**Biogeosciences
Discussions**

Detecting anthropogenic carbon dioxide uptake and ocean acidification in the North Atlantic Ocean

N. R. Bates[1], M. H. P. Best[1], K. Neely[1], R. Garley[1], A. G. Dickson[2], and R. J. Johnson[1]

[1]Bermuda Institute of Ocean Sciences, Ferry Reach, Bermuda
[2]Scripps Institution of Oceanography, University of California San Diego, La Jolla, California, USA

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

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Abstract

Fossil fuel use, cement manufacture and land-use changes are the primary sources of anthropogenic carbon dioxide (CO_2) to the atmosphere, with the ocean absorbing 30 %. Ocean uptake and chemical equilibration of anthropogenic CO_2 with seawater results in a gradual reduction in seawater pH and saturation states (Ω) for calcium carbonate ($CaCO_3$) minerals in a process termed ocean acidification. Assessing the present and future impact of ocean acidification on marine ecosystems requires detection of the multi-decadal rate of change across ocean basins and at ocean time-series sites. Here, we show the longest continuous record of ocean CO_2 changes and ocean acidification in the North Atlantic subtropical gyre near Bermuda from 1983–2011. Dissolved inorganic carbon (DIC) and partial pressure of CO_2 (pCO_2) increased in surface seawater by $\sim 40\,\mu\mathrm{mol\,kg^{-1}}$ and $\sim 50\,\mu\mathrm{atm}$ ($\sim 20\,\%$), respectively. Increasing Revelle factor (β) values imply that the capacity of North Atlantic surface waters to absorb CO_2 has also diminished. As indicators of ocean acidification, seawater pH decreased by ~ 0.05 ($0.0017\,\mathrm{yr^{-1}}$) and Ω values by ~ 7–8 %. Such data provide critically needed multi-decadal information for assessing the North Atlantic Ocean CO_2 sink and the pH changes that determine marine ecosystem responses to ocean acidification.

1 Introduction

The emissions of anthropogenic CO_2 to the atmosphere due to fossil fuel use, cement manufacture and land-use changes (Houghton, 2008) have increased rapidly over the last decade (Friedlingstein et al., 2010). While anthropogenic CO_2 accumulates in the atmosphere, it is also taken up by the terrestrial biosphere and oceans. The annual global ocean uptake is estimated at ~ 1.4 to $2.5\,\mathrm{Pg\,C\,yr^{-1}}$ (e.g., Takahashi et al., 2002; Manning and Keeling, 2006; Takahashi et al., 2009; McKinley et al., 2011; $\mathrm{Pg} = 10^{15}\,\mathrm{g}$), with annual rates of CO_2 uptake increasing with time (Le Quéré et al., 2009). The cumulative total global ocean uptake of anthropogenic CO_2 since pre-industrial time

is estimated at ~ 120–140 Pg C (Sabine et al., 2004; Khatiwala et al., 2009). Ocean uptake of anthropogenic CO_2 and seawater chemistry changes such as reduction in seawater pH and saturation states for calcium carbonate ($CaCO_3$) minerals such as calcite ($\Omega_{calcite}$) and aragonite ($\Omega_{aragonite}$) is termed ocean acidification (e.g., Calderia and Wickett, 2003, 2005; Orr et al., 2005; Doney et al., 2009; Feely et al., 2009), and has likely problematic consequences for marine organisms and ecosystems that are, as yet, poorly understood.

Assessments of rates of ocean CO_2 uptake over multi-decadal timeperiods, changes in the capacity of the ocean to absorb CO_2 and ocean acidification impacts are important for predicting future climate change and marine ecosystem responses (e.g., Fabry et al., 2009). These ocean carbon cycle and ocean acidification data provide critically needed observational tests of global coupled ocean-atmosphere models, and allow attribution of changes to both anthropogenic and natural causes (e.g., Le Quéré et al., 2010). Repeat hydrographic sections provide a means of quantifying basinwide ocean uptake of anthropogenic CO_2 (e.g., Friis et al., 2005; Brown et al., 2010; Wanninkhof et al., 2010). Alternatively, higher frequency observations of the changes in seawater chemistry due to uptake of anthropogenic CO_2 have been collected at a few ocean time-series near various islands, including near Bermuda (Bates, 2001, 2007; Bates and Peters, 2007), Hawaii (e.g., Dore et al., 2003; Brix et al., 2004; Dore et al., 2009), the Canary Islands (Santana-Casiano et al., 2007; Gonzalez-Davila et al., 2010) and Iceland (Olafsson et al., 2010). Here, we examine direct observations of the seawater carbonate chemistry changes resulting from ocean uptake of CO_2 over the last 30 yr in the subtropical gyre of the North Atlantic Ocean near Bermuda from 1983–2011. Seawater samples were collected from two time-series sites near Bermuda (i.e., Bermuda Atlantic Time-series Study; BATS; 31°40′ N, 64°10′ W (Michaels and Knap, 1998; Steinberg et al., 2001); and Hydrostation S, 32°10′ N, 64°30′ W; Keeling, 1993). Samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were analyzed (Bates et al., 1996a; Dickson et al., 2007), multi-decadal checks on accuracy of data are made and computations of other components of the seawater carbonate system computed

(Robbins et al., 2010). These data provide directly observed indicators of ocean acidi-
fication and include pH, carbonate ion concentration ($[CO_3^{2-}]$) and the saturation state
(Ω) for calcium carbonate ($CaCO_3$) minerals. Finally, these data are combined with
a few earlier measurements in the North Atlantic Ocean (from the Geochemical Ocean
5 Section Study, GEOSECS (Kroopnick et al., 1972) and Transient Tracers in the Ocean,
TTO projects; Brewer et al., 1985) extending these trends over the past 40 years.

2 Methods and materials

2.1 Seawater carbonate chemistry sampling at BATS

A time-series of observations of seawater carbonate chemistry observations in the up-
10 per ocean have been collected in the subtropical gyre of the North Atlantic Ocean near
Bermuda since 1983 at the Bermuda Atlantic Time-series Study (BATS) and Hydro-
station S sites (Bates, 2007; Bates and Peters, 2007). The combined ocean time-
series data represent monthly water column sampling for DIC and total alkalinity (TA)
at BATS, with analysis of samples at the Bermuda Institute of Ocean Sciences (BIOS)
15 using highly precise and accurate coulometric and potentiometric techniques, respec-
tively (Bates et al., 1996a, b; Bates, 2001). Addtiional surface samples were collected
at Hydrostation S and analyzed for DIC and TA using manometric and potentiometric
methods, respectively, at Scripps Institution of Oceanography (Keeling, 1993). Here,
DIC is defined as (Dickson et al., 2007):

20 $$DIC = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \tag{1}$$

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

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

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where $[HCO_3^-] + 2[CO_3^{2-}] + B(OH)_4^-$ are the principal components of seawater TA (Dickson et al., 2007).

