diseq}} = \boldsymbol{0}$, i.e. no significant long-term trend in air-sea CO_2 disequilibrium, the accumulated anthropogenic $\Delta \boldsymbol{C_{anth}}$ is defined as:

$$\Delta C_{anth} = \Delta C_{sol} - \Delta C_{diseq} \approx \Delta C_{sol} \quad (5).$$

2.8 Natural CO_2 inventory change

Changes in $C_{soft(AOU)}$ and $C_{soft(NO3)}$ were multiplied by a density factor of 1028 to convert units from μmol kg^{-1} yr^{-1} to μmol m^3 yr^{-1}. Resulting values were integrated along the water column by sum ($C_{soft(AOU)-int}$ and $C_{soft(NO3)-int}$). Assuming lateral homogeneity, $C_{soft(AOU)-int}$ and $C_{soft(NO3)-int}$ were further converted to GtC m^2 yr^{-1} and integrated over the surface of the study area.

2.9 Uncertainty propagation

For GLODAPv2.2022, uncertainties were assigned based on Table 3 of Lauvset et al. (2022) for all data dated from after 1994 (i.e. first use of CRMs). For data prior to 1994, an uncertainty of ±17.2 μmol kg^{-1} was assigned (Dickson, 1992). Most BGC-Argo floats included the error for each adjusted variable. Some uncertainties were missing for T and S_P, for which values were assigned based on Williams et al. (2017) and Mignot et al. (2019), except for the calculated A_T for which the fit RMSE was used (5.5 μmol kg^{-1}, see Section B in supplementary information). Uncertainties for variables calculated with PyCO2SYS v1.8.1 were propagated using the independent uncertainty argument (Humphreys et al., 2022).

In the process of quantifying analysis uncertainty, a multifaceted approach was employed to ensure comprehensive error propagation. To assess the uncertainty in the rates of change, a differential analysis was undertaken, calculating the derivatives for all variables under consideration (i.e. forward-finite differences). Each variable was incrementally altered, specific to the variable's nature, and the impact of these perturbations on the overall outcome was studied through another linear regression on the modified dataset. The differences between the coefficients of the original and modified datasets provided insights into the sensitivity of each variable. After normalization, these differences gave the true derivatives. By juxtaposing these derivatives with known measurement uncertainties, a comprehensive error term for each variable's rate of change was determined, offering a robust assessment of propagated uncertainties. This step provided a foundational understanding of how minor perturbations in each variable could influence the outcome.

Subsequently, to further refine the understanding of the variability and potential uncertainties inherent in the dataset, a bootstrapping technique was applied. Essentially, the data for specific cruises was selectively omitted in a series of simulations, creating a variety of modified datasets. This non-parametric statistical method facilitated the estimation of the distribution of sample statistics by resampling with replacement, thereby offering insights into the potential variability of the results.

Finally, for each measured variable, an internal bias was determined for each cruise or float profile using the standard deviation of each linear regression from the rates of change estimation. All uncertainties were then synthesized to produce a combined error estimate. This layered approach ensured a robust assessment of analysis uncertainty, capturing both the immediate sensitivities of the variables and the broader variability in the dataset.

3 Results

Multi-decadal rates of change for all available and derived carbonate parameters were calculated using GLODAPv2.2022 and BGC-Argo data along latitude 40°S for the period 1972-2023.

Changes in individual variables are reported in Fig. 3, while the calculated change in each component of DIC is shown in Fig. 4. For all variables, little to no change was observed deeper than ~2000 m in the water column thus only data down to this depth are presented here.

On average, surface waters became warmer and fresher, which was reflected in A_T with a slight negative change. Slight decreases of -0.04 ± 0.0006 °C yr^{-1} in θ and -0.01 ± 0.0002 yr^{-1} in S_P were observed in the top ~300 m (γ^n < 27.0 kg m^{-3}), with virtually no change deeper in the water column (Fig. 3a-b). This was closely mirrored by A_T, which showed a maximum decrease of -0.49 ± 0.11 µmol kg^{-1} yr^{-1} within the top ~200 m (γ^n < 26.8 kg m^{-3}), while showing no change deeper in the water column (Fig. 3c).

