



A variable and decreasing sink for atmospheric CO₂ in the North Atlantic

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[1] A time series of observations from merchant ships between the U.K. and the Caribbean is used to establish the variability of sea surface pCO₂ and air-to-sea flux from the mid-1990s to early 2000s. We show that the sink for atmospheric CO₂ exhibits important interannual variability, which is in phase across large regions from year to year. Additionally, there has been an interdecadal decline, evident throughout the study region but especially significant in the northeast of the area covered, with the sink reducing >50% from the mid-1990s to the period 2002–2005. A review of available observations suggests a large region of decrease covering much of the North Atlantic but excluding the western subtropical areas. We estimate that the uptake of the region between 20°N and 65°N declined by ~0.24 Pg C a⁻¹ from 1994/1995 to 2002–2005. Declining rates of wintertime mixing and ventilation between surface and subsurface waters due to increasing stratification, linked to variation in the North Atlantic Oscillation, are suggested as the main cause of the change. These are exacerbated by a contribution from the changing buffer capacity of the ocean water, as the carbon content of surface waters increases.

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1. Introduction

[2] The world's oceans are an important sink for atmospheric CO₂. Currently they absorb 25–30% of the fossil fuel source, and they have taken up almost half of accumulated emissions since the industrial revolution [Sabine *et al.*, 2004]. The air-to-sea surface flux of CO₂ is driven by $\Delta p\text{CO}_2$, the difference between atmospheric and sea surface partial pressures of carbon dioxide (pCO₂). Sea surface pCO₂ is affected by factors such as change of sea surface temperature (SST), mixing with deeper waters that have higher carbon content, and consumption by marine biota linked to the availability of surface nutrients. Models [Orr *et al.*, 2001] and data compilations [Takahashi *et al.*, 2002] suggest atmospheric CO₂ uptake is highest in temperate and subpolar waters where seasonal deep mixing and subsurface water formation allow surface water renewal, and slower in the subtropical gyres where water is trapped at the surface for long periods. The North Atlantic is a particularly strong CO₂ sink region [Takahashi *et al.*, 2002], which is due both to the vertical circulation whereby water moves poleward at the surface, cooling and taking up atmospheric CO₂ before mixing and sinking to depth in wintertime, and to efficient biological uptake of nutrients and carbon.

[3] There are indications of substantial variability in the uptake of CO₂ by the North Atlantic, both spatially [Watson

et al., 1991] and temporally [Gruber *et al.*, 2002], but few observations covering large areas and multiple years. Ocean models suggest that the interannual variability in the global sink is relatively small [Le Quéré *et al.*, 2000], while atmospheric inversions [Bousquet *et al.*, 2000; Patra *et al.*, 2005; Rayner *et al.*, 1999] indicate year-to-year variability that is a substantial fraction of the total sink. Projections suggest that the sink should increase as atmospheric CO₂ continues to rise, but that under anthropogenically induced climate change, increasing stratification and a slowing overturning circulation decrease rates of ventilation and tend to slow the uptake [Fung *et al.*, 2005; Sarmiento and Le Quéré, 1996]. Though time series of measurements have been established at a few locations, there are as yet few observations of surface carbon parameters covering large areas and multiple years with which to test these predictions.

2. Methods

2.1. Measurements

[4] Direct, quasicontinuous autonomous measurements of SST and pCO₂ in the sea surface and overlying atmosphere, were collected between the UK and Caribbean approximately every month (Figure 1). Between the UK and Jamaica they were collected from June 1994 to August 1995 on board MV *Prince of Seas* [Cooper *et al.*, 1998] (these data are available on the CDIAC web site at <http://cdiac.esd.ornl.gov/>). In December 2001 measurements were restarted on MV *Santa Lucia* and continue today on board MV *Santa Maria*, between the UK and Martinique or the Dominican Republic. Data collected from February 2002 to February 2005 are used in this study, consisting of more