2.2 Sampling frequency at BATS

The sampling frequency of the combined dataset from Hydrostation S and BATS was not uniform in time. In the 1980s, samples were collected 9–12 times a year, while since 1992, sampling increased to 14–15 times a year (Fig. 1). The increase in sampling since the middle 1990s was due to supplemental BATS bloom cruises (1 to 4 in number) conducted during the January to April period in addition to BATS core cruises. The increase in sampling frequency over time weights the time-series to springtime which has to be addressed when determining non-seasonally aliased trends.

2.3 Sampling methods

At Hydrostation S, samples were collected into 500 ml Pyrex bottles, poisoned with $HgCl_2$, sealed with ground glass stoppers and then shipped to Scripps Institution of Oceanography (SIO) for analysis (Keeling, 1993; Brix et al., 2004). Storage time for samples before analysis ranged from a few months to several years. Similar sampling protocols were established at BIOS for sampling at the BATS (Bates et al., 1996a,b; Bates, 2001) but in the early 2000s, smaller Pyrex bottles ($\sim$ 350 ml) were used. Samples were typically analyzed within a few months of collection.

2.4 Analytical methods

Hydrostation S samples were analyzed for DIC at SIO using manometric methods (Keeling, 1993) and potentiometric titration methods were used for determination of TA (Keeling, 1993). Analytical precision for both DIC and TA at SIO was typically $< 0.2\%$. At BIOS, DIC was determined using coulometric methods with a SOMMA system (Johnson et al., 1993; Bates et al., 1996a; Dickson et al., 2007). During the

first two years of sampling, DIC samples were analyzed at WHOI (e.g., BATS cruise 1 to 21), and subsequently at BIOS. DIC measurements were calibrated with known volumes of pure CO_2 gas while 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 TA at BIOS (Bates et al., 1996b). At the beginning of the 1990's, a manual alkalinity titrator was used for determination of TA. This was replaced by an automated VINDTA 2S (Versatile Instrument for the Determination of Titration Alkalinity) in the early 2000s. For both manual and automated TA systems, 15–20 titration points past the carbonic acid end point were determined for each sample, with TA computed from these titration data using non-linear least squares methods (Dickson et al., 2007). Surface samples of Sargasso Sea water was also analyzed each day prior to sample analyses and CRM's were used routinely to calibrate the TA measurements. Analytical precision for both DIC and TA at BIOS was typically $< 0.2\%$ for within bottle and between bottle replicate analyses of more than 2000 samples.

2.5 Comparison of replicate samples analyzed at BIOS and SIO

From 1989–2010, selected replicate surface DIC and TA samples at BATS were analyzed *independently* at BIOS and Scripps using different analytical techniques. Replicate surface and 10 m depth samples were collected on BATS cruises over a period of 20 yr from 1990 to 2010. Comparison of DIC samples analyzed independently at BIOS and SIO indicate that the mean difference was $1.24 \pm 3.35 \, \mu\text{mol kg}^{-1}$ (Fig. 2; SIO DIC values higher than BIOS values) with a sample number of 373. Comparison of TA samples analyzed independently at BIOS and SIO indicate that the mean difference was $0.33 \pm 5.02 \, \mu\text{mol kg}^{-1}$ (SIO TA values slightly higher than BIOS values) with a sample number of 290. Thus, over a period of 20 yr, there is no evidence of any systematic analytical biases that would influence the accuracy of data and trends.

2.6 Compilation of a combined BATS/Hydrostation S record

Surface Hydrostation S data from September 1983 to September 1988, and BATS data from October 1988 to present (with exceptions) were combined to produce a continuous time-series. For BATS cruises 22–27, surface DIC data from SIO (Keeling, 1993) was used as water-column samples were not collected for the period July-December 1990. For BATS cruises 21–27 and 30–36, TA samples analyzed at SIO were used (Keeling, 1993). For Hydrostation S cruise 605698101, and BATS cruises 1–3, 4–20, 79A, 90A, 91A, 100A, 101A, 102A, 113A, 114A, 138, 185A, and 186A, TA was calculated from salinity (with an error of $\sim 2.8\,\mu mol\,kg^{-1}$; Bates et al., 1996a). Exclusion of these samples from trend analysis did not change results significantly. The locations of Hydrostation S and BATS are separated in space by $\sim 50\,km$, but analysis of both Hydrostation S and BATS data at SIO suggests that there is no statistical difference between the two locations. Surface data are shown here but no statistical diffference was found if mean DIC and TA were determined for different depth intervals in the mixed layer (using a 0.5 °C temperature criterion to define mixed layer depth).

2.7 Computation of seawater carbonate chemistry

Seawater pCO$_2$, pH, [CO$_3^{2-}$], mineral saturation states for calcite (Ω_{calcite}) and aragonite ($\Omega_{\text{aragonite}}$), and the Revelle factor (β) were computed from DIC, TA, temperature and salinity data using the program CO2calc (Robbins et al., 2010). Carbonic acid dissociation constants (i.e., pK$_1$ and pK$_2$) 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). GEOSECS and Transient Tracers in the Ocean (TTO) DIC, TA, temperature and salinity data were taken from the CDIAC site (http://cidiac.ornl.gov). We used the same dissociation constants to compute surface pCO$_2$, pH and $\Omega_{\text{aragonite}}$ from GEOSECS and Transient Tracers in the Ocean (TTO) DIC, TA, temperature and salinity data. GEOECS and TTO data available through WAVES (Web-Accessible Visualization and Extraction System) that allows access to discrete data that are part of

the Global Ocean Data Analysis Project (GLODAP) and Carbon in the North Atlantic (CARINA) databases.

