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

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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 subtropical mode water (STMW) of the North Atlantic. STMW 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 $+1.51 \pm 0.08 \, \mu mol \, kg^{-1} \, yr^{-1}$ between 1988 and 2011, but also an increase in ocean acidification indicators such as pH at rates ($-0.0022 \pm 0.0002 \, yr^{-1}$) higher than the surface ocean (Bates et al., 2012). It is estimated that the sink of CO_2 into STMW was $0.985 \pm 0.018 \, Pg \, C$ ($Pg = 10^{15}$ g C) between 1988 and 2011 (70 ± 1.8 % of which is due to uptake of C_{ant}). The sink of CO_2 into the STMW is 20 % of the CO_2 uptake in the North Atlantic Ocean between $14°–50° \, N$ (Takahashi et al., 2009). 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 during a predominantly 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 in the North Atlantic 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 $p CO_2$ (partial pressure of 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; Thomas et al., 2008; McKinley et al., 2011; Bates et al., 2012). Complicating any 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 Variability (AMV; McKinley et al., 2004; Ullman et al., 2009; Metzl et al., 2010; McKinley et al., 2011) 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., 2008; 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; Fig. 1a) may contribute substantively to variability in the CO_2 sink in the North Atlantic (Gruber et al., 2002; Bates et al., 2002; Gruber, 2009). These studies indicate that the STMW absorbed 0.030 to $0.240 \, Pg \, C \, yr^{-1}$ in the 1990s (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 approximately $0.100 \, Pg \, C \, yr^{-1}$, 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
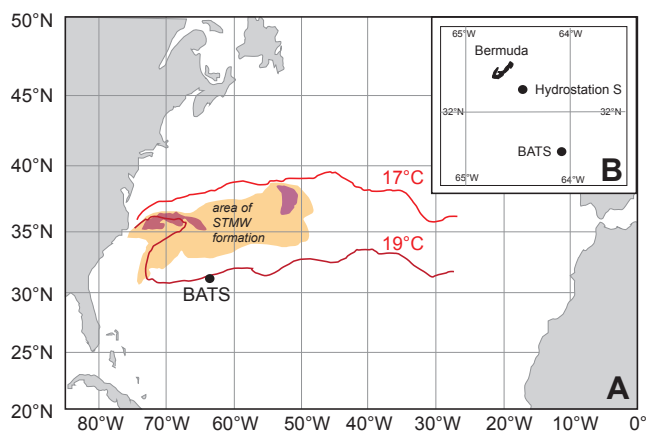
Fig. 1. Location map of general area of STMW outctop and the BATS site near Bermuda in the NW Atlantic Ocean. **(A)** General outcrop area of STMW in the NW Atlantic Ocean, showing locations of climatological 17 °C and 19 °C isotherms and mean STMW formation rate area (orange and purple) for the 2004–2006 period from Marshall et al. (2009). This figure is modified from Fig. 2a and Fig. 12a of Marshall et al. (2009). **(B)** Location of the BATS (Bermuda Atlantic Time-series Study; 31°40′ N, 64°10′ W) site as well as the long-term Hydrostation S ocean time-series.

the site of STMW outcrop during its winter formation (Andersson et al., 2012) 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; Fig. 1b) site near Bermuda are evaluated. Estimates of how much CO_2 has been taken up in STMW over the last 2 decades are made. This is viewed in context with rate of equilibration of the ocean with anthropogenic CO_2 increase in the atmosphere, observed increases in the rates of phytoplankton primary production, and vertical export of sinking organic carbon in the North Atlantic sub-tropical 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 is 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 about 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 approximately 75 to 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 annual fluctuations at 1.4 Svy, respectively. The latter rate implies that the residence time of STMW is 50 yr, but recent studies indicate that approximately 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 increase winter storm frequency and shift the Gulf Stream northward (Hurrell, 1995; Hurrell et al., 2001; Marshall et al., 2001) with a lag of about 1 to 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 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., 1996a, b, 2012; Bates, 2001). DIC is defined as (Dickson et al., 2007):

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

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

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

where $[HCO_3^-], [CO_3^{2-}]$, and $[B(OH)_4^-]$ 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, but the sampling frequency increased to 14–15 times a year over the last 15 years. The time-series of DIC in STMW is not weighted to spring conditions, unlike surface observations where seasonality exerts significant influence on trends in seawater carbonate chemistry (Bates et al., 2012).