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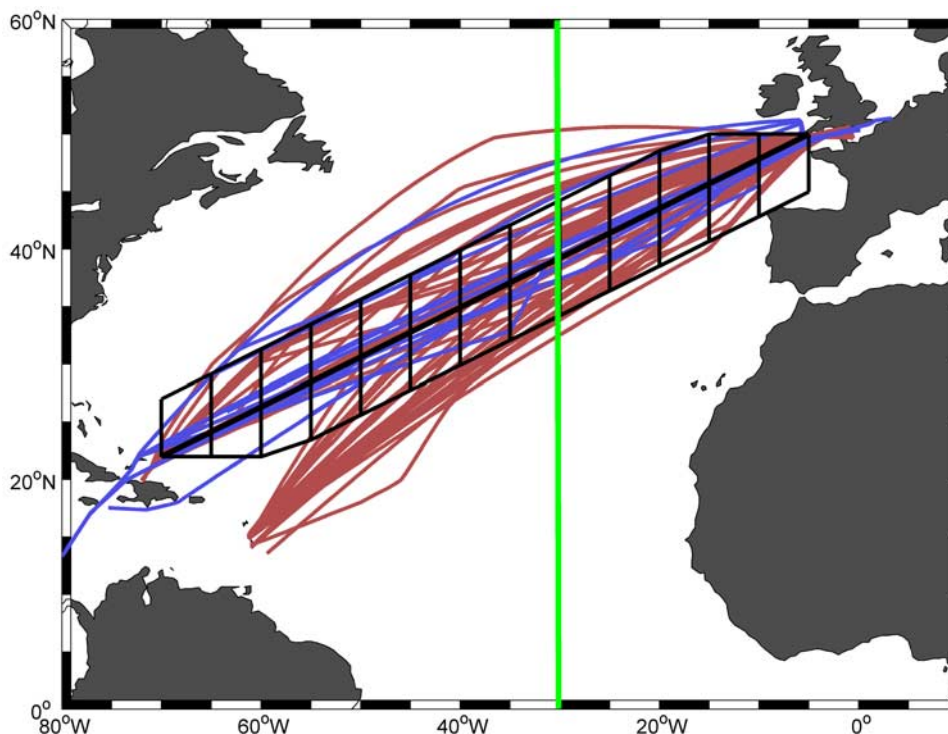


Figure 1. Map showing the locations of ship tracks used in this study. Blue lines, ship tracks in 1994/1995; red lines, tracks in 2002–2005. The thick black line is the center of the band from which data were selected, and the grid along it marks the $10^\circ \times 5^\circ$ areas used for averaging data. The thick green line depicts the border between the northeast temperate/subpolar and the southwest tropical/subtropical region.

than 180,000 point measurements. The design of the system installed on board MV *Santa Lucia* and now on board MV *Santa Maria* is based on the instrument on MV *Prince of Seas* previously described by Cooper *et al.* [1998]. The system consists of three parts: a flowing seawater module in the engine room, an electronics/detector module in the engine control room, and a GPS/air inlet module on the port bridge wing. The flowing seawater unit has an equilibrator (a percolating packed bed type, as described by Cooper *et al.*), located near the seawater inlet at the port sea chest, 3 to 5 m below water level, depending on cargo loading.

[5] Some differences from the system of Cooper *et al.* [1998] have since been incorporated, as follows: A peristaltic pump now regulates the seawater flow to the equilibrator at approximately 3 L min^{-1} . The in situ seawater temperature is now measured by a different sensor (C/T model 3210, Aanderaa Instruments, Norway, that also measures salinity), located immediately at the sea chest. The in situ seawater temperature sensor is regularly recalibrated by the manufacturer. The equilibrator temperature however continues to be measured by platinum resistance thermometers, the calibrations of which are checked against the in situ sensor once per month. As in the installation of Cooper *et al.*, all pipes and sensor housings between the seawater inlet and the equilibrator are thermally insulated, keeping the temperature increase between them below 0.5°C . The control room where the electronics/detector module is now located (due to lack of space in the engine

room) is three decks up from the equilibrator. Power is supplied via an uninterrupted power supply which also filters out spikes in the ship's power. The sample gas is now partially dried by passing through a cold trap at $\sim 5^\circ\text{C}$ prior to the infrared detector to avoid condensation in the detector (Li7000, LiCor Inc., USA; a Li6262 was used in 1994 and 1995). The greater distance between the equilibrator in the engine room and the detector in the control room requires a longer flushing time to ensure newly equilibrated gas reaches the detector. Using a 1/8 inch outer diameter tubing between the equilibrator and detector (approximately 40 m length for the return circuit), gives approximately 300 cm^3 volume; a 30 min flushing time at approximately 100 mL min^{-1} is used to ensure newly equilibrated gas reaches the detector, and only measurements taken at the end of this flushing period were used in this study. This still provides >9000 data points and more-than-adequate spatial and temporal resolution. Secondary gas standards used for the calibration of the detector were run every 3 hours. They are calibrated in the laboratory before and after usage against primary standards from NOAA-CMD-CCGG (<http://www.esrl.noaa.gov/gmd/ccgg/index.html>). All raw data are recorded with coinciding position and time, provided by the GPS module.