Surface waters also showed signs of deoxygenation and increased AOU (Fig. 3h), while the nitrate pool increased (Fig. 3i). [O_2] decreased down to ~900m (γ^n ≈ 27.4 kg m^{-3}), with a minimum Δ[O_2] of -0.56 ± 0.05 µmol kg^{-1} yr^{-1} (Fig. 3g). Deeper than 150 m, AOU increased by a maximum of +0.54 ± 0.02 µmol · kg^{-1} · yr^{-1}, from the surface down to ~2000 m (γ^n ≈ 27.9 kg m^{-3}; Fig. 3h-i). Both AOU and [O_2] converged towards no change at around ~300 m (γ^n ≈ 27.0 kg m^{-3}), before continuing their respective decrease/increase. An important increase in NO_3^- was observed with a peak of +0.14 ± 0.01 µmol · kg^{-1} · yr^{-1} for the first ~150m (γ^n < 26.7 kg m^{-3}), while slowly converging towards no change by ~1000m (γ^n ≈ 27.5 kg m^{-3}; Fig. 3i).

It's important to note that for the analysis of the N/P ratio and [Si], the data is limited to measurements up to 2014. This limitation arises because the BGC-Argo floats are not equipped to measure phosphate and silicate, thus only GLODAPv2.2022 data was used. Nonetheless, within this dataset, there was no significant change observed in the N/P ratio (Fig. 3l). Additionally, [Si] displayed an increase of +0.15 ± 0.08 µmol · kg^{-1} · yr^{-1} near γ^n = 27.4, with no substantial alterations observed in the remaining portions of the water column (Fig. 3k).

Seawater at 40°S became more acidic due to a change in DIC partially caused by biological processes, calcium carbonate formation and CO_2 uptake. A small decrease of -0.24 ± 0.06 µmol kg^{-1} yr^{-1} in the carbonate pump, C_{carb}, was observed within the first ~200m (γ^n < 26.8 kg m^{-3}) of the water column (Fig. 4), correlating closely with the change in A_T (Fig. 3c). DIC showed an increase above ~2000 m (γ^n ≈ 27.9 kg m^{-3}; Fig. 3d and Fig. 4) with a maximum +1.44 ± 0.11 µmol kg^{-1} yr^{-1} in the surface waters (γ^n ≈ 26.7 kg m^{-3}; Fig. 3d and Fig. 4). It is interesting to note that the change in DIC was higher down to 2000m when using all available data, most likely indicative of a deeper penetration depth within the last decade, and noticeable thanks to the high-resolution of BGC-Argo data. Seawater pCO_2 showed a corresponding average increase of +3.83 ± 0.15 µatm yr^{-1}, before slowly converging back to no change deeper than 2000 m (γ^n ≈ 27.9 kg m^{-3}; Fig. 3e). These changes were closely followed by an average decrease of -0.002 ± 0.0001 yr^{-1} in pH_T and a maximum decrease of -0.003 ± 0.0001 yr^{-1} in the shallow subsurface (~150 m, γ^n < 26.7 kg m^{-3}; Fig. 3f), where the pH maximum is often located (Arroyo et al., 2022). This change in pH_T is consistent with most recent globally averaged rate of surface ocean pH change, −0.0016 ± 0.0006 yr^{-1} (Garcia-Soto et al., 2021).

Change in DIC appears to be mostly caused by an accumulation of C_{anth}, in the surface waters, which was further supported by a parallel increase in seawater pCO_2 (Figs. 3e and Fig.). Not all DIC change was attributed to C_{anth}, as there also appeared to be a significant increase in the soft

tissue pump (Fig. 4). If calculated using AOU, $C_{soft(AOU)}$ increased by +0.20 ± 0.03 μmol · kg^{-1} · yr^{-1} down to ~2000m ($\gamma^n \approx 27.9$ kg m^{-3}; Fig. 4), while being close to no change near ~300 m ($\gamma^n \approx 27.0$ kg m^{-3}; Fig. 4). The corresponding $C_{anth(AOU)}$ thus represented most of the DIC change, with an increase of +1.48 ± 0.13 μmol · kg^{-1} · yr^{-1} close to the surface ($\gamma^n < 26.7$ kg m^{-3}; Fig. 4). However, if calculated using NO_3^-, $C_{soft(NO3)}$ showed an increase ~4 times greater than $C_{soft(AOU)}$, with +0.85 ± 0.07 μmol kg^{-1} yr^{-1} in the surface waters ($\gamma^n < 26.8$ kg m^{-3}; Fig. 4), and $C_{anth(NO3)}$ then contributing half of $C_{anth(AOU)}$, with an average increase of +0.67 ± 0.14 μmol kg^{-1} yr^{-1} down to 1000 m ($\gamma^n \approx 27.5$ kg m^{-3}; Fig. 4).

