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Multi-decadal uptake of carbon dioxide into subtropical mode water of the North Atlantic Ocean

N. R. Bates

Bermuda Institute of Ocean Sciences, Ferry Reach, Bermuda

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Correspondence to: N. R. Bates (nick.bates@bios.edu)

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Abstract

Natural climate variability impacts the multi-decadal uptake of anthropogenic carbon dioxide (C_{ant}) into the North Atlantic Ocean subpolar and subtropical gyres. Previous studies have shown that there is significant uptake of CO_2 into the subtropical mode water (STMW) that forms south of the Gulf Stream in winter and constitutes the dominant upper-ocean water mass in the subtropical gyre of the North Atlantic Ocean. Observations at the Bermuda Atlantic Time-series Study (BATS) site near Bermuda show an increase in dissolved inorganic carbon (DIC) of $+1.51 \pm 0.08\,\mu\text{mol kg}^{-1}\,\text{yr}^{-1}$ between 1988 and 2011. It is estimated that the sink of CO_2 into STMW was 0.985 ± 0.018 Pg C ($\text{Pg} = 10^{15}$ g C) between 1988 and 2011 (~70 % of which is due to uptake of C_{ant}). However, the STMW sink of CO_2 was strongly coupled to the North Atlantic Oscillation (NAO) with large uptake of CO_2 into STMW during the 1990s (NAO positive phase). In contrast, uptake of CO_2 into STMW was much reduced in the 2000s during the NAO neutral/negative phase. Thus, NAO induced variability of the STMW CO_2 sink is important when evaluating multi-decadal changes in North Atlantic Ocean CO_2 sinks.

1 Introduction

The North Atlantic Ocean contributes approximately 25 % to the global ocean sink of anthropogenic carbon dioxide (CO_2) from the atmosphere (Takahashi et al., 2002, 2009). Recent studies have suggested that the basinwide CO_2 sink has decreased over the last decade (Schuster and Watson, 2007; Watson et al., 2009). However, ocean observations conducted over longer timescales indicate that surface ocean $p\text{CO}_2$ has increased at the same rate as the atmosphere with the implication that the North Atlantic Ocean CO_2 sink has not changed significantly over multi-decadal timescales (McKinley et al., 2004, 2011; Thomas et al., 2007). Complicating assessment of change in the CO_2 sink-source strength of the North Atlantic Ocean is a recognition that natural interannual variability imparted by modes of climate variability such as the North Atlantic Oscillation (NAO) (Hurrell and Deser, 2009), Atlantic Multidecadal Oscillation (McKinley et al., 2004, 2011; Ullman et al., 2009) and El Niño-Southern Oscillation (ENSO) play important roles in controlling air-sea CO_2 fluxes in the subtropical and subpolar gyres of the basin (Gruber et al., 2002; Bates et al., 2002; Thomas et al., 2009; Gruber, 2009; Levine et al., 2011).

In the subtropical gyre of the North Atlantic Ocean, the formation of subtropical mode water (STMW) or Eighteen Degree Water (EDW; Worthington, 1959, 1976; Hanawa and Talley, 2001) in winter just south of the Gulf Stream (Marshall et al., 2009) may contribute substantively to variability in the CO_2 sink (Gruber et al., 2002; Bates et al., 2002; Gruber, 2009). These studies indicated that the STMW absorbed 0.030 to 0.240 Pg C yr^{-1} in the 1990's (Gruber et al., 2002; Bates et al., 2002), while model studies suggest that the wintertime replenishment of CO_2 to the storage of anthropogenic CO_2 in STMW varies by $\sim$0.100 Pg C yr^{-1} depending on the state of the NAO (Levine et al., 2011). More recently, studies have focussed on determining the rate of CO_2 uptake at the site of STMW outcrop during it's winter formation (Andersson et al., 2011) as part of the CLIMODE (Climate of Mode Water) project (Marshall et al., 2009). In this paper, multi-decadal changes from 1988 to 2011 in the dissolved inorganic carbon (DIC) content of the STMW observed at the Bermuda Atlantic Time-series Study (BATS; 31° 40′ N, 64° 10′ W) site near Bermuda are evaluated. Estimates of how much CO_2 has been taken up in STMW over the last two decades are made. This is viewed in context with rate of equilibration of the ocean with anthropogenic CO_2 increase in the atmosphere, and observed increases in the rates of primary production and export of sinking organic carbon in the North Atlantic subtropical gyre (Lomas et al., 2010). Finally, relationships between the DIC content of STMW and NAO state are examined to determine whether the uptake and storage of CO_2 in STMW has changed contemporaneously with the NAO.

STMW forms during winter just south of the Gulf Stream in a region of very high heat loss from the ocean which triggers intense convective mixing (Marshall et al., 2009) and subsequent isopycnal transfer into the thermocline of the subtropical gyre.

STMW is a classically identified water mass that has a temperature and salinity range of 17.8–18.4 °C and 36.5 ± 0.05, respectively, and commonly identified by a characteristic minimum in the vertical gradient of potential density or potential isopycnic vorticity (Jenkins, 1982). The volume of STMW formed each winter ranges from ~ 4.6 to 8 Svy (where 1 Svy = 3.15×10^{13} m^3 and corresponds to a 1 Sv (10^6 m^3 s^{-1}) flow sustained for 1 yr; Speer and Tziperman, 1992; Kwon and Riser, 2004; Maze et al., 2009; Forget et al., 2011). The volume of STMW in the subtropical gyre is ~ 75–80 Svy (Worthington, 1976; Forget et al., 2011) with seasonal and annual fluctuations ranging from 3.5 to 8.6 Svy (Kwon and Riser, 2004; Forget et al., 2011) and 1.4 Svy, respectively. The latter rate implies that the residence time of STMW is 50 yr but recent studies indicate that ~ 8 yr is sufficient to ventilate STMW (Forget et al., 2011).

The outcrop and volume of STMW formation is coupled to the NAO which is the dominant climate mode that influences interannual and multi-decadal variability in the North Atlantic Ocean (Hurrell and Deser, 2009; Jenkins, 1982; Hurrell, 1995). During NAO positive phases, stronger atmospheric pressure gradients between the subpolar and subtropical region increases winter storm frequency and shifts the Gulf Stream northward (Hurrell, 1995; Hurrell et al., 2001; Marshall et al., 2004) with a lag of ~ 1–2 yr. During NAO negative phases, the Icelandic atmospheric low pressure shifts winter storm tracks southward, winter storms tend to be fewer in number and the Gulf Stream shifts southward. The outcrop area, extent and formation rate of STMW south of the Gulf Stream also shift in concert with NAO variability (Alfutis and Cornillon, 2001; Joyce et al., 2000; Levine et al., 2011).