2.8 Computation of seawater carbonate chemistry

The computation of seawater pCO_2 was compared to direct measurements of pCO_2 from the R/V *Atlantic Explorer* (AE) and Bermuda Testbed Mooring (BTM) from 2005 to 2010 (Fig. 3). During this period, 42 direct comparisons were made. Observed seawater pCO_2 was collected from BIOS ship R/V *Atlantic Explorer* at the BATS site (31°43′ N, 64°10′ W) using a pCO_2 system calibrated with 4 CO_2-in-air standards similar to previous methods used at BIOS (Bates et al., 1998). Seawater pCO_2 measurements were also made using a pCO_2 sensor attached to the Bermuda Testbed Mooring (BTM; 31°41.77′ N, 64°10.52′ W; Dickey et al., 2009, http://cidiac.ornl.gov). This system was calibrated with one CO_2-in-air standards and deployed from 2005 to 2007. Both seawater pCO_2 systems were calibrated with CO_2-in-air standards calibrated at CMDL (NOAA).

At the time of sampling for DIC and TA at the BATS site (i.e., time that Niskin sampler was tripped and filled), mean observed R/V *Atlantic Explorer* and BTM seawater pCO_2 were averaged over 1 h with the mid-point exactly contemporaneous with the time of sampling. Compared to the observed R/V *Atlantic Explorer* and BTM seawater pCO_2 data, computed pCO_2 from DIC and TA was lower by a mean of -4.7 ± 13.6 µatm. However, there were slight differences in sampling temperatures, and thus, R/V *Atlantic Explorer* and BTM seawater pCO_2 data were corrected to the SST's at time of DIC/TA sampling at BATS. The mean difference between temperature corrected seawater pCO_2 computed at BATS, and directly observed from the R/V *Atlantic Explorer* and BTM was small (-3.1 ± 10.8 µatm). No systematic bias in the computation of seawater pCO_2 was apparent.

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2.9 Trend analysis and statistics

Trend analyses of the time-series of surface temperature and salinity, seawater carbonate chemistry (DIC, TA, pCO$_2$, Revelle factor, β) and ocean acidification indicators (pH, [CO$_3^{2-}$], $\Omega_{calcite}$ and $\Omega_{aragonite}$) was conducted. Here, trend analysis of salinity normalized DIC (nDIC) and TA (nTA) data were also made in order to account for local evaporation and precipitation changes. These data were normalized to a salinity of 36.6, as this represents the mean salinity observed at the BATS site (Bates, 2007). Trend analysis was performed with observed data (Table 1) and seasonally detrended data (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 at the 99 % confidence level.

2.10 Seasonal detrending of data

Trends analyses with observed data exhibits seasonal aliasing due to sampling weighting to spring conditions. For example, sea surface temperature (SST) apparently cooled during the 1983–2011 period at a rate of -0.075 decade^{-1}, but, this largely reflects a sampling bias that is weighted to springtime conditions. To account for seasonal weighting, the data were also seasonally detrended. Seasonal detrending of the BATS/Hydrostation S data was accomplished by binning data into appropriate month, with mean values calculated from 2 or more cruises conducted within a representative month each year. This provides a uniform timestep of approximately 1 month (i.e., 365 or 366 days/12) throughout the time-series, thereby removing any potentially seasonal weighting especially to springtime conditions. The mean seasonality of all parameters are shown in Fig. 4. Second, a mean and standard deviation is then determined each month for the 1983–2011 (Fig. 4), and anomalies computed from monthly data minus mean values. Trends and regression statistics for seasonally detrended data are given in Table 2. Removing any potentially seasonal weighting allowed trend analysis of data that had any non-temporal uniformity reduced as much as possible. The caveat to this

approach and other approaches (e.g., using a 12 month harmonic fit to the data) is that energy may be lost or gained from this time-series data.

3   Results

3.1   Seawater carbonate chemistry changes in surface waters

The time-series of surface temperature and salinity, seawater carbonate chemistry (DIC, TA, $p\text{CO}_2$, Revelle factor, β) and ocean acidification indicators (pH, [CO_3^{2-}], Ω_{calcite} and $\Omega_{\text{aragonite}}$) off Bermuda in the North Atlantic Ocean are shown in Fig. 5. However, these data are subject to seasonal weighting due to additonal sampling in springtime and thus, seasonal detrended data are shown in Fig. 6. Trends and regression statistics for seasonally detrended data are given in Table 2.

3.2   Warming and salinity increases in surface waters

There is evidence for warming and increased salinity of surface waters observed in the North Atlantic subtropical gyre near Bermuda. Time series analysis of data at BATS reveal significant long-term trends in the temperature and salinity of the surface ocean increasing at rates of $\sim 0.011 \pm 0.006 \,^{\circ}\text{C yr}^{-1} (\sim 0.11 \,^{\circ}\text{C decade}^{-1})$ and $0.0054 \pm 0.0001 \,\text{yr}^{-1}$, respectively (Table 2; Fig. 6). However, it should be noted that the surface temperature trend is not statistically significant at the 95 % level (p-value > 0.05), but similar temperature trends that are statistically significant have been observed within the upper 400 m at BATS and Hydrostation S over the last 55 yr with temperature and salinity increasing at rates of $\sim 0.01 \,^{\circ}\text{C yr}^{-1}$ and $0.002 \,\text{yr}^{-1}$, respectively (Joyce et al., 1999). Similar long-term changes in surface temperatures have been observed across the subtropical gyre of the North Atlantic Ocean (Grist et al., 2010) indicating a system level change in the marine environment. The observed increase in surface salinity near Bermuda is also evident across the North Atlantic Ocean subtropical gyre (Zhang et al.,

2011), that appears related to coordinated changes in freshwater fluxes and modes of climate variability such as the North Atlantic Oscillation (Hurrell and Deser, 2010).

3.3 Trends in seawater carbonate chemistry of surface waters

Our observations near Bermuda also show multi-decadal changes in seawater carbonate chemistry in response to anthropogenic CO_2 uptake by surface waters. Direct observations of DIC, computed seawater pCO_2 and Revelle factor (β) exhibit significant increases over the last 3 decades (Fig. 6; Table 2). Surface DIC and salinity normalized DIC (i.e., nDIC) have increased by 1.39 ± 0.06 and $1.08 \pm 0.06 \, \mu mol \, kg^{-1} \, yr^{-1}$, respectively, a change of nearly $40 \, \mu mol \, kg^{-1}$, or $\sim 2\%$ from 1983 to 2011. Similar changes were observed previously at BATS (Bates, 2007) and attributed to the uptake of anthropogenic CO_2 from the atmosphere (Gruber et al., 2002; Bates et al., 2002). Similar changes in DIC over shorter timescales have been observed elsewhere off Hawaii (Dore et al., 2003, 2009) and the Canary Islands (Santana-Casiano et al., 2007; Gonzalez-Davila et al., 2010). For example, total alkalinity, TA increased slightly by $0.48 \pm 0.07 \, \mu mol \, kg^{-1} \, yr^{-1}$, attributed here to gradual increase in the salinity of surface subtropical gyre waters. Salinity normalized TA (nTA) increased slightly at a rate of $0.10 \pm 0.03 \, \mu mol \, kg^{-1} \, yr^{-1}$ but since this trend was not statistically significant, there was no definitive evidence that nTA has changed during the last 3 decades (Table 2).