[6] Routine measurement of CO₂ in marine air is also carried out, using an air line from the outside of the port bridge wing. Periods in which the standard deviation of these measurements rose above 0.7 ppm were examined for possible contamination from the ship and excluded if there

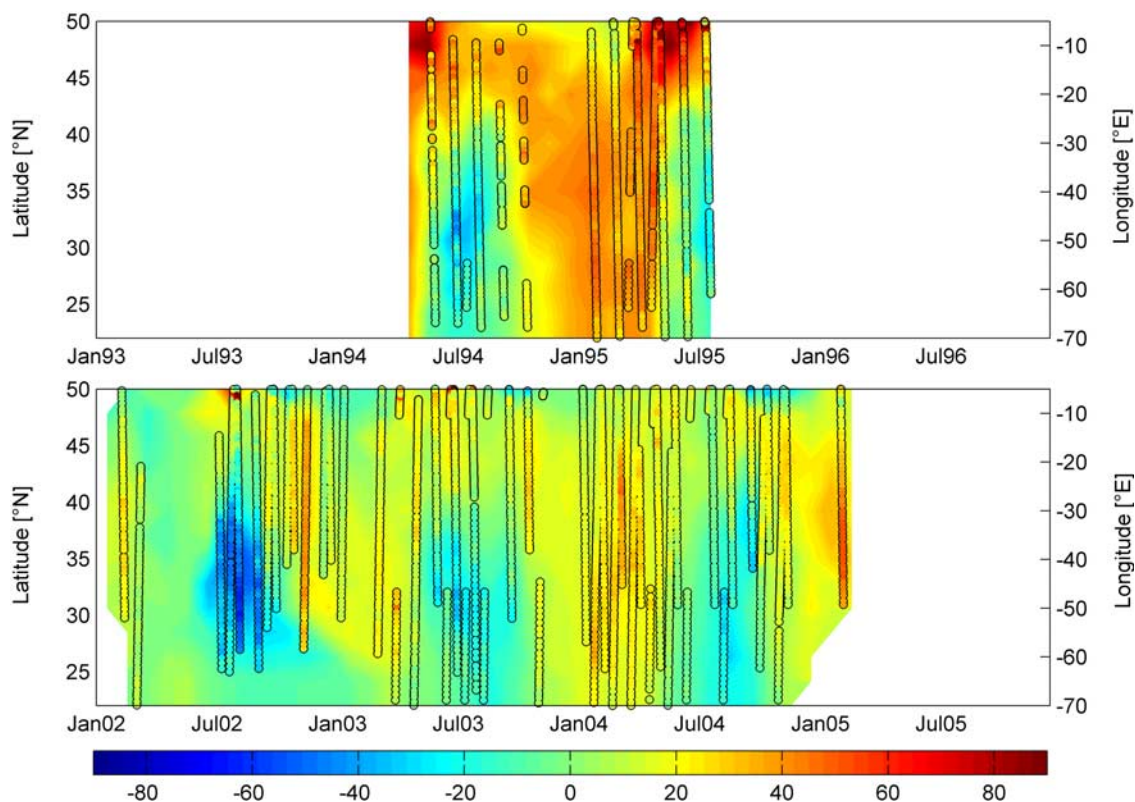


Figure 2. Hovmöller plots of $\Delta p\text{CO}_2$ (μatm) (defined as the atmosphere minus sea surface), for (top) 1994/1995 and (bottom) 2002/2005, calculated as described in the text.

was any doubt as to their quality. The air measurements provide an important check on the operation of the system, but in this study, the air measurements were not used to calculate air-sea $p\text{CO}_2$ differences. Instead the air-side $p\text{CO}_2$ was derived from monthly averages of mixing ratios from [GLOBALVIEW-CO₂, 2006] for both the 1994/1995 period and the 2002/2005 periods, as described in more detail below. We took the view that these large-area background estimates are more appropriate for the calculation than our instantaneous measurements, though there was in practice very little difference in the results using either source of atmospheric $p\text{CO}_2$.