2 Methods and materials

2.1 Determining long-term trends

A time-series of observations of seawater carbonate chemistry observations in the upper ocean have been collected in the subtropical gyre of the North Atlantic Ocean near

Bermuda since 1988 at the Bermuda Atlantic Time-series Study (BATS) site (Bates, 2007; Bates and Peters, 2007). This includes monthly, water column sampling for DIC and total alkalinity (TA) with analysis of samples at the Bermuda Institute of Ocean Sciences (BIOS) using highly precise and accurate coulometric and potentiometric techniques, respectively (Bates et al., 1996; Bates, 2001). DIC is defined as (Dickson et al., 2007):

$$\mathrm{DIC} = [\mathrm{CO_2}^*] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] \tag{1}$$

where $[\mathrm{CO_2}^*]$ represents the concentration of all unionized carbon dioxide, whether present as H_2CO_3 or as CO_2. The total alkalinity of seawater (TA) is defined as:

$$\begin{aligned}\mathrm{TA} = {} & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] + [\mathrm{HPO_4^{2-}}] + 2[\mathrm{PO_4^{3-}}] + [\mathrm{SiO(OH)_3^-}] \\ & + [\mathrm{HS^-}] + [\mathrm{NH_3}] + \ldots - [\mathrm{H^+}] - [\mathrm{HSO_4^-}] - [\mathrm{HF}] - [\mathrm{H_3PO_4}] - \ldots \end{aligned} \tag{2}$$

where $[\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + \mathrm{B(OH)_4^-}$ are the principal components of seawater TA.

2.2 Sampling frequency at BATS

The frequency of sampling at BATS was not uniform in time. Beginning in 1988, samples were collected 9–12 times a year but not always at the depth of the STMW, with the sampling frequency increased to 14–15 times a year over the last 15 yr. However, the time-series of $\mathrm{DIC^{STMW}}$ is not weighted to spring conditions, unlike surface observations where seasonality exerts significant influence on trends in seawater carbonate chemistry (Bates et al., 2011).

2.3 Sampling methods

Samples from the BATS site were collected into 500 ml Pyrex bottles, poisoned with Hg_2Cl, sealed with ground glass stoppers and subsequently analyzed at BIOS (Bates et al., 1996; Bates, 2007). Since the early 2000's, smaller Pyrex bottles (~ 350 ml) were used. Samples were typically analyzed within a few months of collection.

2.4 Analytical methods

At BIOS, DIC was determined using coulometric methods with a SOMMA system (Bates et al., 1996; Bates, 2007). During the first two years of sampling (1988–1990), DIC samples from BATS cruise 1 to 21 were analyzed at WHOI, thereafter at BIOS. Each day, DIC was calibrated with known volumes of pure CO_2 gas and certified reference materials (CRM's; Dickson et al., 2007) were routinely analyzed each day of analysis. Potentiometric titration methods were also used for determination of alkalinity at BIOS (Bates et al., 1996). In the 1990's, a manual alkalinity titrator was used, replaced by an automated VINDTA 2S (Versatile Instrument for the Determination of Titration Alkalinity; manufactured by Marianda Co.) in the early 2000's. In both systems, at least 15–20 titration points past the carbonic acid end point were determined for each sample, and TA then computed using non-linear least squares methods (Dickson et al., 2007). Surface Sargasso Sea water was typically used to condition the titrator while CRM's were routinely used. Analytical precision for both DIC and TA at BIOS was typically $< 0.2\,\%$ for > 1000 within bottle and between bottle replicate analyses.

2.5 Identifying changes in STMW CO_2 content

The time-series of seawater carbonate chemistry for STMW was compiled using temperature criteria (i.e., 17.8–18.4 °C) to identify STMW water as in previous studies (Bates et al., 2002). During a few cruises, total alkalinity was not determined analytically, and it was computed from salinity with an error of $\sim 2.8\,\mu\text{moles}\,\text{kg}^{-1}$. (Bates et al., 1996).

2.6 Seawater carbonate chemistry computations

The complete seawater carbonic acid system (i.e., CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+) can be calculated from a combination of two carbonate system parameters DIC, TA, pCO$_2$ and pH, along with temperature and salinity. Seawater pCO$_2$, pH, $[CO_3^{2-}]$, mineral saturation states for calcite ($\Omega_{calcite}$) and aragonite ($\Omega_{aragonite}$), and the Revelle factor (β; $= \partial \ln p\mathrm{CO}_2/\partial \ln \mathrm{DIC}$) were computed from DIC, TA, temperature and salinity data using the program CO2calc (Robbins et al., 2010). Carbonic acid dissociation constant of Mehrbach et al. (1973), as refit by Dickson and Millero (1987) were used for the computation, as well as dissociation constants for HSO_4^- (Dickson, 1990). Here, $p\mathrm{CO}_2$ is the partial pressure of CO_2 in equilibrium with seawater, while pH is expressed on the total seawater scale.

Salinity normalized DIC (i.e., nDIC) and TA (i.e., nTA) data were also determined to account for local evaporation and precipitation changes. Trends and regression statistics for CO_2 changes in the STMW are given in Table 1 (using a 17.8–18.4 °C temperature criterion to define STMW; Fig. 1; Table 1). A density criterion (i.e., 26.4 σ_Θ isopycnal surface) can also be used define STMW but does not give significantly different results. Surface trends are also discussed here for comparative purposes but more detailed information about surface seawater carbonate chemistry changes are given elsewhere (Bates et al., 2011).

2.7 Trend anlysis and statistics

Trend analysis was performed with observed data in STMW (Table 1). Trends were also computed for the two time periods (1988–2000; 2000–2011; Table 2). Regression statistics given were slope, error, r^2, p-value and n. Trends with p-values greater than 0.01 were deemed statistically not significant. Monthly and winter JFM mean NAO index data was obtained from the NOAA Climate Prediction Office (http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/nao_index.html). Correlations between winter NAO, mixed layer depth, and surface and STMW DIC contents are shown in Table 3.