The depth-integrated increase in the soft tissue pump was approximately +0.004 ± 0.002 GtC yr^{-1} for $C_{soft(AOU)}$ and +0.006 ± 0.002 GtC yr^{-1} for $C_{soft(NO3)}$ within the study area.

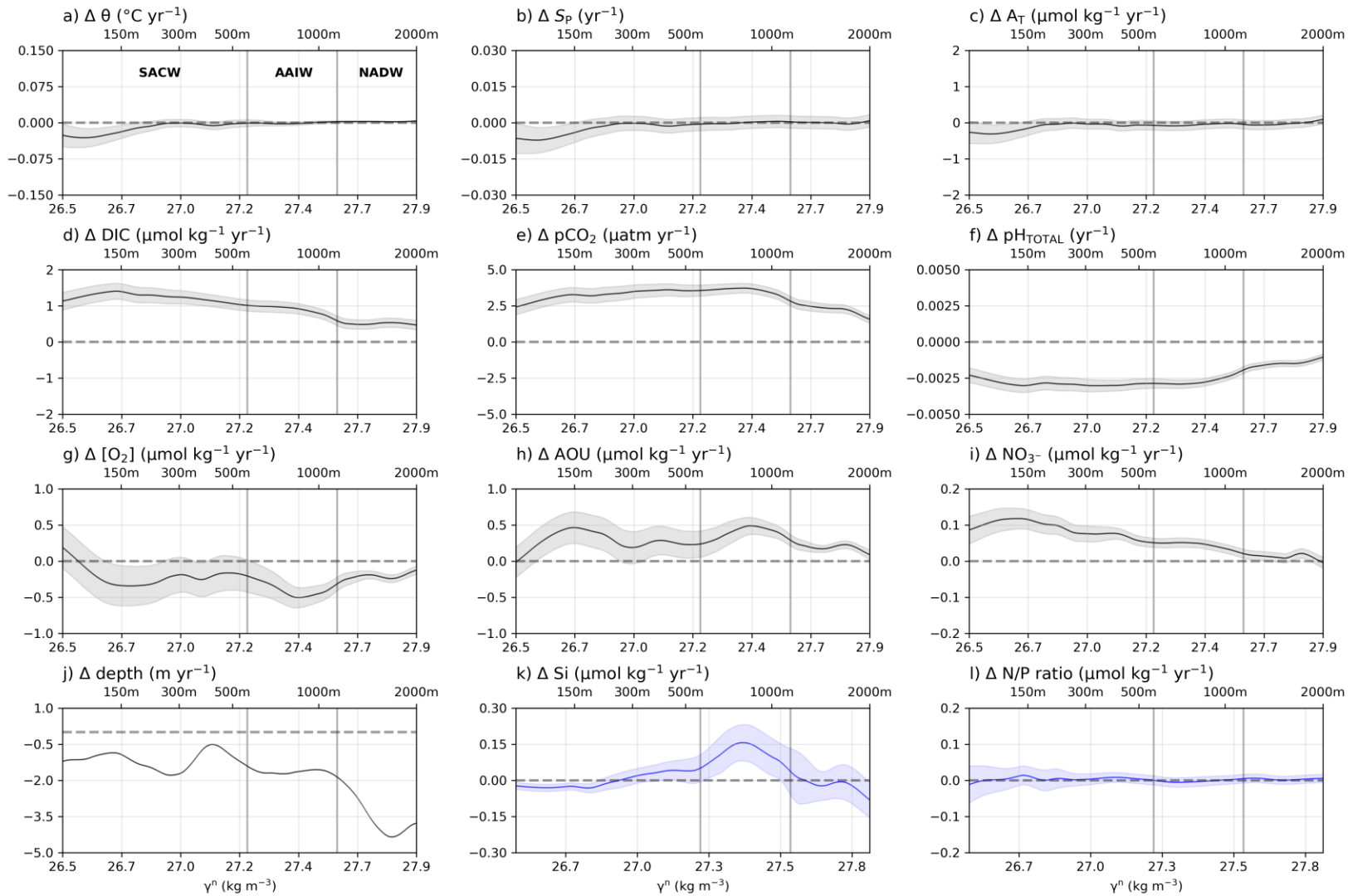

Figure 3. Change in biogeochemical parameters across 40°S in the Atlantic Ocean for all available dataApproximate depths are shown at the top of each plot, along water masses as part of subplot a. Note that blue panels k and l only include data up to 2014 as BGC-Argo floats are not equipped for phosphate and silicate measurements. MLD is off the x-axis (54m, $\gamma^n \approx 25.8$).