2.2. Data Reduction

[7] Calculation of sea surface $p\text{CO}_2$ values from raw measurements followed the previously published procedure [Cooper *et al.*, 1998]. The initial measure of CO_2 in the equilibrated gas was $x\text{CO}_2$, the mole fraction of CO_2 in the detector cell recorded after correction for band broadening by the detector software. A dilution correction for water vapor was first made to this to yield the $x\text{CO}_2$ in dry air, since a Li7000, used since 2002, does not internally correct for water vapor dilution. True $x\text{CO}_2$ was calculated by correcting this for detector drift, applying a linear interpolation between secondary gas standard concentrations. Equilibrator $p\text{CO}_2$ was found by correcting the true $x\text{CO}_2$ to 100% humidity at equilibrator temperature and pressure, using the saturated water vapor pressure appropriate to seawater given by [Cooper *et al.*, 1998]: $p_{\text{H}_2\text{O}} = 0.981 \exp(14.32602 - 5306.83/\text{SST} [\text{Kelvin}])$. The in situ sea surface $p\text{CO}_2$ was then calculated by correcting the equil-

ibrator $p\text{CO}_2$ for the difference ΔT between in situ and equilibrator temperature, applying the relationship given by Takahashi *et al.* [1993]: $p\text{CO}_2$ (in situ) = $p\text{CO}_2(\text{equ}) \exp(-0.0423 \Delta T)$.

[8] To examine trends in the open ocean, we first excluded data south of 22°N, west of 70°W, east of 5°W, and north of 50°N to avoid coastal influences. Sea surface $p\text{CO}_2$ and SST from each voyage were averaged into 1° latitude by 1° longitude bins. Individual measurements separated by such short scales are very highly correlated, and this step yields values with uniform area weighting, while discarding information only on variability at the finest scales, which are not the focus of this study. Averages of these values falling within a 10° wide latitude band centered on the line shown in Figure 1 were then calculated. The selected data were then 2-D interpolated by Delaunay triangulation onto a grid of 1 month by 5° longitude along the line (or 2.15° latitude, since latitude and longitude are linearly related along the line). Each grid point therefore yields a value for the respective grid box in Figure 1 for each month of measurement. Use of a relatively broad band of 10° width allows the inclusion of the largest possible number of data and ensures that any trends detected are applicable to a large area, but it is wide enough that systematic changes in the latitudes of routes, occurring between periods being compared, might lead to biases. We investigated this possibility (see auxiliary material Figure S3a)¹ by repeating the anal-

¹Auxiliary materials are available in the HTML. doi:10.1029/2006JC003941.