3 Results

3.1 Seawater carbonate chemistry changes in STMW

Over the last 2 decades (1988–2011), the inorganic carbon content of STMW such as DIC (i.e., DIC^{STMW}) and $p\text{CO}_2$ has significantly changed while temperature, salinity and total alkalinity did not change over time (Fig. 1a; Table 1). For example, the long-term trend of DIC (i.e., $\delta\text{DIC}^{\text{STMW}}/\delta t_{1988-2011}$) and salinity normalized nDIC in STMW exhibits increases of $+1.51 \pm 0.08$ and $+1.46 \pm 0.06\,\mu\text{mol kg}^{-1}\,\text{yr}^{-1}$, respectively. This constitute a $\sim 40\,\mu\text{moles kg}^{-1}$ change in DIC^{STMW} since 1988 (Fig. 1b). Contemporaneously, the computed seawater $p\text{CO}_2$ of STMW increased at a rate of $+2.13 \pm 0.16\,\mu\text{atm kg}^{-1}\,\text{yr}^{-1}$ (an increase of nearly 50 µatm or 12 % from 1988 to 2011; Fig. 1c), higher than the increase in atmospheric $p\text{CO}_2$ observed over the same period (Bates et al., 2011). The Revelle factor (β), which indicates the capacity of seawater to absorb CO_2, has also increased at a rate of $+0.025 \pm 0.002\,\text{yr}^{-1}$ (Fig. 1c). This infers that the capacity of STMW to absorb CO_2 has gradually reduced over time, similar to the model studies of Thomas et al. (2009).

3.2 Detecting rates of ocean acidification in STMW

Trend analysis indicates that relevant indicators of ocean acidification in STMW such as pH have also significantly decreased. The pH of STMW decreased at a rate of $-0.0022 \pm 0.0002\,\text{yr}^{-1}$, a seawater pH decline of ~ 0.05 over the past 2 decades (Fig. 1d; Table 1). This rate of pH decrease is higher than surface waters at BATS ($-0.0017 \pm 0.0001\,\text{yr}^{-1}$) and off Hawaii and the Canary Islands (-0.0014 to $-0.0019\,\text{yr}^{-1}$ (Dore et al., 2009; Gonzalez-Davila et al., 2010). This change in pH of the STMW represents a $\sim 12\,\%$ increase in hydrogen ion (H^+) since 1988. Other indicators of ocean acidification at BATS such as $[\text{CO}_3^{2-}]$, Ω_{calcite} and $\Omega_{\text{aragonite}}$ have also decreased by $-0.87 \pm 0.07\,\mu\text{mol kg}^{-1}\,\text{yr}^{-1}$, $-0.022 \pm 0.002\,\text{yr}^{-1}$, and $-0.014 \pm 0.001\,\text{yr}^{-1}$, respectively (Fig. 1d,e; Table 1). The ecosystem response in the mesopelagic (i.e., at the depth of STMW within the subtropical gyre) to ocean acidification is unknown at present.

4 Discussion

4.1 Determining the rates of CO_2 uptake into STMW over the last 2 decades

Trend analyses reveal that DIC^{STMW} has increased at a significantly higher rate than observed for surface waters in the subtropical gyre (1988–2011). For example, the DIC of surface waters (i.e., $DIC^{surface}$), expressed here as $\delta DIC^{surface}/\delta t_{1988-2011}$, increased at a rate of $+1.08 \pm 0.05\,\mu mol\,kg^{-1}\,yr^{-1}$ (Bates et al., 2011; Fig. 2a). This trend is similar to that expected from equilibration of STMW with increasing atmospheric CO_2 due to the anthropogenic CO_2 transient. Here, this term (i.e., $\delta DIC^{anthropogenic}/\delta t_{1988-2011}$) is calculated using mean hydrographic, DIC and TA values for STMW with the observed atmospheric pCO_2 increases (due to anthropogenic CO_2) over the same time period (i.e., $+1.72 \pm 0.01\,ppm\,yr^{-1}$; 30). The trend for $\delta DIC^{anthropogenic}/\delta t_{1988-2011}$ is $+1.06\,\mu mol\,kg^{-1}\,yr^{-1}$ and this effectively represents the uptake rate of anthropogenic CO_2 (C_{ant}) from the atmosphere.

Examination of trends in seawater carbonate chemistry indicate that the DIC content of surface and STMW waters observed at the BATS site have increased at divergent rates over the last 2 decades (Fig. 2a). Once STMW is formed during winter, isopycnal mixing and subduction emplaces STMW between surface/seasonal thermocline waters and the permanent thermocline in the subtropical gyre. STMW is ultimately subducted to deeper depths with time (Behringer and Stommel, 1980; Spall, 1992; Fig. 3a). Using the $\delta DIC^{STMW}/\delta t_{1988-2011}$ trend of $+1.51 \pm 0.08\,\mu mol\,kg^{-1}\,yr^{-1}$, and given that the volume of STMW in the North Atlantic subtropical gyre is ~ 75 Svy (Forget et al., 2011), it is estimated that the STMW has accumulated 0.985 ± 0.018 Pg C since 1988 (Fig. 3b).

The error in the amount of CO_2 taken up into STMW relates to that propagated from the trend error. However, the volume of SMTW could be underestimated by 10 % (Forget et al., 2011) which implies that the estimate of 0.985 ± 0.018 Pg C, and other estimations discussed later in the paper, may be higher by 10 %. The separation of STMW from contact with the atmosphere within the subtropical gyre (with exceptions discussed later) and eventual subduction to deeper waters constitutes a mechanism for transferring CO_2 from the air-sea interface to the deep ocean and thus constitutes a sink for CO_2. Thus, over the last 2 decades, the STMW has been a quantitatively important additional CO_2 sink term in the sink-source CO_2 budget of the North Atlantic Ocean.