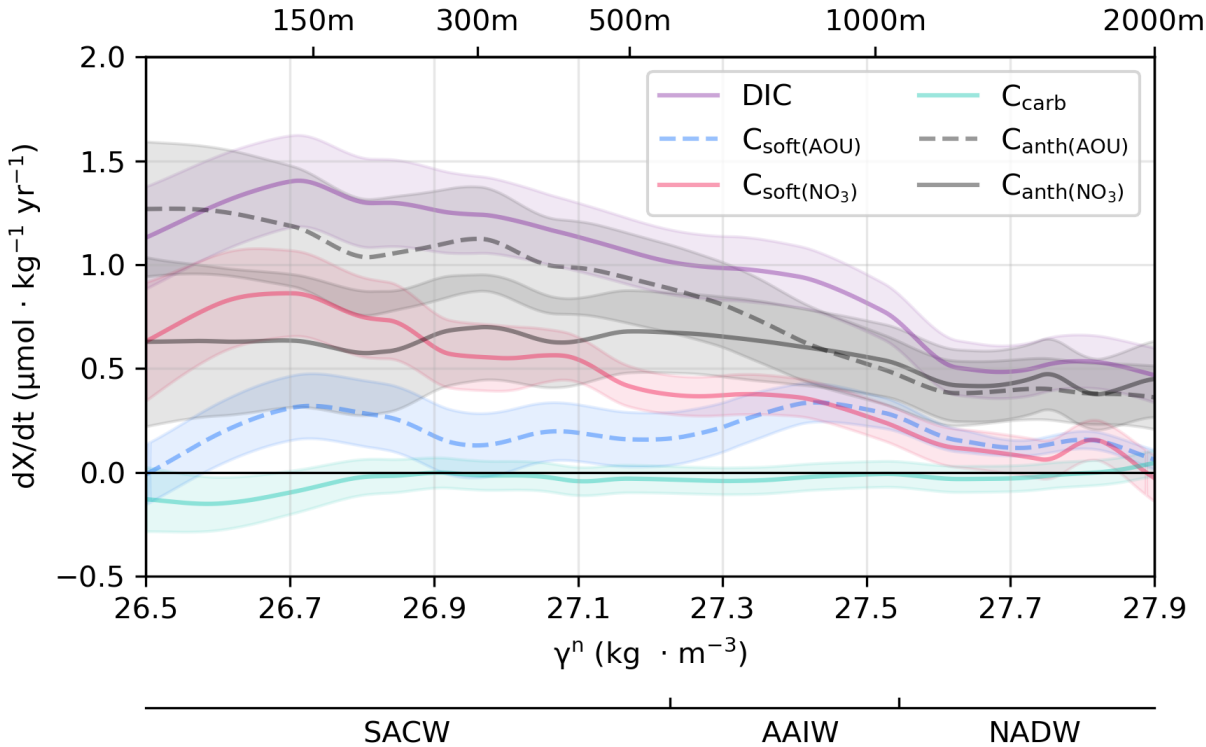

Figure 4. Rates of change in DIC (purple) and its components, C_{carb} (turquoise), $C_{soft(NO3)}$ estimated from NO_3^- (red), $C_{soft(AOU)}$ estimated from AOU (dashed blue), with corresponding $C_{anth(NO3)}$ in solid black and $C_{anth(AOU)}$ in dashed black. Results are for the compilation of all available data. Approximate depths are showed at the top and water masses at the bottom of the axes. MLD is off the x-axis (54m, $\gamma^n \approx 25.8$).

4 Discussion

Although the biological pump at 40°S has clearly increased, the magnitude remains uncertain, depending on whether NO3 or AOU is used to estimate the soft tissue pump component. Below, we discuss this uncertainty and the implications of our findings, first looking at the physical factors and subsequently the influence of biology.

4.1 Influence of Physical Factors on BCP Dynamics

4.1.1 Melting Ice

Variability in oxygen content at 40°S is largely influenced by sea ice dynamics affecting gas exchange, temperature and salinity (Hofmann et al., 2011). The stratification induced by meltwater creates a barrier that inhibits deep water mixing. As a result, vertical water exchange between the surface and deeper ocean layers is slowed, retaining carbon and nutrients in the upper water column for longer, marking a transition from a system that exports carbon and nutrients to one that retains them (Gjelstrup et al., 2022; Priest et al., 2023; von Appen et al., 2021). However, the melting of sea ice cools seawater, enhancing the solubility of CO_2 and O_2 without affecting NO_3^-. Subsequent air-sea gas exchange will thereby increase DIC and [O_2], but

it will not alter AOU, because $[O_2]$ changes to match its new saturation level ($[O_2]_{sat}$). The impact varies with the supersaturation or undersaturation of surface waters with respect to atmospheric CO_2 and O_2 (Council, 2010; Figuerola et al., 2021). In scenarios of reduced gas exchange due to diminished sea ice in the Southern Ocean, there should be a decrease in DIC and AOU, as the melting sea ice enhances the ocean's capacity to absorb atmospheric CO_2 and O_2, which would lead the concentrations of these dissolved gases to increase thus changing $C_{softAOU}$ but not NO_3^- and $C_{soft(NO3)}$.