4 Discussion

4.1 Changes in seawater pCO_2 with time and its attribution

Surface seawater pCO_2 exhibited significant increases over the last 3 decades, increasing at a rate of $1.80 \pm 0.09 \, \mu atm \, kg^{-1} \, yr^{-1}$ and representing an increase of nearly $55 \, \mu atm$ or 20% from 1983 to 2011 (Fig. 6; Table 2). The increasing trend in seawater pCO_2 can be attributed to changes in DIC, TA, temperature and salinity (Fig. 7). The

trend in observed DIC would increase seawater pCO_2 by +122 %, but this effect is counteracted by a small increase in TA that decreases pCO_2 (−33 %). Trends in temperature (+8 %) and salinity (+3 %) have minor impacts on calculated seawater pCO_2. Similar trends and attribution of trends have been shown for observed pCO_2 across the North Atlantic in the seasonally stratified subtropical gyre (Bates, 2011) where the increase in seawater pCO_2 can be attributed to non-temperature effects (i.e., sum of DIC, TA and salinity changes). Over shorter timescales, similar trends in surface seawater pCO_2 have been observed elsewhere off Hawaii (Dore et al., 2003, 2009) and the Canary Islands (Santana-Casiano et al., 2007; Gonzalez-Davila et al., 2010).

4.2 Changes in the ocean CO$_2$ sink?

These observations infer that the ocean CO_2 sink in the subtropical gyre has not changed significantly over the last three decades. Similar to previous observations at BATS, seawater pCO_2 has increased at a comparable rate to atmospheric pCO_2 (Bates, 2007; Takahashi et al., 2009; Table 2, $1.72 \pm 0.01\,\mu\mathrm{atm\,kg^{-1}\,yr^{-1}}$) from 1983 to present. These trends indicate that the driving force for air-sea CO_2 gas exchange (i.e., ΔpCO_2; pCO_2 difference between atmosphere and seawater) has not changed significantly over the last 3 decades. One might therefore think that the ocean CO_2 sink near Bermuda has not changed significantly over time. However, it should be noted that windspeed also contributes in addition to ΔpCO_2 to the magnitude of air-sea CO_2 gas exchange. There is some evidence that the annual CO_2 sink has increased slightly due to higher annual windspeeds in the 2000's observed near Bermuda (Bates, 2007) perhaps in response to shift in the winter North Atlantic Oscillation from positive to neutral/negative over the last 2 decades (Hurrell and Deser, 2010; Bates, 2011). Other studies have also shown that with observations conducted over time periods longer than 2 decades, seawater pCO_2 has increased at the same rate as the atmosphere (Bates et al., 2002; McKinley et al., 2011) with longer term observations smoothing out shorter term variability. Such studies suggest that analysis of the CO_2 sink or source status using data that has a relatively short duration (<10 yr) may not be sufficient to

determine whether the North Atlantic Ocean CO_2 sink has decreased over time (e.g., Schuster and Watson, 2007; Schuster et al., 2009; Watson et al., 2009). Such assessments may require a longer term view especially in light of this and other studies (McKinley et al., 2011); and especially when deciphering anthropogenic secular trends from natural variability imparted by such phenomena as the NAO (Joyce et al., 1999; Gruber et al., 2002; Hurrell and Deser, 2010) and Atlantic Multidecadal Oscillation (McKinley et al., 2011). In summary, it appears that $\Delta p CO_2$ values have not changed significantly over the last 30 yr, and there is little evidence of any change in the CO_2 sink in the subtropical gyre of the North Atlantic near Bermuda.

In addition, over the 1983–2011 period, the Revelle factor (β) has increased at a rate of $0.0137 \pm 0.0008 \, \text{yr}^{-1}$ or ~ 0.41 over the last 3 decades. This indicates that the buffer capacity of subtropical gyre surface waters to absorb CO_2 has gradually reduced over time, confirming previous model studies that predict an increasing trend in β at BATS and for the North Atlantic Ocean in response to the ocean uptake of anthropogenic CO_2 from the atmosphere (Thomas et al., 2007).

4.3 The signal of ocean acidification in the North Atlantic Ocean

The BATS/Hydrostation S time-series data allow direct detection of the signal of ocean acidification in surface waters of the North Atlantic. The uptake of anthropogenic CO_2 from the atmosphere by the ocean changes seawater chemistry through chemical equilibrium of CO_2 with seawater. Dissolved CO_2 forms a weak acid and the pH and $[CO_3^{2-}]$ decrease as seawater absorbs CO_2, a process termed ocean acidification (Caldeira and Wickett, 2003, 2005). The effects of ocean acidification are potentially far-reaching in the global ocean, particularly for organisms that secrete $CaCO_3$ skeletons, tests or shells and for marine ecosystems where calcification and pH controls on biogeochemical processes are important factors (e.g., Fabry et al., 2009). Relevant indicators of ocean acidification include seawater pH, but also $[CO_3^{2-}]$ and thus saturation states for $CaCO_3$ minerals (i.e., $\Omega_{calcite}$ and $\Omega_{aragonite}$). The typical pH range of surface waters is between 7.8 and 8.4 in the open ocean and the ocean remains mildly alkaline at

present. At BATS, the mean pH is 8.094 with a range of 8.00–8.18 (Fig. 5).

The BATS site near Bermuda constitutes the longest time-series record of ocean acidification anywhere in the global ocean (Fig. 6; Bates, 2007). Trend analysis shows that the primary indicator of ocean acidification, seawater pH, has decreased at a rate of $-0.0017 \pm 0.0001\,\mathrm{yr}^{-1}$, a total decline in seawater pH of ~ 0.05 over the past 3 decades (Fig. 6; Table 2). This represents a $\sim 12\%$ increase in hydrogen ion concentration since 1983. Other indicators of ocean acidification at BATS such as $[CO_3^{2-}]$, $\Omega_{\mathrm{calcite}}$ and $\Omega_{\mathrm{aragonite}}$ have also decreased at a rate of $-0.58 \pm 0.041\,\mu\mathrm{mol\,kg^{-1}\,yr^{-1}}$, $-0.0141 \pm 0.0009\,\mathrm{yr}^{-1}$, and $-0.0091 \pm 0.0006\,\mathrm{yr}^{-1}$, respectively (Table 2). Trend analysis at BATS, and other published trends for three other ocean time-series sites indicate that surface seawater pH has decreased at a rate of -0.0014 to $-0.0019\,\mathrm{yr}^{-1}$ (e.g., Bates and Peters, 2007; Bates, 2007; Dore et al., 2009; Gonzalez-Davila et al., 2010; Byrne et al., 2010).