4.2 The STMW CO_2 sink and it's attribution

The change in DIC content of the STMW (i.e., $\delta \mathrm{DIC}^{\mathrm{STMW}}/t_{1988-2011}$) potentially results from a number of factors, including: (1) equilibration at the STMW outcrop with the anthropogenic CO_2 increase in the atmosphere (i.e., $\delta \mathrm{DIC}^{\mathrm{anthropogenic}}/t_{1988-2011)}$); (2) physical changes at the outcrop site of STMW winter formation encompasses the summed changes due to changes in air-sea gas exchange of CO_2, the preformed DIC content of waters that contribute to STMW formation during winter, formation rate of STMW and its subsequent dispersion rates in the subtropical gyre (here termed $\delta \mathrm{DIC}^{\mathrm{outcrop}}/t_{1988-2011}$), and; (3) changes imparted by biological processes including respiration/remineralization acting on STMW during it's transit through the subtropical gyre (here termed $\delta \mathrm{DIC}^{\mathrm{biology}}/t_{1988-2011}$). Thus:

$$\begin{aligned}\delta \mathrm{DIC}^{\mathrm{STMW}}/t_{1988-2011} = {} & \delta \mathrm{DIC}^{\mathrm{anthropogenic}}/t_{1988-2011} + \delta \mathrm{DIC}^{\mathrm{biology}}/t_{1988-2011} \\ & + \delta \mathrm{DIC}^{\mathrm{outcrop}}/t_{1988-2011} \end{aligned} \tag{3}$$

The $\delta \mathrm{DIC}^{\mathrm{anthropogenic}}/t_{1988-2011}$ term was estimated earlier at 1.06 μmol kg^{-1} yr^{-1}, with the implication that the uptake of anthropogenic CO_2 constitutes ~70 % of the observed increase in $\mathrm{DIC}^{\mathrm{STMW}}$. We estimate that the uptake of anthropogenic CO_2

into STMW since 1988 was 0.692 ± 0.018 Pg C (Fig. 3b) or ~70 % of the STMW CO_2 sink. The remaining terms in Eq. (3) comprise the remaining ~30 % of the observed changes.

Term 3 ($\delta \mathrm{DIC}^{\mathrm{biology}}/t_{1988-2011}$) can be approximated by examining changes in organic carbon export and remineralization and/or biogeochemical properties (e.g., dissolved oxygen and inorganic nutrients). Term 2 ($\delta \mathrm{DIC}^{\mathrm{outcrop}}/t_{1988-2011}$) is difficult to determine directly due to the lack of sustained observations at the STMW site of formation but some field (Andersson et al., 2011) and model studies (Levine et al., 2011) provide some inferences on this term. Thus, Eq. (4) can be solved by difference, with the caveat that there are many uncertainties underlying this approach:

$$\delta \mathrm{DIC}^{\mathrm{outcrop}}/t_{1988-2011} = \delta \mathrm{DIC}^{\mathrm{STMW}}/t_{1988-2011} - (\delta \mathrm{DIC}^{\mathrm{anthropogenic}}/t_{1988-2011} + \delta \mathrm{DIC}^{\mathrm{biology}}/t_{1988-2011}) \quad (4)$$

Since 1990, integrated rates of in situ primary production (0–140 m) have increased at BATS by 44 % (+0.85 mmol C m^{-2} d^{-1} yr^{-1}) and since 1996 by 98 % (Lomas et al., 2010). During the 1990–2007 period, the sinking particulate organic carbon (POC) flux record at 150 m has increased by 71 % (+0.12 mmol C m^{-2} d^{-1} yr^{-1}). However, at 300 m, no long-term change is observed in POC flux (Lomas et al., 2010), with the implication that the observed increase in ocean carbon export is attenuated by mesopelagic remineralization of sinking organic carbon back to CO_2 in the 150 m to 300 m depth zone. Since this depth zone coincides approximately with the upper/middle portion of the STMW, enhanced mesopelagic remineralization likely contributes to the observed increase in $\mathrm{DIC}^{\mathrm{STMW}}$. The increase in DIC due to enhanced remineralization is estimated at ~0.29 ± 0.05 µmol kg^{-1} yr^{-1} (i.e., $\delta \mathrm{DIC}^{\mathrm{biology}}/t_{1988-2011}$) or approximately 19 % of $\delta \mathrm{DIC}^{\mathrm{STMW}}/t_{1988-2011}$. Dissolved oxygen (DO) and nitrate contents also change by −0.15 ± 0.07 µmol kg^{-1} yr^{-1} and −0.01 ± 0.01 µmol kg^{-1} yr^{-1}, respectively ($r^2 < 0.02$). However, both DO and nitrate are also likely to vary depending on preconditioning and physical changes at the winter outcrop site of STMW formation. Despite these caveats, it appears that increase in $\mathrm{DIC}^{\mathrm{STMW}}$ due to changes at the STMW outcrop (i.e., term 2, $\delta\mathrm{DIC}^{\mathrm{outcrop}}/t_{1988-2011}$) contribute the remaining 10 % to $\delta\mathrm{DIC}^{\mathrm{STMW}}/t_{1988-2011}$ (i.e., $\delta\mathrm{DIC}^{\mathrm{outcrop}}/t_{1988-2011} = 0.16 = 1.51 - [1.06 + 0.29]$).

4.3 A multi-decadal change in the STMW CO$_2$ sink and it's relation to NAO variability

A closer inspection of the trends in $\mathrm{DIC}^{\mathrm{STMW}}$ reveal considerable difference between the 1990s and 2000s. The trend for $\mathrm{DIC}^{\mathrm{STMW}}$ determined for 1988 to 2001 was much higher at 2.06 ± 0.26 µmol kg^{-1} yr^{-1} (Bates et al., 2002,and recalculated here) when compared to that observed for the 2001–2011 period (0.56 ± 0.21 µmol kg^{-1} yr^{-1}; Fig. 2a; Table 2). Over the last 2 decades, the NAO (JFM) winter state has transitioned from mostly positive values in the 1990s to neutral and negative values in the 2000s (Fig. 2b). Contemporaneous with the change in winter NAO, the mean winter mixed layer depth (MLD) has also deepened significantly from ~ 110 m to ~ 150 m (Fig. 2b). Notably, a significant decline in $\mathrm{DIC}^{\mathrm{STMW}}$ was observed in 2011 that coincides with a strongly negative NAO (JFM) winter phase (Figs. 1f; 2b). If data from 2011 is not included in the trend analysis, the $\delta\mathrm{DIC}^{\mathrm{STMW}}/t_{1988-2010}$ was significantly higher at ~ 1.74 ± 0.08 µmol kg^{-1} yr^{-1} (see Table 1).