Melting land ice also enhances ocean stratification and introduces micronutrients like iron, fueling biological productivity in near-surface waters (Lannuzel et al., 2010; Lannuzel et al., 2016; Morley et al., 2020).Sediment-derived iron, accounting for 54 ± 15% of total iron flux, is carried from continental shelves via benthic diffusion and sediment resuspension (De Jong et al., 2012; Tian et al., 2023). This transport may influence nutrient dynamics and productivity as far as 3500 km from the Antarctic Peninsula (De Jong et al., 2012). An influx of micronutrients leads to a higher uptake of DIC and also nitrate NO_3^-, resulting in an decrease in $C_{soft(NO3)}$. These changes, predominantly affecting near-surface photosynthesis, align with the Redfield Ratio, which predicts a decrease in NO_3^- proportional to the decrease in DIC. However, this would impact AOU and hence also $C_{soft(AOU)}$ less because O_2 more quickly re-equilibrates with the atmosphere than DIC. Enhanced remineralization at greater depths due to the increased productivity would change DIC, AOU and NO_3^- in line with the Redfield ratio (Henley et al., 2020). As the composition of the water we observe at 40°S is the result of transport of this water from south to north it also reflects the initial preformed value from the enhanced productivity near the Antarctic as well as processes happening at 40°S and during transport (Morley et al., 2020).

A component of the observed increase in DIC at 40°S could hence reflect both melting of sea and land ice, which in turn impact the BCP. But unlike for NO_3^-, the AOU change from increased productivity is quickly erased by air-sea gas exchange. Changes in AOU observed at 40°S therefore cannot result from these melting processes, while the changes in NO_3^- could stem from these changing endmember conditions.

4.1.2 Interior ocean mixing

Recent studies have highlighted changes in ocean circulation patterns, which most likely are also reflected at 40°S. Decrease in the ages of Subantarctic Mode Water (SAMW) and Circumpolar Deep Water (CDW) were observed across the South Atlantic Ocean since the 1990s, suggesting enhanced ventilation, a phenomenon partly attributed to shifts in westerly winds (Fine et al., 2017; Tanhua et al., 2017; Waugh et al., 2013). This trend in SAMW indicates potentially increased isopycnal mixing, which elevates surface DIC due to the upward transport of DIC-rich deep waters which may drive part of the observed increase in DIC at 40°S (Fig. 3d). Additionally, Wei et al. (2022), focusing on a transect from the Rio Grande Rise to the Mid-Atlantic Ridge, demonstrated increases in diapycnal diffusivities, again indicating intensified mixing, thus implying enhanced vertical circulation of nutrient-rich deep waters. This observation is consistent with the observed rise in NO_3^- and $C_{soft(NO3)}$ at 40°S (Fig. 3i and 4). Both the isopycnal and diapycnal mixing introduce oxygen-poor deep water to the surface, increasing SACW AOU, especially in regions with high remineralization (Fig.3h; Fine et al., 2017; Tanhua et al., 2017; Waugh et al., 2013. This suggests that the apparent increase in

remineralization within the BCP as inferred from DIC, AOU, and NO_3^- measurements, is primarily due to the enhanced advection of older deep waters to the surface.

Piñango et al. (2022) also reported increased organic matter remineralization in the AAIW likely indicating deoxygenation. This is due to an enhanced flux of organic matter, which increases microbial oxygen consumption, and enhanced ventilation. While the latter introduces oxygen, it also brings in more anthropogenic carbon, exacerbating the oxygen demand for remineralization. This is especially true along the AAIW from 50°S to 30°S where increased AOU was observed at a mean rate of AOU change of 0.23 ± 0.68 μmol kg^{-1} yr^{-1} south of 30°S which concurs with our results (Fig. 3; Piñango et al., 2022). This is consistent with the deoxygenation trend reported by Santos et al. (2016) for the AAIW in the South Atlantic subtropical gyre from 1960 to 2015, which was -0.18 ± 0.04 μmol kg−1 yr−1. It also aligns with the AOU rate observed by Fontela et al. (2021)in the Argentine Basin, which was 0.38 ± 0.13 μmol kg−1 yr−1. Additionally, these results agree with the AAIW deoxygenation documented by Schmidtko et al. (2017) over the last two decades.