5 Conclusions

The long term ocean observations near Bermuda constitute the longest running time-series of changes in seawater carbonate chemistry due to the uptake of anthropogenic CO$_2$ and resulting ocean acidification impacts. Such records and those from other time-series sites (Dore et al., 2009; Gonzalez-Davila et al., 2010; Olafsson et al., 2010) provide critically needed data showing that such changes are due to anthropogenic CO$_2$ release and absorption by the global ocean and to test ocean-atmosphere models (e.g., Bates, 2007; McKinley et al., 2011) that are used for predictive climate-change purposes. Before regular sampling began at the Hydrostation S in 1983 and later at the BATS site in 1988, there was occasional sampling in the North Atlantic subtropical gyre near Bermuda through the GEOSECS and Transient Tracers in the Ocean (TTO) projects. Here, we compute surface pCO$_2$, pH and $\Omega_{\mathrm{aragonite}}$ from surface GEOSECS and TTO DIC and total alkalinity data (Kroopnick et al., 1972; Brewer et al.,

1985). Combined with BATS/Hydrostation S data, this extends the time-series records of computed surface pCO$_2$, pH and $\Omega_{aragonite}$ back to the early 1970s (Fig. 8; Supplementary Information). These data were sampled within 200 km of Bermuda (but not at BATS/Hydrostation) and both surface pCO$_2$, pH and $\Omega_{aragonite}$ data from GEOSECS and TTO fall close to the regression lines for these parameters (from Table 1, Fig. 2). Thus, the trends established at BATS/Hydrostation S appear to extend back to the early 1970s, constituting a nearly continuous 40 yr record of changing seawater carbonate chemistry and ocean acidification indicators.

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Table 1. Long-term trends (1983–2011) of surface hydrography and seawater carbonate chemistry with regression statistics (slope and error, n, r^2 and p-value). This includes surface seawater temperature, salinity, DIC, nDIC, TA, nTA, atmospheric $p\mathrm{CO}_2$ ($p\mathrm{CO}_2^{atm}$), and calculated seawater $p\mathrm{CO}_2$ ($p\mathrm{CO}_2^{sea}$) and Revelle factor (β) from the BATS (31°50′ N, 64°10′ W)/Hydrostation S (32°10′ N, 66°30′ W) sites in the North Atlantic Ocean. Please see text for details on the CO_2-carbonic acid system computation and salinity normalization procedures. Observations of atmospheric $p\mathrm{CO}_2$ data come from two atmospheric monitoring sites (Terceira Island, Açores, September 1983–September 1988; Bermuda, August 1988–December 2010).

Parameter	Period	Slope and std error	n	r^2	p-value
Hydrography					
Temperature	09/1983–07/2011	$-0.0075 \pm 0.021\,°\mathrm{C\,yr^{-1}}$	362	0.00	0.72
Salinity	09/1983–07/2011	$+0.0058 \pm 0.0010\,\mathrm{yr^{-1}}$	362	0.08	<0.01
Ocean acidification indicators					
pH	09/1983–07/2011	$-0.0016 \pm 00022\,\mathrm{yr^{-1}}$	358	0.13	<0.01
CO_3^{2-}	09/1983–07/2011	$-0.64 \pm 0.06\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	358	0.24	<0.01
$\Omega_{calcite}$	09/1983–07/2011	$-0.0152 \pm 0.0016\,\mathrm{yr^{-1}}$	358	0.21	<0.01
$\Omega_{aragonite}$	09/1983–07/2011	$-0.0100 \pm 0.0012\,\mathrm{yr^{-1}}$	358	0.16	<0.01
Seawater carbonate chemistry					
DIC	09/1983–07/2011	$+1.53 \pm 0.12\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	361	0.32	<0.01
nDIC	09/1983–07/2011	$+1.20 \pm 0.09\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	361	0.35	<0.01
TA	09/1983–07/2011	$+0.50 \pm 0.07\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	361	0.12	<0.01
nTA	09/1983–07/2011	$+0.12 \pm 0.03\,\mathrm{\mu mol\,kg^{-1}\,yr^{-1}}$	361	0.04	<0.01
$p\mathrm{CO}_2^{sea}$	09/1983–07/2011	$+1.62 \pm 0.21\,\mathrm{\mu atm\,yr^{-1}}$	358	0.16	<0.01
$p\mathrm{CO}_2^{atm}$	09/1983–12/2010	$+1.72 \pm 0.01\,\mathrm{ppm\,yr^{-1}}$	1825	0.89	<0.01
Revelle factor (β)	09/1983–07/2011	$+0.015 \pm 0.0014\,\mathrm{yr^{-1}}$	358	0.24	<0.01

Table 2. Seasonally detrended long-term trends (1983–2011) of surface hydrography and seawater carbonate chemistry with regression statistics (slope and error, n, r^2 and p-value). This table includes trend analysis of surface hydrography including temperature and salinity, seawater carbonate chemistry (i.e., DIC, nDIC, TA, nTA, atmospheric pCO$_2$ (pCO$_2^{atm}$), and calculated seawater pCO$_2$ (pCO$_2^{sea}$) and Revelle factor (β) anomalies) and indicators of seawater carbonate chemistry changes (e.g., pH, [CO$_3^{2-}$], and mineral saturation states of calcite ($\Omega_{calcite}$) and aragonite (Ω_{arag}) from the BATS (31°40′ N, 64°10′ W) and Hydrostation S (32°10′ N, 64°30′ W) sites in the North Atlantic Ocean. Please see text for details on the seawater carbonate chemistry computation and salinity normalization procedures. Observations of atmospheric pCO$_2$ data come from two atmospheric monitoring sites (Terceira Island, Açores, September 1983–September 1988; Bermuda, August 1988–December 2010). Please see text for details on the methods for removing seasonal trends.