If winter $\mathrm{DIC}^{\mathrm{STMW}}$ and surface DIC are compared, the trends are convergent (Fig. 2c) rather than divergent (Fig. 2a). While winter $\mathrm{DIC}^{\mathrm{STMW}}$ trends are similar to that determined for all annual data (+1.46 µmol kg^{-1} yr^{-1}), winter $\mathrm{DIC}^{\mathrm{surface}}$ increased at a rate of 1.80 µmol kg^{-1} yr^{-1} (i.e., ~ 0.70 µmol kg^{-1} yr^{-1} greater than the trend determined for $\mathrm{DIC}^{\mathrm{surface}}$ with all monthly data; Table 1). As the winter NAO has declined to neutral status, over the last decade, winter $\mathrm{DIC}^{\mathrm{surface}}$ has increased as mixed layers have deepened (with standout high values during NAO negative winters; Fig. 2d). In contrast, winter $\mathrm{DIC}^{\mathrm{STMW}}$ appears to lag NAO by up to 1–2 yr (Levine et al., 2011). NAO, mixed layer depth and the difference between surface and STMW DIC also appear well correlated with each other (Fig. 2e,f; r^2 values of 0.25–0.45; Table 3).

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
|◀ | ▶|
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

In the 1990s, contemporaneous with DIC^{STMW} increase of 2.06 ± 0.26 µmol kg^{-1} yr^{-1} (Bates et al., 2022), recalculated here; Fig. 4b; Table 2), DO and nitrate decreased (increased) at −0.55 ± 0.14 and +0.03 ± 0.02 µmol kg^{-1} yr^{-1}, respectively (although the r^2 values were low, < 0.10). With the volume of STMW at ~ 75 Svy (Forget et al., 2011), this is equivalent to an increase of 0.760 Pg C (Figs. 3c, 4d), or approximately 77 % of the 1988–2011 increase of DIC^{STMW}. In contrast, the δDIC^{STMW}/t$_{2001-2011}$ trend is only +0.56 µmol kg^{-1} yr^{-1} for the 2000s (Fig. 4c). The increase in DIC^{STMW} is much reduced compared to the 1990s as is the estimate of the CO_2 sink into STMW (i.e., 0.159 Pg C, Figs. 3d, 4e).

The two periods of observation, 1988–2001 and 2001–2011, correspond approximately to a decade of positive winter NAO (mean of +0.73, 1989–2001) followed by a decade of neutral/negative NAO (mean of +0.10, 2001–2011). Levine et al. (2011) suggest that STMW takes up more CO_2 during NAO positive phase as the Gulf Stream and STMW outcrop moves northward in response to NAO. During an NAO neutral negative phase the Gulf Stream and STMW outcrop moves south with less CO_2 taken up by STMW. Levine et al. (2011) show a STMW CO_2 uptake variability of ~ 0.100 Pg C yr^{-1} depending on the state of the NAO.

In the 1990s, trend analysis and STMW sink CO_2 estimates indicate that the accumulation of CO_2 into STMW was large during the NAO positive phase with C$_{ant}$ computed to be 0.391 Pg C or ~ 51 % of the total 0.760 Pg C sink in the 1990's (Fig. 4d). Furthermore, it is estimated that enhanced remineralization of sinking organic carbon in STMW (Lomas et al., 2010) may have contributed 0.109 Pg C or ~ 14 % to the total sink. The remainder (i.e., 0.262 Pg C or 34 % of the total sink) must be due to changes in DIC contents during formation of the STMW at the outcrop due to a combination of changes in air-sea gas exchange rates and water mass contributions to STMW. With movement northward of the Gulf Stream and STMW outcrop during an NAO positive period, entrainment of high DIC from deeper water (as shown in DIC sections across the STMW outcrop, Marshall et al., 2009; Andersson et al., 2011), and less mixing with relatively low DIC subtropical gyre waters during winter STMW formation, potentially contribute to higher DIC input into the STMW (Fig. 4e).

In the 2000s, the observed uptake was much reduced compared to the 1990s at ~0.159 Pg C (Fig. 4f). Indeed this is much less than predicted from equilibration with anthropogenic CO_2 in the atmosphere (i.e., ~0.301 Pg C). Furthermore, during this period, an additional ~0.082 Pg C may have accumulated in STMW due to enhanced remineralization of organic carbon in STMW. These two terms have to be balanced by reduced input of DIC to the STMW during winter formation of STMW (here computed at −0.025 Pg C; Fig. 4f) and loss from STMW due to mixing with surface waters/seasonal thermocline and/or enhanced diapycnal mixing with deeper waters than STMW. Given that the winter $\mathrm{DIC}^{\mathrm{surface}}$ increases by 0.70 μmol kg^{-1} yr^{-1}, we estimate that STMW may have lost ~0.198 Pg C (Fig. 4f) due to mixing with surface waters. The implication is that much of the anthropogenic CO_2 uptake into STMW during the 2000s will have been lost to surface waters (in contact with the atmosphere) and thus ventilated over a shorter timeframe. Thus, in contrast to the 1990s, the STMW appears not to have been a sink for anthropogenic CO_2 in the 2000s. Indeed without the potential increase in $\mathrm{DIC}^{\mathrm{STMW}}$ due to enhanced remineralization of organic carbon, the DIC content of STMW would have declined during the 2000s.

The observations at BATS thus indicate that the phase of the NAO is important for determining the long-term or short-term sink of CO_2 into STMW. During NAO positive phases, the CO_2 sink into SMTW appears to be long-term (i.e., > 10 yr), whilst short-term (i.e., < 10 yr), during the NAO neutral/negative period of the 2000s. As such, the reduced potential for uptake and long-term storage of CO_2 in STMW during the 2000s likely contributed to the observed decline in the North Atlantic Ocean CO_2 sink during this decade. It may be that the 1990s uptake and storage of CO_2 into the STMW reflects an anomalous decade since the winter NAO was predominantly neutral/negative in the 1950s to 1980s, with a return to this state in the 2000s. This study supports the findings of other studies (Gruber et al., 2002; Bates et al., 2002; McKinley et al., 2004, 2011; Thomas et al., 2007; Gruber, 2009; Ullman et al., 2009) that natural climate variability such as NAO imparts a significant influence on CO_2 sinks in the North Atlantic Ocean.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

5 Conclusions

The observations at BATS thus indicate that the phase of the NAO is important for determining the long-term or short-term sink of CO_2 into STMW. During NAO positive phases, the CO_2 sink into SMTW appears to be long-term (i.e., > 10 yr), whilst short-term (i.e., < 10 yr), during the NAO neutral/negative period of the 2000s. As such, the reduced potential for uptake and long-term storage of CO_2 in STMW during the 2000s likely contributed to the observed decline in the North Atlantic Ocean CO_2 sink during this decade. It may be that the 1990s uptake and storage of CO_2 into the STMW reflects an anomalous decade since the winter NAO was predominantly neutral/negative in the 1950s to 1980s, with a return to this state in the 2000s. Thus the NAO imparts a significant influence on CO_2 sinks in the North Atlantic Ocean.