2.3 Sampling methods

Samples from the BATS site were collected into 500 ml Pyrex bottles, poisoned with $HgCl_2$, sealed with ground glass stoppers and subsequently analyzed at BIOS (Bates et al., 1996a; Bates, 2007). Since the early 2000s, 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., 1996a; Bates, 2007). During the first two years of sampling (1988–1990), DIC samples from BATS cruises 1 to 21 were analyzed at WHOI, and thereafter at BIOS. Each day of analysis, DIC was calibrated with known volumes of pure CO_2 gas, and certified reference materials (CRMs; 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., 1996b). In the 1990s, 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 2000s. In both systems, at least 15–20 titration points past the carbonic acid end point were determined for each sample, and TA was then computed using non-linear least squares methods (Dickson et al., 2007). Surface water from Sargasso Sea was typically used to condition the titrator while CRMs were routinely used. Analytical precision for both DIC and TA at BIOS was typically < 0.2 % for more than 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, but it was computed from salinity with an error of 2.8 µmoles kg^{-1} (Bates et al., 1996b; TA $= -47.155 + 66.576 \times S$).

2.6 Seawater carbonate chemistry computations

The complete seawater carbonic acid system (i.e. CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}, and H^+) can be calculated from a combination of two carbonate system parameters (i.e. DIC, TA, pCO$_2$ and/or pH) and temperature and salinity. Seawater pCO$_2$, pH, $[CO_3^{2-}]$, mineral saturation states for calcite ($\Omega_{\mathrm{calcite}}$) and aragonite ($\Omega_{\mathrm{aragonite}}$), 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). The carbonic acid dissociation constants of Mehrbach et al. (1973) as refit by Dickson and Millero (1987) was used for the computation, as well as dissociation constants for HSO_4^- (Dickson, 1990). Here, pCO$_2$ 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. 2; Table 1). A density criterion (i.e. 26.4 σ_Θ isopycnal surface) can also be used to 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., 2012).

2.7 Trend analysis and statistics

Trend analysis was performed with observed data for 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 (January, February, March) 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. Mixed layer depth (MLD) was computed from the depth at which temperature was less than 0.5 °C cooler than surface temperatures.

# 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$^{\mathrm{STMW}}$) and pCO$_2$, has significantly changed while temperature, salinity and total alkalinity did not change significantly over time (Fig. 2a; Table 1). Short-term changes (Bates et al., 1996b) and longer term trends in total alkalinity have been observed in surface waters but not at depth in the STMW. For example,

Table 1. Long-term trends (1988–2011) of STMW hydrography and seawater carbonate chemistry with regression statistics (slope and error, n, r^2 and p-value). This table includes trend analyses of STMW including temperature, salinity, seawater carbonate chemistry (i.e. DIC, nDIC, TA, nTA, atmospheric pCO$_2$ (pCO$_2^{\mathrm{atm}}$), calculated seawater pCO$_2$ (pCO$_2^{\mathrm{sea}}$) and Revelle factor (β) anomalies), and indicators of seawater carbonate chemistry changes (i.e. pH, [CO$_3^{2-}$], and mineral saturation states of calcite ($\Omega_{\mathrm{calcite}}$) and aragonite ($\Omega_{\mathrm{aragonite}}$)) from the BATS (31°40′ 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	$18.10 \pm 0.17\,°C$	-0.26	$-0.011 \pm 0.002\,°C\,yr^{-1}$	214	0.14	< 0.01
Salinity	Sep 1988– Jul 2011	36.540 ± 0.035	0.015	$0.0006 \pm 0.0004\,yr^{-1}$	214	0.01	0.13
Seawater carbonate chemistry							
DIC	Sep 1988–Jul 2011	$2098.09 \pm 11.1\,\mu mol\,kg^{-1}$	$+34.6$	$+1.51 \pm 0.08\,\mu mol\,kg^{-1}\,yr^{-1}$	209	0.63	< 0.01
DIC	Sep 1988–May 2010	$2098.06 \pm 11.4\,\mu mol\,kg^{-1}$	$+40.0$	$+1.74 \pm 0.08\,\mu mol\,kg^{-1}\,yr^{-1}$	195	0.73	< 0.01
nDIC	Sep 1988–Jul 2011	$2101.6 \pm 11.5\,\mu mol\,kg^{-1}$	$+33.6$	$+1.46 \pm 0.09\,\mu mol\,kg^{-1}\,yr^{-1}$	209	0.55	< 0.01
TA	Sep 1988–Jul 2011	$2387.4 \pm 5.3\,\mu mol\,kg^{-1}$	$+3.6$	$+0.15 \pm 0.06\,\mu mol\,kg^{-1}\,yr^{-1}$	208	0.03	0.02
nTA	Sep 1988–Jul 2011	$2391.2 \pm 4.9\,\mu mol\,kg^{-1}$	$+2.4$	$+0.11 \pm 0.06\,\mu mol\,kg^{-1}\,yr^{-1}$	208	0.02	0.07
pCO$_2^{\mathrm{sea}}$	Sep 1988–Jul 2011	$354.4 \pm 18.5\,\mu atm$	$+48.9$	$+2.13 \pm 0.16\,\mu atm\,yr^{-1}$	208	0.45	< 0.01
Revelle (β)	Sep 1988–Jul 2011	10.07 ± 0.22	$+0.58$	$+0.025 \pm 0.002\,yr^{-1}$	208	0.44	< 0.01
Ocean acidification indicators							
pH	Sep 1988–Jul 2011	8.078 ± 0.020	-0.053	$-0.0022 \pm 0.0002\,yr^{-1}$	208	0.44	< 0.01
CO$_3^{2-}$	Sep 1988–Jul 2011	$204.68 \pm 7.9\,\mu mol\,kg^{-1}$	-20.0	$-0.87 \pm 0.07\,\mu mol\,kg^{-1}\,yr^{-1}$	208	0.41	< 0.01
$\Omega_{\mathrm{calcite}}$	Sep 1988–Jul 2011	2.99 ± 0.13	-0.33	$-0.022 \pm 0.0019\,yr^{-1}$	208	0.40	< 0.01
$\Omega_{\mathrm{aragonite}}$	Sep 1988–Jul 2011	4.59 ± 0.20	-0.51	$-0.014 \pm 0.0012\,yr^{-1}$	208	0.40	< 0.01