A component of the observed changes in DIC, AOU, NO_3^- and therefore the BCP at 40°S is thus mechanistically linked to enhanced mixing through an increased influence of deeper waters on overlying water masses.

4.1.3 Wind-driven circulation

Increased wind-driven circulation has been invoked to explain changes in marine biogeochemical cycles, including effects on DIC and nutrients (England et al., 2014; Keppler & Landschützer, 2019; Liu et al., 2023).

The rate of gas exchange between the ocean and atmosphere is controlled by a set of physical processes that scale with wind speed (Wanninkhof, 2014). Because the South Atlantic Ocean is a net sink for CO_2 (i.e., seawater pCO_2 is lower than atmospheric pCO_2), enhanced gas exchange due to stronger surface winds would increase surface ocean pCO_2 and DIC. The same process decreases AOU, which is positive in surface waters here (Fig. 3h), due to the absorption of atmospheric oxygen. In contrast, dissolved nutrients such as NO_3^- (and therefore $C_{soft(NO3)}$), which are primarily controlled by biological uptake and nutrient cycling, are not directly affected by intensified gas exchange.

However, increased winds also drive enhanced upwelling. Deep waters are high in DIC, AOU and NO_3^- due in a large part to remineralization of organic matter, so enhanced upwelling elevates all these properties in the SACW roughly in line with the Redfield ratio (Fig. 3d,h,i; England et al., 2014; Liu et al., 2023). Accordingly, changes in wind-driven circulation would increase both $C_{soft(NO3)}$ and $C_{soft(AOU)}$ in SACW, but likely in agreement with the Redfield ratio and true change in C_{soft}. This aspect therefore cannot cause the observed discrepancy between $C_{soft(NO_3)}$ and $C_{soft(AOU)}$ observed at 40°S.

Additionally, increased mixing due to stronger winds leads to a more uniform distribution of DIC in the upper part of the water column as the surface mixed layer thickens (England et al., 2014), as seen at 40°S (Fig. 3j). This mixing increases AOU near the surface and lowers it at depth. Mixing also results in a more even distribution of nutrients like NO_3^- throughout the water

column, redistributing these vertically rather than straightforwardly increasing or decreasing the soft tissue pump.

4.2 Biological effects on quantifying the BCP

The increase in NO_3^- at 40°S, especially in the first 500m (Fig. 3i), could reflect increased remineralization, possibly caused by enhanced organic matter export at 40°S (Boyd & Trull, 2007; Sarmiento, 2006). This should be accompanied by an [O_2] decline in the same waters, increasing AOU, which in the surface mixed layer could then be attenuated by oxygen exchange with the atmosphere. Consequently, $C_{soft(AOU)}$ in the near surface would underestimate the actual change in C_{soft}, while in deeper waters beneath the mixed layer (without the associated air-sea gas exchange causing a bias in $C_{soft(AOU)}$), $C_{soft(AOU)}$ would be consistent with $C_{soft(NO3)}$ (Fig. 4). However, $C_{soft(AOU)}$ and $C_{soft(NO3)}$ differ significantly from each other down to around 800 m (or 27.4 kg m^{-3}), which is deeper than the mixed layer here (54m, $\gamma^n \approx 25.8$), so this is not a complete explanation for the discrepancy.

In shallower waters, other factors might explain the observed discrepancy between $\Delta C_{soft(AOU)}$ and $\Delta C_{soft(NO3)}$, such as changes in the stoichiometry of organic matter. Variations from standard plankton biomass elemental ratios (i.e., the Redfield ratio; Redfield, 1958) have been observed spatially and temporally (Inomura et al., 2022; Martiny et al., 2013; Tanioka & Matsumoto, 2020) , which may contribute to the difference between $C_{soft(AOU)}$ and $C_{soft(NO3)}$ observed here (Fig. 4; Anderson and Sarmiento, 1994). South of 40°S, the carbon to nitrogen (C:N) ratio is closely aligned with the Redfield ratio (Johnson et al., 2022). Conversely, north of 40°S, dissolved organic matter (DOM) has higher C:N ratios, with 10.4 ± 4.1 at 30°S, 14.0 ± 4.8 at 35°S, and 9.7 ± 1.7 at 40°S, all surpassing the Redfield ratio of 6.6 (Johnson et al., 2022). The elevated C:N observed at 40°S could then also result from a changing balance between water masses from the north and the south. Organic matter (OM)with higher C:N requires more oxygen for its remineralization, thereby accelerating the consumption of dissolved oxygen (Matsumoto et al., 2020; Szewczyk et al., 2023). Climate change is expected to cause significant stoichiometric shifts in plankton biomass, with warmer temperatures and rising CO_2 levels promoting higher C:P and N:P ratios (Ayo et al., 2017; DeVries, 2018; DeVries et al., 2017; Toseland et al., 2013; van de Waal et al., 2010; Yvon-Durocher et al., 2017) which may result in increased oxygen consumption during remineralization and thus higher AOU (DeVries, 2018).