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Table 1. Long-term trends (1983–2011) of STMW hydrography and seawater carbonate chemistry with regression statistics (slope and error, n, r^2 and p-value). This table includes trend analysis of STMW including temperature and salinity, seawater carbonate chemistry (i.e., DIC, nDIC, TA, nTA, atmospheric $p\text{CO}_2$ ($p\text{CO}_2^{\text{atm}}$), and calculated seawater $p\text{CO}_2$ ($p\text{CO}_2^{\text{sea}}$) and Revelle factor ($\beta$) anomalies) and indicators of seawater carbonate chemistry changes, including pH, [CO_3^{2-}], and mineral saturation states of calcite (Ω_{calcite}) and aragonite (Ω_{arag}) from the BATS (31° 50′ N, 64° 10′ W) site in the North Atlantic Ocean. Please see text for details on the seawater carbonate chemistry computation and salinity normalization procedures.

Parameter	Period	Mean (std dev)	1988–2011 change	slope and std error	n	r^2	p-value
Hydrography							
Temperature	Sep 1988–Jul 2011	18.10 ± 0.17 °C	−0.26	−0.011 ± 0.002 °C yr^{-1}	214	0.14	< 0.01
Salinity	Sep 1988–Jul 2011	36.540 ± 0.035	0.015	0.0006 ± 0.0004 yr^{-1}	214	0.01	0.13
Seawater carbonate chemistry							
DIC	Sep 1988–Jul 2011	2098.09 ± 11.1 µmol kg^{-1}	+34.6	+1.51 ± 0.08 µmol kg^{-1} yr^{-1}	209	0.63	< 0.01
DIC	Sep 1988–May 2010	2098.06 ± 11.4 µmol kg^{-1}	+40.0	+1.74 ± 0.08 µmol kg^{-1} yr^{-1}	195	0.73	< 0.01
nDIC	Sep 1988–Jul 2011	2101.6 ± 11.5 µmol kg^{-1}	+33.6	+1.46 ± 0.09 µmol kg^{-1} yr^{-1}	209	0.55	< 0.01
TA	Sep 1988–Jul 2011	2387.4 ± 5.3 µmol kg^{-1}	+3.6	+0.15 ± 0.06 µmol kg^{-1} yr^{-1}	208	0.03	0.02
nTA	Sep 1988–Jul 2011	2391.2 ± 4.9 µmol kg^{-1}	+2.4	+0.11 ± 0.06 µmol kg^{-1} yr^{-1}	208	0.02	0.07
$p\text{CO}_2^{\text{sea}}$	Sep 1988–Jul 2011	354.4 ± 18.5 µatm	+48.9	+2.13 ± 0.16 µatm yr^{-1}	208	0.45	< 0.01
Revelle (β)	Sep 1988–Jul 2011	10.07 ± 0.22	+0.58	+0.025 ± 0.002 yr^{-1}	208	0.44	< 0.01
Ocean acidification indicators							
pH	Sep 1988–Jul 2011	8.078 ± 0.020	−0.053	−0.0022 ± 0.0002 yr^{-1}	208	0.44	< 0.01
CO_3^{2-}	Sep 1988–Jul 2011	204.68 ± 7.9 µmol kg^{-1}	−20.0	−0.87 ± 0.07 µmol kg^{-1} yr^{-1}	208	0.41	< 0.01
Ω_{calcite}	Sep 1988–Jul 2011	2.99 ± 0.13	−0.33	−0.022 ± 0.0019 yr^{-1}	208	0.40	< 0.01
$\Omega_{\text{aragonite}}$	Sep 1988–Jul 2011	4.59 ± 0.20	−0.51	−0.014 ± 0.0012 yr^{-1}	208	0.40	< 0.01

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀I | ▶I
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Table 2. Long-term trends (1983–2011) of STMW hydrography and seawater carbonate chemistry with regression statistics (slope and error, n, r^2 and p-value) separated into time-periods. This table includes trend analysis of STMW including temperature and salinity, seawater carbonate chemistry (i.e., DIC, nDIC, TA, nTA, atmospheric $p\mathrm{CO}_2$ ($p\mathrm{CO}_2^{\mathrm{atm}}$), and calculated seawater $p\mathrm{CO}_2$ ($p\mathrm{CO}_2^{\mathrm{sea}}$) and Revelle factor ($\beta$) anomalies) and indicators of seawater carbonate chemistry changes, including pH, $[\mathrm{CO}_3^{2-}]$, and mineral saturation states of calcite ($\Omega_{\mathrm{calcite}}$) and aragonite ($\Omega_{\mathrm{arag}}$) from the BATS (31° 50′ N, 64° 10′ W) site in the North Atlantic Ocean. Please see text for details on the seawater carbonate chemistry computation and salinity normalization procedures.

Parameter	Period	slope and std error	n	r^2	p-value
1988–2011					
Temperature	Sep 1983–Jul 2011	$-0.011 \pm 0.002\,^{\circ}\mathrm{C\,yr^{-1}}$	214	0.14	< 0.01
Salinity	Sep 1983–Jul 2011	$+0.0064 \pm 0.0004\,\mathrm{yr^{-1}}$	212	0.01	0.13
Dissolved oxygen	Sep 1983–Mar 2009	$-0.15 \pm 0.07\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	227	0.02	0.04
Nitrate	Sep 1983–Mar 2009	$+0.01 \pm 0.01\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	219	0.01	0.26
DIC	Sep 1983–Jul 2011	$+1.51 \pm 0.08\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	209	0.63*	< 0.01
DIC	Sep 1983–Jul 2010	$+1.74 \pm 0.08\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	196	0.73*	< 0.01
1988–2001					
Temperature	Sep 1983–Jul 2001	$-0.019 \pm 0.005\,^{\circ}\mathrm{C\,yr^{-1}}$	87	0.17	< 0.01
Salinity	Sep 1983–Jul 2001	$-0.0014 \pm 0.0008\,\mathrm{yr^{-1}}$	86	0.32	< 0.01
Dissolved oxygen	Sep 1983–Jul 2001	$-0.55 \pm 0.14\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	144	0.10	< 0.01
Nitrate	Sep 1983–Jul 2001	$+0.03 \pm 0.02\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	139	0.02	0.14
DIC	Sep 1983–Jul 2001	$+2.06 \pm 0.21\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	85	0.53*	< 0.01
2001–2011					
Temperature	Jul 2001–Jul 2011	$+0.007 \pm 0.005\,^{\circ}\mathrm{C\,yr^{-1}}$	127	0.01	0.23
Salinity	Jul 2001–Mar 2009	$+0.006 \pm 0.001\,\mathrm{yr^{-1}}$	127	0.17	< 0.01
Dissolved oxygen	Jul 2001–Mar 2009	$+1.29 \pm 0.27\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	84	0.21	< 0.01
Nitrate	Jul 2001–Jul 2011	$-0.05 \pm 0.04\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	78	0.02	0.28
DIC	Jul 2001–Jul 2011	$+0.56 \pm 0.21\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	124	0.06	< 0.01