Table 2. Long-term trends of STMW hydrography and seawater carbonate chemistry with regression statistics (slope and error, n, r^2 and p-value) separated into time-periods (1988–2011; 1988–2000; 2001–2011).

Parameter	Period	Slope and std error	n	r^2	p-value
1988–2011					
Temperature	Sep 1988–Jul 2011	$-0.011 \pm 0.002\,°C\,yr^{-1}$	214	0.14	<0.01
Salinity	Sep 1988–Jul 2011	$+0.0064 \pm 0.0004\,yr^{-1}$	212	0.01	0.13
Dissolved oxygen	Sep 1988–Mar 2009	$-0.15 \pm 0.07\,\mu mol\,kg^{-1}\,yr^{-1}$	227	0.02	0.04
Nitrate	Sep 1988–Mar 2009	$+0.01 \pm 0.01\,\mu mol\,kg^{-1}\,yr^{-1}$	219	0.01	0.26
DIC	Sep 1988–Jul 2011	$+1.51 \pm 0.08\,\mu mol\,kg^{-1}\,yr^{-1}$	209	0.63	<0.01
DIC	Sep 1988–Jul 2010	$+1.74 \pm 0.08\,\mu mol\,kg^{-1}\,yr^{-1}$	196	0.73	<0.01
1988–2001					
Temperature	Sep 1988–Jul 2001	$-0.019 \pm 0.005\,°C\,yr^{-1}$	87	0.17	<0.01
Salinity	Sep 1988–Jul 2001	$-0.0014 \pm 0.0008\,yr^{-1}$	86	0.32	<0.01
Dissolved oxygen	Sep 1988–Jul 2001	$-0.55 \pm 0.14\,\mu mol\,kg^{-1}\,yr^{-1}$	144	0.10	<0.01
Nitrate	Sep 1988–Jul 2001	$+0.03 \pm 0.02\,\mu mol\,kg^{-1}\,yr^{-1}$	139	0.02	0.14
DIC	Sep 1988–Jul 2001	$+2.06 \pm 0.21\,\mu mol\,kg^{-1}\,yr^{-1}$	85	0.53	<0.01
2001–2011					
Temperature	Jul 2001–Jul 2011	$+0.007 \pm 0.005\,°C\,yr^{-1}$	127	0.01	0.23
Salinity	Jul 2001–Mar 2009	$+0.006 \pm 0.001\,yr^{-1}$	127	0.17	<0.01
Dissolved oxygen	Jul 2001–Mar 2009	$+1.29 \pm 0.27\,\mu mol\,kg^{-1}\,yr^{-1}$	84	0.21	<0.01
Nitrate	Jul 2001–Jul 2011	$-0.05 \pm 0.04\,\mu mol\,kg^{-1}\,yr^{-1}$	78	0.02	0.28
DIC	Jul 2001–Jul 2011	$+0.56 \pm 0.21\,\mu mol\,kg^{-1}\,yr^{-1}$	124	0.06	<0.01
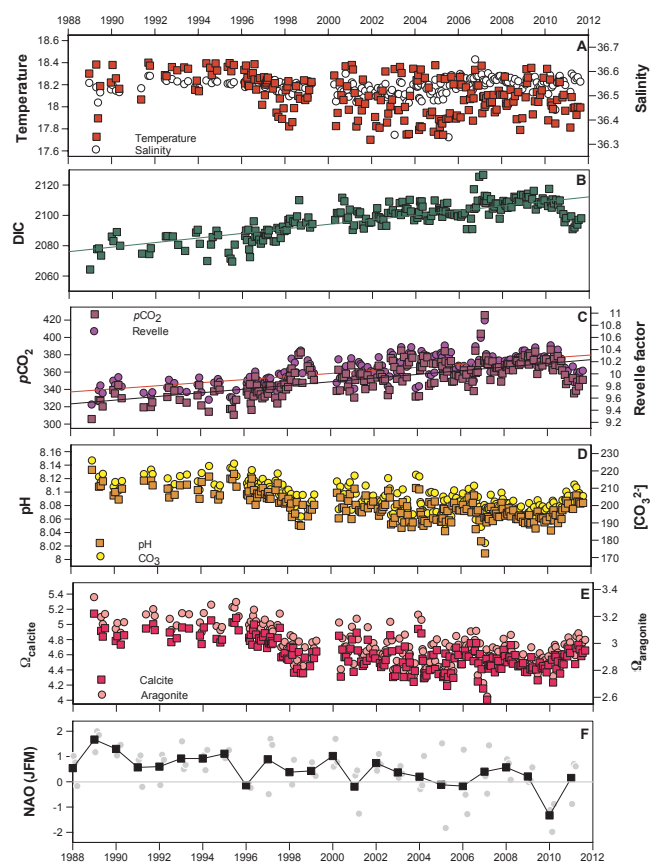
Fig. 2. Long-term observations and trends of STMW hydrography, seawater carbonate chemistry and ocean acidification indicators from 1988 to 2011 at the BATS (Bermuda Atlantic Time-series Study; 31°40′ N, 64°10′ W) site located near Bermuda in the NW Atlantic Ocean. Slopes and statistics of regressions are listed in Table 1. **(A)** Sea surface temperature (°C; black symbol) and salinity (red symbol). **(B)** Surface dissolved inorganic carbon (DIC, μmol kg^{-1}, green symbol). **(C)** Seawater pCO$_2$ (μatm; purple symbol) and Revelle factor (β) (fuchsia symbol). **(D)** Surface seawater pH (orange symbol) and [CO$_3^{2-}$] (μmol kg^{-1}, yellow symbol). **(E)** Surface saturation state of calcite (Ω_{calcite}) (pink symbol) and aragonite ($\Omega_{\text{aragonite}}$) (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).