| Parameter	Period	30 yr change (and units if applicable)	slope and std error (and units if applicable)	n	r^2	p-value
Hydrography and seawater carbonate chemistry						
Temperature	09/1983–07/2011	+0.33 °C	+0.011 ± 0.006 °C yr^{-1}	320	0.01	0.06
Salinity	09/1983–07/2011	+0.162	+0.0054 ± 0.0001	320	0.09	< 0.01
DIC	09/1983–07/2011	+41.7 µmol kg^{-1}	+1.39 ± 0.06 µmol kg^{-1} yr^{-1}	319	0.63	< 0.01
nDIC	09/1983–07/2011	+32.4 µmol kg^{-1}	+1.08 ± 0.05 µmol kg^{-1} yr^{-1}	319	0.61	< 0.01
TA	09/1983–07/2011	+14.6 µmol kg^{-1}	+0.48 ± 0.07 µmol kg^{-1} yr^{-1}	319	0.14	< 0.01
nTA	09/1983–07/2011	+3.0 µmol kg^{-1}	+0.10 ± 0.03 µmol kg^{-1} yr^{-1}	319	0.03	< 0.01
pCO$_2^{sea}$	09/1983–07/2011	+54.4 µatm	+1.80 ± 0.09 µatm yr^{-1}	319	0.53	< 0.01
pCO$_2^{atm}$	09/1983–12/2010	+51.6 µatm	+1.72 ± 0.01 ppm yr^{-1}	1825	0.89	< 0.01
Revelle	09/1983–07/2011	+0.41	+0.0137 ± 0.0008	319	0.50	< 0.01
Ocean acidification indicators						
pH	09/1983–07/2011	−0.0501	−0.00174 ± 0.0001	319	0.50	< 0.01
CO$_3^{2-}$	09/1983–07/2011	−17.5 µmol kg^{-1}	−0.58 ± 0.04 µmol kg^{-1} yr^{-1}	319	0.41	< 0.01
$\Omega_{aragonite}$	09/1983–07/2011	−0.246	−0.0091 ± 0.0006	319	0.39	< 0.01
$\Omega_{calcite}$	09/1983–07/2011	−0.391	−0.0141 ± 0.0009	319	0.42	< 0.01
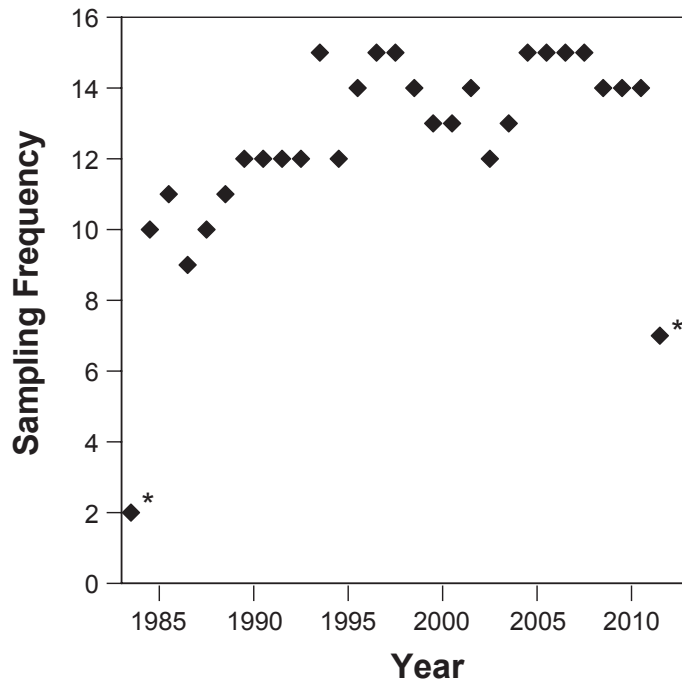
Fig. 1. Sampling frequency or number of cruises each year when seawater carbonate chemistry and other parameters were collected. From September 1988, only BATS cruises are shown with Hydrostation S cruise beforehand. The * symbol denotes years when the full year was not sampled.
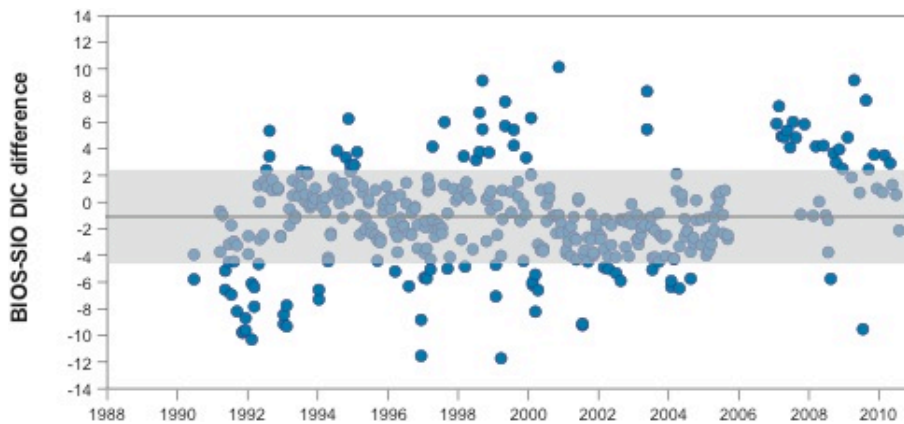
Fig. 2. Comparison of DIC analyzed at BIOS and SIO. Differences shown in $\mu mol\,kg^{-1}$.
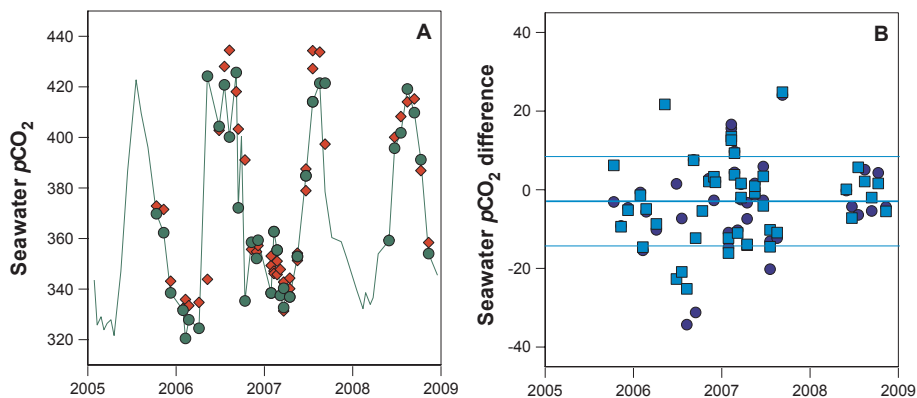
Fig. 3. Comparison of computed seawater pCO_2 (µatm) with pCO_2 directly measured from the R/V *Atlantic Explorer* or Bermuda Testbed Mooring (BTM). **(A)**. time-series of computed seawater pCO_2 at BATS (black line) with directly measured pCO_2 from the R/V *Atlantic Explorer* and BTM (red symbols). The green symbols denote directly measured pCO_2 corrected to the temperature of sampling at BATS. **(B)** difference between computed seawater pCO_2 and directly measured pCO_2 from the R/V *Atlantic Explorer* and BTM (blue symbols; µatm). The cyan symbols denote directly measured pCO_2 corrected to the temperature of sampling at BATS. Mean and 1 standard deviation are shown in the figure.
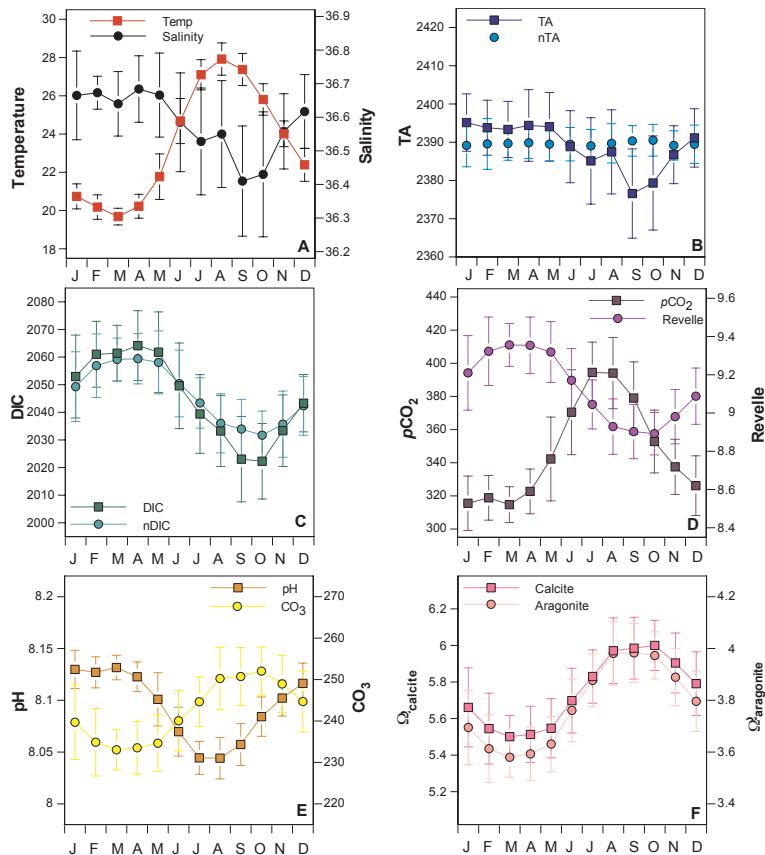
Fig. 4. Mean monthly values for surface temperature and salinity **(A)**, total alkalinity (**B**, $\mu mol\,kg^{-1}$); DIC (**C**, $\mu mol\,kg^{-1}$), seawater pCO_2 (**D**, μatm), pH and $[CO_3^{2-}]$ (**E**, $\mu mol\,kg^{-1}$ for $[CO_3^{2-}]$), and $\Omega_{calcite}$ and $\Omega_{aragonite}$ (**E**), at BATS/Hydrostation S for the period 1983–2011. The standard deviation is shown by *y* error bars.