Table 3. Correlation table of selected mean winter (JFM) variables. Within each cell, the first row = correlation coefficient and second row = p-value. For each correlation, $N = 22$–23. Only those correlations with $P \leq 0.1$ are shown, with $P \leq 0.01$ in bold.

MLD	$\mathrm{DIC}^{\mathrm{surface}}$	$\mathrm{DIC}^{\mathrm{STMW}}$	$\mathrm{DIC}^{\mathrm{STMW-surf}}$	
NAO	**−0.34** < **0.01**	**−0.66** < **0.01**	**−0.30** < **0.01**	**0.45** < **0.01**
MLD		0.23 0.02	–	**−0.39** < **0.01**
$\mathrm{DIC}^{\mathrm{surface}}$			**0.63** < **0.01**	**−0.32** < **0.01**
$\mathrm{DIC}^{\mathrm{STMW}}$				–

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◂◂
▸▸
◂
▸
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

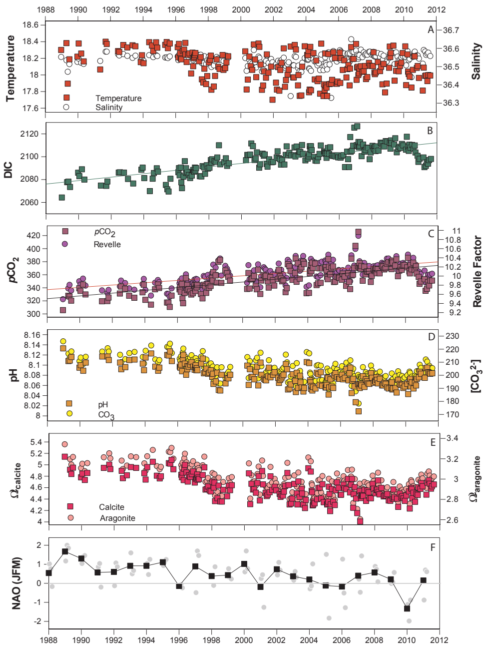

Fig. 1. Long-term observations and trends of surface hydrography, seawater carbonate chemistry and ocean acidification indicators from 1983 to 2011 at the BATS (Bermuda Atlantic Time-series Study; 31° 40′ N, 64° 10′ W) and Hydrostation S (32° 10′ N, 64° 30′ W) sites located near Bermuda in the NW Atlantic Ocean. Slopes and statistics of regressions are listed in Table 1. **(A)** Sea surface temperature (°C; black line) and salinity (red line). **(B)** Surface dissolved inorganic carbon (DIC, µmol kg^{-1}, green symbol) and salinity normalized DIC (nDIC; µmol kg^{-1}, light green symbol). **(C)** Seawater $p\mathrm{CO}_2$ (µatm; purple symbol) and Revelle factor (*b*) (fuchsia symbol). **(D)** Surface seawater pH (orange symbol) and $[\mathrm{CO}_3^{2-}]$ (µmol kg^{-1}, yellow symbol). **(E)** Surface saturation state of calcite ($\Omega_{\mathrm{calcite}}$) (pink symbol) and aragonite ($\Omega_{\mathrm{calcite}}$) (light pink symbol). **(F)** Time-series of January, February and March NAO index (grey circles; and mean winter NAO (JFM; black square symbols and line)).

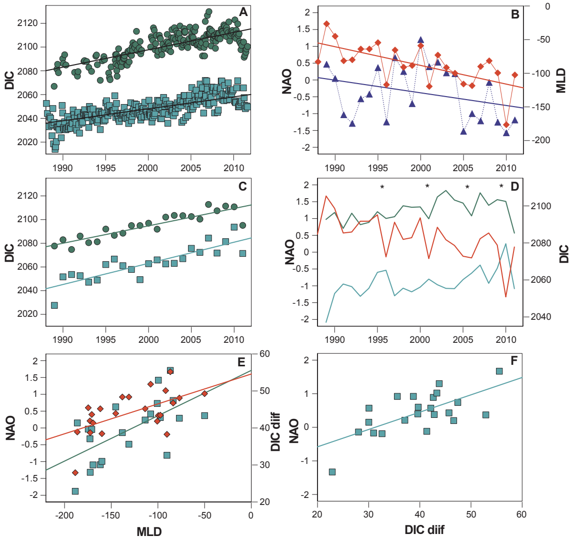

Fig. 2. Time-series and relationships between DIC, mixed layer depths (MLD) and NAO index from 1983 to 2011 at the BATS (Bermuda Atlantic Time-series Study; 31° 40′ N, 64° 10′ W) site located near Bermuda in the NW Atlantic Ocean. Slopes and statistics of regressions are listed in Table 1. **(A)** Time series of DIC in surface (DIC$^{\text{surface}}$; µmol kg^{-1}; light green) and STMW (DIC$^{\text{STMW}}$; µmol kg^{-1}; dark green) waters. **(B)** Time-series of winter NAO (JFM; red symbols and line) and mixed layer depth (m; blue symbols and line). **(C)** Time series of winter (JFM) DIC in surface (µmol kg^{-1}; light green) and STMW (µmol kg^{-1}; dark green) waters. **(D)** Time series of winter (JFM) DIC in surface (µmol kg^{-1}; light green) and STMW (µmol kg^{-1}; dark green) waters winter NAO (JFM; red line). The surface and STMW DIC data are corrected for long-term trends and so represent anomalies relative to long-term trends. **(E)** Scatter plot of winter (JFM) NAO (red symbols) and DIC difference between surface and STMW (µmol kg^{-1}; green symbol) against mixed layer depth (m). **(F)** Scatter plot of winter (JFM) NAO (red symbols) against DIC difference between surface and STMW (µmol kg^{-1}; green symbol).