the long-term trends of DIC (i.e. $\delta\text{DIC}^{\text{STMW}}/\delta t_{1988-2011}$) and salinity normalized nDIC in STMW exhibit increases of $+1.51 \pm 0.08$ and $+1.46 \pm 0.06\,\mu\text{mol kg}^{-1}\,\text{yr}^{-1}$, respectively. This constitutes a 40 μmoles kg^{-1} change in DIC$^{\text{STMW}}$ since 1988 (Fig. 2b). Contemporaneously, the computed seawater pCO$_2$ 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. 2c), which is higher than the increase in atmospheric pCO$_2$ observed over the same period ($+1.72 \pm 0.01\,\mu\text{atm yr}^{-1}$; Bates et al., 2012). The Revelle factor (β), which indicates the capacity of seawater to absorb CO$_2$, has also increased at a rate of $+0.025 \pm 0.002\,\text{yr}^{-1}$

Table 3. Correlation table of selected mean winter (JFM) variables. Within each cell, the first row is the correlation coefficient and second row is the 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	DIC$^{\text{surface}}$	DIC$^{\text{STMW}}$	DIC$^{\text{STMW-surf}}$
NAO	**−0.34**	**−0.66**	**−0.30**	**0.45**
	< 0.01	**< 0.01**	**< 0.01**	**< 0.01**
MLD		0.23	–	**−0.39**
		0.02		**<0.01**
DIC$^{\text{surface}}$			**0.63**	**−0.32**
			< 0.01	**< 0.01**
DIC$^{\text{STMW}}$				–

(Fig. 2c). 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. (2007).