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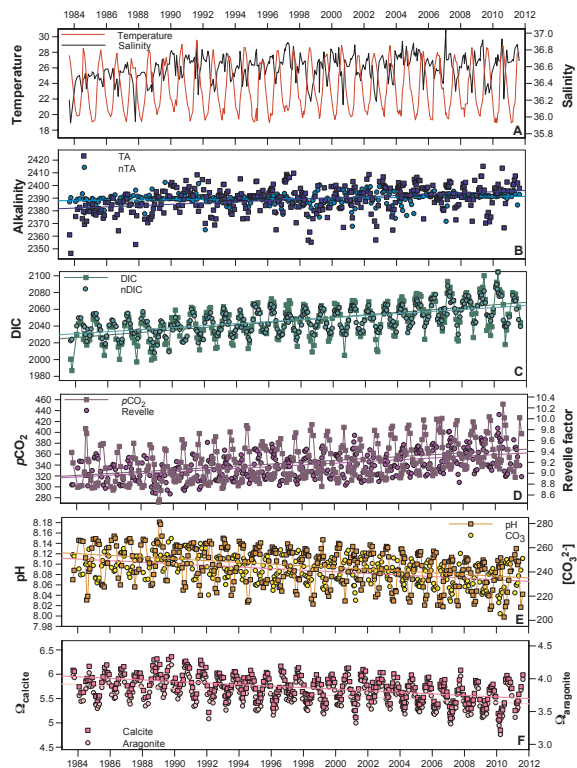
Fig. 5. Long-term observations and trends of surface hydrography, seawater carbonate chemistry and ocean acidification indicators from 1983 to 2011 at the BATS (Bermuda Atlantic Time-series Study; 31°40′ N, 64°10′ W) and Hydrostation S (32°10′ N, 64°30′ W) sites located near Bermuda in the NW Atlantic Ocean. Slopes and statistics of regressions are listed in Table 1. **(A)** Sea surface temperature (°C; black line) and salinity (red line). **(B)** Surface total alkalinity (TA, µmol kg⁻¹, blue symbol) and salinity normalized TA (nTA; µmol kg⁻¹, cyan symbol). **(C)** Surface dissolved inorganic carbon (DIC, µmol kg⁻¹, green symbol) and salinity normalized DIC (nDIC; µmol kg⁻¹, light green symbol). **(D)** Seawater $p\text{CO}_2$ (µatm; purple symbol) and Revelle factor (β) (fuchsia symbol). **(E)** Surface seawater pH (orange symbol) and $[\text{CO}_3^{2-}]$ (µmol kg⁻¹, yellow symbol) **(F)** Surface saturation state of calcite (Ω_{calcite}) (pink symbol) and aragonite (Ω_{calcite}) (light pink symbol).
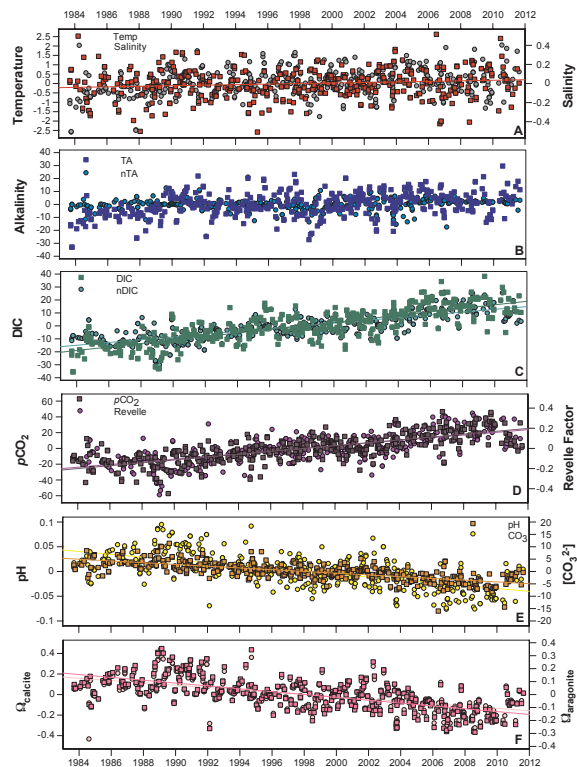
Fig. 6. Long-term anomalies and trends of surface hydrography, seawater carbonate chemistry and ocean acidification indicators from 1983 to 2011 at the BATS (Bermuda Atlantic Time-series Study; 31°40′ N, 64°10′ W) and Hydrostation S (32°10′ N, 64°30′ W) sites located near Bermuda in the NW Atlantic Ocean. Slopes and statistics of regressions are listed in Table 2. **(A)** Sea surface temperature (°C; black line) and salinity (red line). **(B)** Surface total alkalinity (TA, µmol kg^{-1}, blue symbol) and salinity normalized TA (nTA; µmol kg^{-1}, cyan symbol). **(C)** Surface dissolved inorganic carbon (DIC, µmol kg^{-1}, green symbol) and salinity normalized DIC (nDIC; µmol kg^{-1}, light green symbol). **(D)** Seawater pCO$_2$ (µatm; purple symbol) and Revelle factor (β) (fuchsia symbol). **(E)** Surface seawater pH (orange symbol) and [CO$_3^{2-}$] (µmol kg^{-1}, yellow symbol) **(f)**. Surface saturation state of calcite ($\Omega_{calcite}$) (pink symbol) and aragonite ($\Omega_{calcite}$) (light pink symbol).
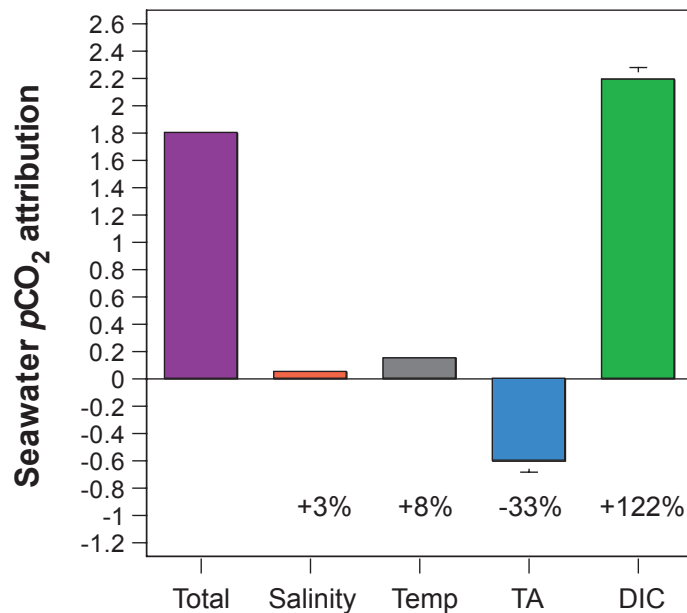
Fig. 7. Long-term trend in seawater pCO_2 (purple) and its attribution to long-term changes in salinity, temperature, TA and DIC (green). The relative attribution of change was computed using CO2calc (Robbins et al., 2010) using mean temperature, salinity, TA and DIC values observed at BATS. Mean values and trends taken from Table 2.