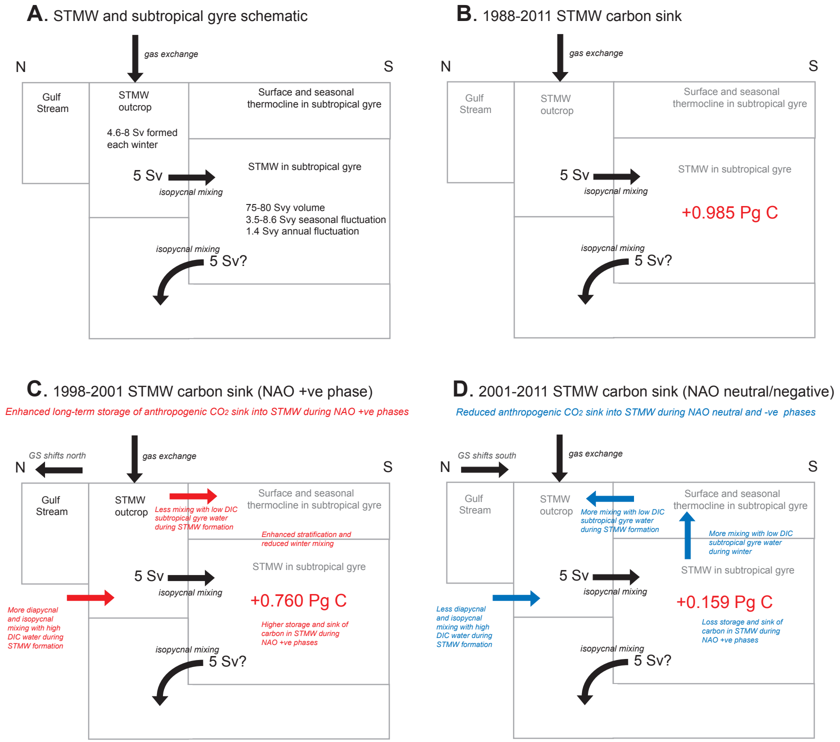

Fig. 3. Schematic of water masses and CO_2 sink estimates in STMW for different time-periods from 1988–2011. **(A)** Schematic of North Atlantic subtropical gyre showing Gulf Stream, STMW outcrop, surface and seasonal thermocline layer (not to scale). Range of winter STMW formation rates (Sv; Speer and Tziperman, 1992; Kwon and Riser, 2004; Forget et al., 2011), volume of STMW (Svy; Maze et al., 2009; Forget et al., 2011), and seasonal/annual fluctuations in the volume of STMW (Kwon and Riser, 2004; Forget et al., 2011) are given. **(B)** Estimate of CO_2 sink into STMW (Pg C) for 1988–2011 period. **(C)** Estimate of CO_2 sink into STMW (Pg C) for 1988–2001 period. **(D)** Estimate of CO_2 sink into STMW (Pg C) for 2001–2011 period.

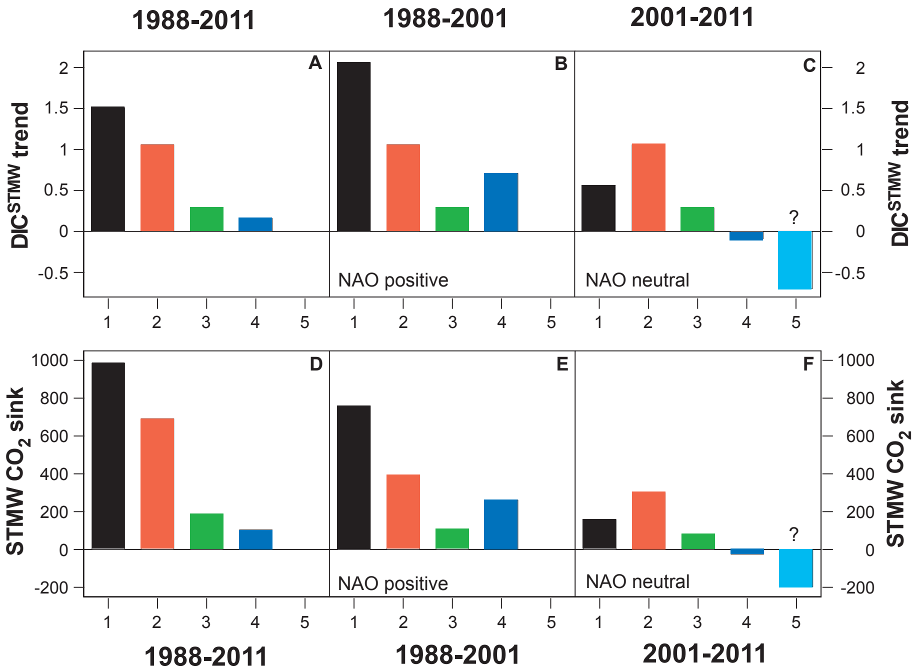

Fig. 4. Trends in $\mathrm{DIC}^{\mathrm{STMW}}$ (**A–C**; µmol kg^{-1} yr^{-1}) and estimate of CO_2 sink into STMW (**D–F**; Pg C) for the 1988–2001, 1988–2001, and 2001–2011 periods, respectively. The trend and CO_2 sink in STMW is given in row 1 in each panel ($\delta\mathrm{DIC}^{\mathrm{STMW}}/t$; black). In each panel, row 2 denotes potential uptake due to anthropogenic CO_2 (C_{ant} or $\delta\mathrm{DIC}^{\mathrm{anthropogenic}}/t$); red; row 3 denotes increase due to remineralization of organic carbon in STMW to CO_2 (i.e., $\delta\mathrm{DIC}^{\mathrm{biology}}/t$; green); row 4 denotes increase (decrease) at the STMW outcrop (i.e., $\delta\mathrm{DIC}^{\mathrm{outcrop}}/t$; blue). In row 5, the potential change due to mixing of STMW with surface/seasonal thermocline waters is shown (i.e., $\mathrm{dDIC}^{\mathrm{mixing}}/t$; cyan).