## 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. 2d; Table 1). This rate of pH decrease is higher than that for surface waters at BATS ($-0.0017 \pm 0.0001\,\text{yr}^{-1}$) as well as off Hawaii and the Canary Islands (-0.0014 to $-0.0019\,\text{yr}^{-1}$) (Dore et al., 2009; González-Dávila et al., 2010). This change in pH of the STMW represents a 12 % increase in hydrogen ions (H$^+$) since 1988. Other indicators of ocean acidification at BATS such as [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. 2d and 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$^{\text{STMW}}$ 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$^{\text{surface}}$), expressed here as $\delta\text{DIC}^{\text{surface}}/\delta t_{1988-2011}$, increased at a rate of $+1.08 \pm 0.05\,\mu\text{mol kg}^{-1}\,\text{yr}^{-1}$ (Bates et al., 2012; Fig. 3a). 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. $\delta\text{DIC}^{\text{anthropogenic}}/\delta t_{1988-2011}$) is calculated using mean hydrographic, DIC and TA values for STMW
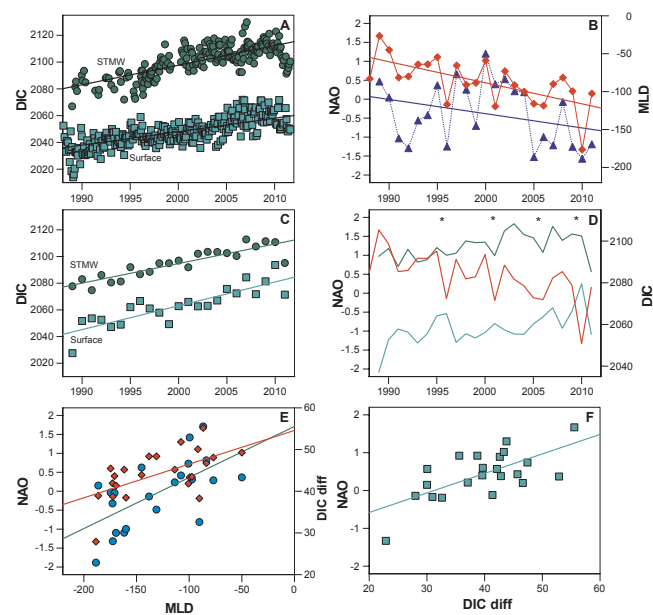
Fig. 3. Time-series and relationships between DIC, mixed layer depths (MLD) and NAO index from 1988 to 2011 at the BATS (Bermuda Atlantic Time-series Study; 31°40′ N, 64°10′ W) site located near Bermuda in the NW Atlantic Ocean. Slopes and statistics of regressions are listed in Table 1. **(A)** Time-series of DIC in surface ($DIC^{surface}$; μmol kg^{-1}; light green symbols) and STMW (DIC^{STMW}; μmol kg^{-1}; dark green symbols) 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 symbols and line) and STMW (μmol kg^{-1}; dark green symbols and line) waters. **(D)** Time series of winter (JFM) DIC in surface (μmol kg^{-1}; light green line) and STMW (μmol kg^{-1}; dark green line) waters and 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)**. Scatterplot of winter (JFM) NAO (red symbols) and DIC difference between STMW and surface (μmol kg^{-1}; blue symbols) against mixed layer depth (m). **(F)**. Scatterplot of winter (JFM) NAO against DIC difference between surface and STMW (μmol kg^{-1}; green symbols).

with the observed atmospheric pCO$_2$ increases (due to anthropogenic CO$_2$) over the same time 1988–2011 period (i.e. $+1.72 \pm 0.01$ ppm yr^{-1}). The trend for $\delta DIC^{anthropogenic}/\delta t_{1988-2011}$ is $+1.06$ μmol 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. 3a). Once STMW is formed during winter, isopycnal mixing and subduction adds to the existing pool of STMW found between surface/seasonal thermocline waters and the permanent thermocline in the subtropical gyre (approximately

250–450 m deep). STMW is ultimately subducted to deeper depths with time (Behringer and Stommel, 1980; Spall, 1992; Fig. 4a). Using the $\delta DIC^{STMW}/\delta t_{1988-2011}$ trend of $+1.51 \pm 0.08$ μmol kg^{-1} yr^{-1}, and given that the volume of STMW in the North Atlantic subtropical gyre is about 75 Svy (Forget et al., 2011), it is estimated that the STMW has accumulated 0.985 ± 0.018 Pg C since 1988 (Fig. 4b). The error in the amount of CO$_2$ taken up into STMW relates to that propagated from the trend error. However, the volume of STMW 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$_2$. The sink of CO$_2$ into the STMW, averaged annually for the period 1988–2011 (0.042 Pg C yr^{-1}), is approximately 20 % of the CO$_2$ uptake in the North Atlantic Ocean in the zone between 14° and 50° N (0.220 Pg C yr^{-1}; Takahashi et al., 2009). 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 its attribution

The change in DIC content of the STMW (i.e. $\delta DIC^{STMW}/t_{1988-2011}$) 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. $\delta DIC^{anthropogenic}/t_{1988-2011}$); (2) physical changes at the outcrop site of STMW winter formation encompasses the summed changes due to variability 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 $\delta DIC^{outcrop}/t_{1988-2011}$), and; (3) changes imparted by biological processes, including respiration/remineralization, acting on STMW during its transit through the subtropical gyre (here termed $\delta DIC^{biology}/t_{1988-2011}$). Thus:

$$\delta DIC^{STMW}/t_{1988-2011} =$$
$$\delta DIC^{anthropogenic}/t_{1988-2011} + \delta DIC^{biology}/t_{1988-2011}$$
$$+ \delta DIC^{outcrop}/t_{1988-2011} \qquad (3)$$