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Interactive Discussion

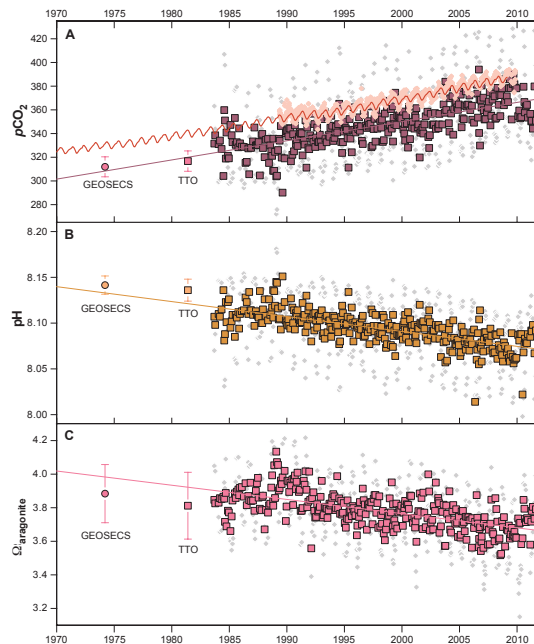**Fig. 8.** Time-series of atmospheric and ocean pCO$_2$, pH and aragonite saturation states. **(A)** time-series of atmospheric pCO$_2$ (ppm) from Mauna Loa, Hawaii (red line), and Bermuda (pink symbol), and surface ocean seawater pCO$_2$ (µatm) at the Bermuda Atlantic Time-series Study (BATS) site off Bermuda. Observed (grey) and seasonally detrended (purple) surface ocean seawater pCO$_2$ levels are shown. Earlier seawater data from the GEOSECS and TTO expeditions in the North Atlantic Ocean are also shown in this and following panels. **(B)** time-series of surface ocean seawater pH at the BATS site off Bermuda. Observed (grey) and seasonally detrended (orange) seawater pH are shown. **(C)** time-series of surface ocean aragonite saturation state ($\Omega_{\text{aragonite}}$) for calcium carbonate at the BATS site off Bermuda. Observed (purple) and seasonally detrended (purple line) seawater $\Omega_{\text{aragonite}}$ are shown.