The enhanced remineralization and possible changes in C:N observed at 40°S may be due to increased diatom populations further south (Arrigo et al., 1999; Arrigo et al., 2015; Soppa et al., 2016). Diatoms are reliant on silicate and significant nitrate consumers. Also enhanced inputs of iron are known to stimulate diatom productivity (Sect. 4.1.1). Diatoms secrete transparent exopolymeric particles (TEP), which act like glue to hold aggregates together, leading to faster sinking of marine particles and a more efficient biological pump (Chen & Thornton, 2015; Toullec & Moriceau, 2018). TEP production also increases the C:N ratio (Kim et al., 2021; Passow, 2002). Boosted silicate availability, most likely due to enhanced upwelling and glacial runoff (Henley et al., 2020), may accordingly reduce NO_3^- levels at the sea surface and increase NO_3^- and AOU in the AAIW, due to enhanced sinking and remineralization of algal diatom biomass. If driven by diatoms, we would expect the increased NO3 and AOU in deeper waters to be accompanied by an increase in [Si] in AAIW (Cael et al., 2021), which is what we observe at 40°S (Fig. 3k). Either through remote or via locally enhanced productivity an increased

abundance of diatoms, caused by higher iron and [Si], could be responsible for the changes in the BCP that we observe.

4.3 Consequences of Changes in the Biological Carbon Pump

4.3.1 Implications for Marine CO_2 Sink

Previous studies have shown that the South Atlantic Ocean is a sink of atmospheric CO_2, with an average net air-to-sea CO_2 flux of 0.3 Pg C yr−1 (Takahashi et al., 1997; Takahashi et al., 2002). Recent work has highlighted strong seasonality in the South Atlantic CO_2 flux, acting as a strong sink during the spring when most primary production takes place, and shifting towards a source during autumn (Lencina-Avila et al., 2016; Padin et al., 2010). Monitoring whether the South Atlantic acts as a source or sink of CO_2 is vital for understanding its role in the global carbon cycle, as it directly influences the atmospheric CO_2 concentration and therefore Earth's climate (Lencina-Avila et al., 2016; Padin et al., 2010). As these variations are connected to the biological productivity of the South Atlantic Ocean, it is especially important to understand the biological pump's contribution to changes in DIC, which has a direct impact on whether the ocean basin acts as a source or sink of CO_2.

The observed increase in surface ocean pCO_2 at 40°S is consistent with the growth in atmospheric pCO_2 (Fig. 3e). If the changes in the BCP were to lead seawater pCO_2 to rise faster or slower than atmospheric pCO_2, this would cause an decrease or increase respectively of the ocean CO_2 sink (DeVries et al., 2017).

4.3.2 Carbon Export & BCP Role in Climate Responses

Our findings at 40°S indicate that the biological pump is experiencing shifts due to a mix of chemical changes in water mass formation regions and biological factors across the Atlantic Ocean. Model results suggest that the anticipated increase in iron supply and improved light availability for phytoplankton—owing to enhanced near-surface stratification and prolonged ice-free periods—will likely amplify primary production. This could, in turn, boost carbon export around the Antarctic region (Henley et al., 2020). These observations at 40°S may be the early signs of the impacts of global change in the Southern Ocean.