The $\delta DIC^{anthropogenic}/t_{1988-2011}$ term (Eq. 3) was estimated earlier at 1.06 μmol kg^{-1} yr^{-1}, with the implication that the uptake of anthropogenic CO$_2$ constitutes approximately 70 % of the observed increase in DIC^{STMW}. The rate of increase in atmospheric CO$_2$ at Bermuda has not changed significantly over the past couple of decades (Bates, 2007; Bates et al., 2012), and thus it is assumed that the equilibration rate of anthropogenic CO$_2$ with surface waters
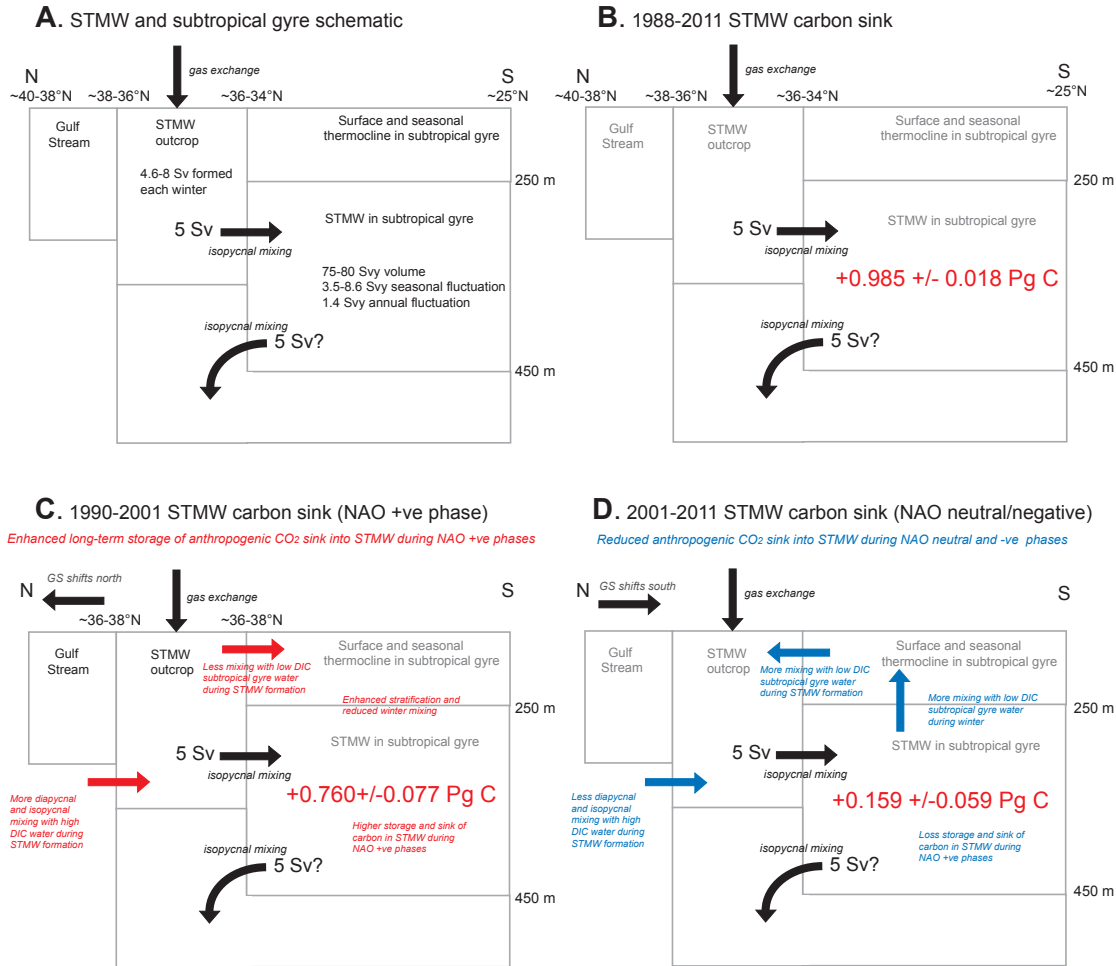
Fig. 4. Schematic of water masses and CO_2 sink estimates in STMW for different time-periods from 1988–2011. **(A)** Schematic of North Atlantic subtropical gyre showing Gulf Stream, STMW outcrop, surface and seasonal thermocline layer (not to scale). Range of winter STMW formation rates (Sv; Speer and 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.

(i.e. $\delta DIC^{anthropogenic}/t_{1988-2011}$) has also not changed significantly. It is estimated that the uptake of anthropogenic CO_2 into STMW since 1988 was 0.692 ± 0.018 Pg C or approximately $70 \pm 1.8\%$ of the total STMW CO_2 sink (0.985 ± 0.018 Pg C; Fig. 3b). The remaining terms in Eq. (1) comprise the remaining 30 % of the observed changes.