Building on these observations, the depth-integrated increase in organic carbon export flux was between 0.004 ± 0.002 ($C_{soft(AOU)}$) and 0.006 ± 0.002 GtC yr^{-1} ($C_{soft(NO3)}$) for the study area. For comparison, a recent estimate of global export production accounting for both POC and DOC was 8.37 ± 1.57 GtC yr^{-1} (Sulpis et al., 2023), which amounts to 0.017 ± 0.003 GtC yr^{-1} when scaled down to the study area. This suggests that the increase in the BCP that we observed could represent an increase in the amount of carbon remineralised by 23% to 35% each year. However, if the study region is a biological "hotspot" with high baseline productivity and remineralization, the global average would be an underestimate for this region, so the 23% to 35% increase is an upper bound. Regardless of its size as a fraction of the baseline remineralization rate, the magnitude of the DIC increase associated with the BCP is of the same order of magnitude as the anthropogenic increase in DIC (Fig. 3d and Fig. 4). Thus, while changes in the biological carbon pump are often considered less significant than anthropogenic CO_2 uptake, they should still be considered in global carbon budgets.

4.3.3 Anthropogenic Influence and CO_2 Dynamics

Since the early 1960s, the primary driver behind the long-term trend in the ocean carbon sink has been the rising uptake of anthropogenic CO_2 (Gruber et al., 2023). From 2004 through to 2019, the global oceanic DIC pool increased at an average rate of 3.2 ± 0.7 Pg C yr^{-1}, with no statistically detectable difference between the total DIC change and Canth accumulation between 2004 and 2020 (Keppler et al., 2023). This implies no global net change in C_{soft} but does not rule out a spatial redistribution, driven by various factors including ocean warming, alterations in marine biology, and other physical changes within the oceans, as discussed above for 40°S. Thus, our study may be an example of this redistribution effect—as also witnessed in the northeast Atlantic Ocean (Humphreys et al., 2016). The role of the biological carbon pump relative to anthropogenic CO_2 uptake in the changing marine DIC pool may be more important than previously thought.

5 Conclusions

At 40°S in the Atlantic Ocean, from 1972 to 2023, DIC increased, down to approximately 2000 m ($\gamma n \approx 27.9$ kg m^{-3}), with a near-surface maximum rate of 1.52 ± 0.11 μmol kg^{-1} yr^{-1}. Although at least half of this change can be attributed to anthropogenic CO_2 accumulation, the intensification of the BCP in this region is evident, with contributions ranging from 0.20 ± 0.03 μmol kg^{-1} yr^{-1} to 0.85 ± 0.07 μmol kg^{-1} yr^{-1} (using $C_{soft(AOU)}$ and $C_{soft(NO3)}$, respectively). While we cannot definitively select one soft tissue pump estimation over another due to inherent uncertainties in the influence of different processes, the concurrent increase in both $C_{soft(AOU)}$ and $C_{soft(NO3)}$ estimates serves as a robust indicator of the intensifying nature of the BCP at this location amidst various influencing factors.

This study at 40°S in the Southern Ocean has also provided valuable insights into the complex interplay of physical, biological, and anthropogenic factors influencing the dynamics of the BCP. Our investigation reveals that changes in sea ice dynamics, ocean stratification, wind patterns, and biological activity, including photosynthesis and organic matter degradation, could all have played a role in the observed changes in efficiency of the BCP.

These findings also highlight the implications of these changes for CO_2 sink behavior and carbon export. The observed increase in pCO_2 at 40°S and the depth-integrated increase in organic carbon export flux imply shifts in the region's role in the global carbon cycle. These shifts are not only vital for understanding the evolution of atmospheric CO_2 concentration but also for potential future climate change mitigation efforts.

Finally, the study addresses anthropogenic influence on CO_2 dynamics. The increasing uptake of anthropogenic CO_2 and its interplay with the biological carbon pump indicate that the role of the BCP in DIC changes might be more intricate and significant than previously assumed. This highlights the need for comprehensive consideration of the biological carbon pump in global carbon budgets and climate models.

Supplement

The supplement related to this article is available online at: https://doi.org/

Author contributions

LD and MPH conceptualized the project. LD and MPH curated the data. LD, MPH and OS performed the investigation. LD conceptualized the methodology, used the necessary software, visualized the data and prepared the original draft of the paper. LD, MPH, OS and GJR reviewed and edited the paper.

Competing interests

The contact author has declared that neither they nor their co-authors have any competing interests.

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Open Research Data Availability Statement

All data and code used in this analysis will be available in the GitHub repository at https://github.com/louisedelaigue/changing-BCP-40S by the time of publication. PyCO2SYS v1.8.1 (Humphreys et al., 2022) was used to solve for the carbonate system, with software available at https://doi.org/10.5281/zenodo.3744275 (Humphreys et al., 2024). The Gibbs-SeaWater (GSW) Oceanographic Toolbox was used to calculate neutral density, with software available at https://www.teos-10.org/. Figures were made with Python version 3.9 (van Rossum & Drake Jr, 2009).

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