Term two of Eq. (3) (i.e. $\delta DIC^{biology}/t_{1988-2011}$) can be approximated by examining changes in organic carbon export and remineralization and/or biogeochemical properties (e.g. dissolved oxygen and inorganic nutrients). Term three of Eq. (3) (i.e. $\delta DIC^{outcrop}/t_{1988-2011}$) is difficult to determine directly due to the lack of sustained observations at the STMW site of formation, but some field (Andersson et al., 2012) and model studies (Levine et al., 2011) provide some inferences on this term. Thus, Eq. (3) can be solved by

difference, with the caveat that there are many uncertainties underlying this approach:

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

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 increased by 71 % ($+0.12$ mmol C m^{-2} d^{-1} yr^{-1}). However, at 300 m, no long-term change was 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 DIC^{STMW}. Here, the increase in POC flux (i.e. $+0.12$ mmol C m^{-2} d^{-1} yr^{-1}) observed at BATS is converted to DIC change over time, assuming a 150 m thickness of STMW at BATS. The increase in DIC due to enhanced remineralization is estimated at $+0.29 \pm 0.05$ µmol kg^{-1} yr^{-1} (i.e. $\delta DIC^{biology}/t_{1988-2011}$), or approximately 19 ± 3.2 % of $\delta DIC^{STMW}/t_{1988-2011}$. Thus, it is estimated that the enhanced remineralization within STMW since 1988 has contributed 0.187 ± 0.036 Pg C of the total STMW CO_2 sink (0.985 ± 0.018 Pg C; Fig. 4b). Dissolved oxygen (DO) and nitrate contents also changed 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 DIC^{STMW} due to changes at the STMW outcrop (i.e. term three in Eq. (3), $\delta DIC^{outcrop}/t_{1988-2011}$) contributes the remaining 11 % to $\delta DIC^{STMW}/t_{1988-2011}$ (i.e. $\delta DIC^{outcrop}/t_{1988-2011} = 0.16 = 1.51 - [1.06 + 0.29]$), or approximately 0.099 Pg C.

4.3 A multi-decadal change in the STMW CO_2 sink and its relation to NAO variability

A closer inspection of the trends in DIC^{STMW} reveals considerable difference between the 1990s and 2000s. The trend for DIC^{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) compared to that observed for the 2001 to 2011 period at 0.56 ± 0.21 µmol kg^{-1} yr^{-1} (Fig. 3a; 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. 3b). Contemporaneous with the change in winter NAO, the mean winter mixed layer depth (MLD) has also deepened significantly from 110 to 150 m (Fig. 3b). Notably, a significant decline in DIC^{STMW} was observed in 2011 that coincides with a strongly negative NAO (JFM) winter phase (Figs. 2f and 3b). If data from 2011 is not included in the trend analysis, the $\delta DIC^{STMW}/t_{1988-2010}$ was significantly higher at 1.74 ± 0.08 µmol kg^{-1} yr^{-1} (see Table 1).

If winter DIC^{STMW} and surface DIC are compared, the trends are convergent (Fig. 3c) rather than divergent (Fig. 3a). While winter DIC^{STMW} trends are similar to those determined for all annual data ($+1.46$ µmol kg^{-1} yr^{-1}), winter $DIC^{surface}$ 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 $DIC^{surface}$ with all monthly data; Table 1). As the winter NAO
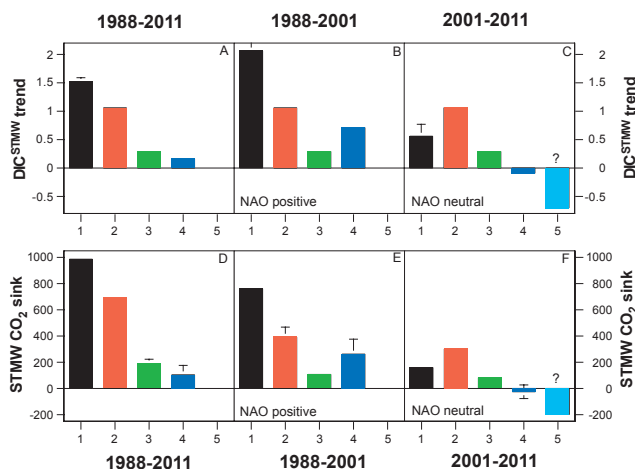
Fig. 5. Trends in DIC^{STMW} (**A–C**; µmol kg^{-1} yr^{-1}) and estimates of CO_2 sink into STMW (**D–F**; Pg C) for the 1988–2011, 1988–2001, and 2001–2011 periods. The trend and CO_2 sink in STMW is given in row 1 in each panel ($\delta DIC^{STMW}/t$; black). In each panel, row 2 denotes potential uptake due to anthropogenic CO_2 (C_{ant} or $\delta DIC^{anthropogenic}/t$; red) row 3 denotes increase due to remineralization of organic carbon in STMW to CO_2 (i.e. $\delta DIC^{biology}/t$; green); row 4 denotes increase (decrease) at the STMW outcrop (i.e. $\delta DIC^{outcrop}/t$; blue); and row 5 denotes the potential change due to mixing of STMW with surface/seasonal thermocline waters (i.e. $dDIC^{mixing}/t$).

has declined to neutral status over the last decade, winter $DIC^{surface}$ has increased as mixed layers have deepened (with standout high values during NAO negative winters; Fig. 3d). In contrast, winter DIC^{STMW} appears to lag NAO by up to 1–2 yr (Levine et al., 2011), with the lag observed at BATS greater during NAO positive phases. NAO, mixed layer depth and the difference between surface and STMW DIC also appear well correlated with each other (Fig. 3e and f; r^2 values of 0.25–0.45; Table 3).

In the 1990s, contemporaneous with DIC^{STMW} increase of 2.06 ± 0.26 µmol kg^{-1} yr^{-1} (Bates et al., 2002, and recalculated here; Fig. 5; Table 2), DO decreased and nitrate increased at -0.55 ± 0.14 and $+0.03 \pm 0.02$ 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 ± 0.077 Pg C (Figs. 4c and 5d), or approximately 77 ± 10 % of the 1988–2011 increase of DIC^{STMW}. Thus, in the 1990s, the sink of CO_2 into the STMW was 27 % of the long-term CO_2 uptake in the North Atlantic Ocean in the zone between 14° and 50° N (i.e. 0.220 Pg C yr^{-1}; Takahashi et al., 2009). In contrast, the $\delta DIC^{STMW}/t_{2001-2011}$ trend was only $+0.56$ µmol kg^{-1} yr^{-1} for the 2000s (Fig. 5c). The increase in DIC^{STMW} is much reduced compared to the 1990s, as is the estimate of the CO_2 sink into STMW of 0.159 ± 0.059 Pg C (Figs. 4d and 5e), or only about 7 % of the North Atlantic Ocean CO_2 sink between 14° and 50° N (Takahashi et al., 2009).

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 move northward in response to NAO. During an NAO neutral to negative phase, the Gulf Stream and STMW outcrop move south with less CO_2 taken up by STMW. Levine et al. (2011) show a STMW CO_2 uptake variability of $0.100\,\mathrm{Pg\,C\,yr^{-1}}$, depending on the state of the NAO.

In the 1990s, trend analyses 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 $0.391 \pm 0.077\,\mathrm{Pg\,C}$ or approximately $51 \pm 10\,\%$ of the total $0.760\,\mathrm{Pg\,C}$ sink in the 1990s (Fig. 3c). Furthermore, it is estimated that enhanced remineralization of sinking organic carbon in STMW (Lomas et al., 2010) may have contributed $0.109 \pm 0.019\,\mathrm{Pg\,C}$ or $14 \pm 2\,\%$ to the total sink. The remainder (i.e. $0.262\,\mathrm{Pg\,C}$ 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., 2012) and less mixing with relatively low DIC subtropical gyre waters during winter STMW formation potentially contribute to higher DIC input into the STMW (Fig. 5e).

In the 2000s, the observed uptake was much reduced compared to the 1990s at $0.159\,\mathrm{Pg\,C}$ (Fig. 5f). Indeed, this is much less than predicted from equilibration with anthropogenic CO_2 in the atmosphere (i.e. $0.301 \pm 0.030\,\mathrm{Pg\,C}$). Furthermore, an additional $0.082 \pm 0.014\,\mathrm{Pg\,C}$ may have accumulated in STMW during this period 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 $-0.025\,\mathrm{Pg\,C}$; Fig. 5f) and loss from STMW due to mixing with surface waters/seasonal thermocline and/or enhanced diapycnal mixing with waters deeper than STMW. Given that the winter $DIC^{surface}$ increases by $0.70\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$, we estimate that STMW may have lost $0.198\,\mathrm{Pg\,C}$ (Fig. 5f) 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 DIC^{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 and short-term sinks of CO_2 into STMW. During NAO positive phases, the CO_2 sink into STMW appears to be long-term (i.e. more than 10 yr), whilst it is short-term (i.e. less than 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 (Schuster and Watson, 2007; Watson et al., 2009). 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 from 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; Thomas et al., 2008; Gruber, 2009; Ullman et al., 2009; McKinley et al., 2011) that natural climate variability such as NAO imparts a significant influence on CO_2 sinks in the North Atlantic Ocean.

5 Conclusions

The observations at BATS thus indicate that the phase of the NAO is important for determining the long-term and short-term sinks of CO_2 into STMW. During NAO positive phases, the CO_2 sink into STMW appears to be long-term (i.e. more than 10 yr), whilst it is short-term (i.e. less than 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 from 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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