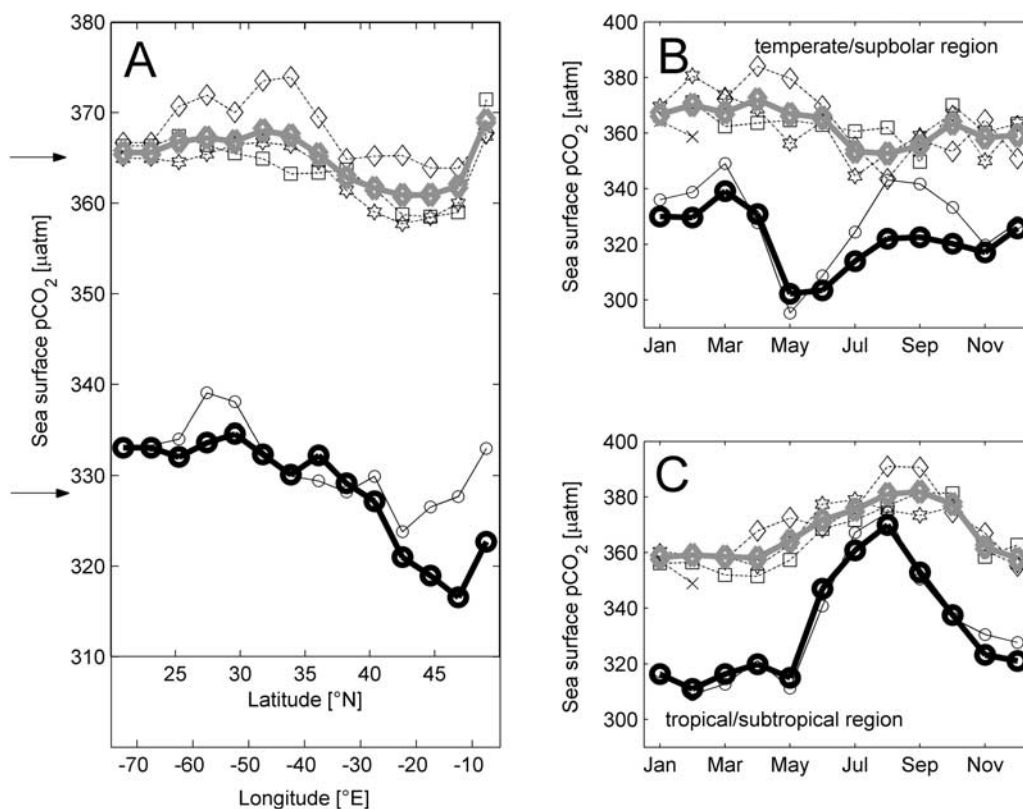


Figure 3. Annual and monthly mean sea surface pCO₂ (μatm). (a) Annual means versus latitude or longitude of each grid box shown in Figure 1, and monthly means averaged over (b) the temperate/subpolar region and (c) the tropical/subtropical region. For the annual averages (Figure 3a), the thick black line indicates averages of 1994/1995, the thick grey line averages of 2002/2005. The thin line with circles are the 1994/1995 averages recalculated assuming constant alkalinity and total CO₂ content, but accounting for the change in SST between 1994/1995 and 2002/2005. The thin lines with other markers give the average for individual years (from March to February, diamonds for 2002/2003, stars for 2003/2004, squares for 2004/2005). The horizontal arrows to the left of A indicate the annual means for 1994/1995 at 328 μatm and for 2002/2005 at 365 μatm. For the monthly means in the temperate/subpolar region (Figure 3b; grid boxes east of 30°W), the thick black line, the thick grey line, and the thin line with circles are the same as in Figure 3a); diamonds are monthly means for 2002, stars for 2003, squares for 2004, and crosses for 2005. For the monthly mean in the tropical/subtropical region (C, grid boxes west of 30°W), patterns are the same as for the temperate/subpolar region.

ysis with a narrower, 5° wide band centered on the line. This results in better collocation of the data but at the cost of excluding a substantial proportion of the observations. The results shown in the auxiliary material remained essentially unchanged from those with the 10° band discussed below, and we conclude that use of the latter is justified.

[9] Atmospheric pCO₂ values were calculated from the monthly, latitudinal atmospheric xCO₂ values given by [GLOBALVIEW-CO₂, 2006]. These were selected for the appropriate month, latitude-interpolated onto the same time-space grid as our sea surface data, and converted into atmospheric pCO₂ values by using NCEP/NCAR reanalysis estimates of barometric pressure and SST (6-hourly and 2.5° × 2.5° resolution [Kalnay et al., 1996], also averaged onto the same time-space grid). The ΔpCO₂ was then calculated as atmospheric pCO₂ minus sea surface pCO₂ (note a positive ΔpCO₂ therefore depicts an uptake of CO₂ by the ocean surface). A Hovmöller plot of the gridded

ΔpCO₂ is shown in Figure 2, together with the color-coded values and position of the 1° × 1°-binned data. Similar plots for SST and sea surface pCO₂ are included in the auxiliary material (auxiliary material Figures S1 and S2). The gridded sea surface pCO₂ and ΔpCO₂ were then further averaged into two regions: temperate/subpolar from, 39°N–50°N and 30°W–5°W, and subtropical/tropical from 22°N–39°N, 70°W–30°W, the Azores front making the approximate boundary between these regions. Figure 3a shows the annual average sea surface pCO₂ along the route for the different periods, while Figures 3b and 3c show the annual pCO₂ cycle in the temperate/subpolar region and the subtropical/tropical region respectively. Figures 4a, 4b, and 4c show the equivalent plots for ΔpCO₂.

2.3. Flux Calculations

[10] Air-to-sea fluxes of CO₂ were calculated from the ΔpCO₂ values obtained above, using the time and area

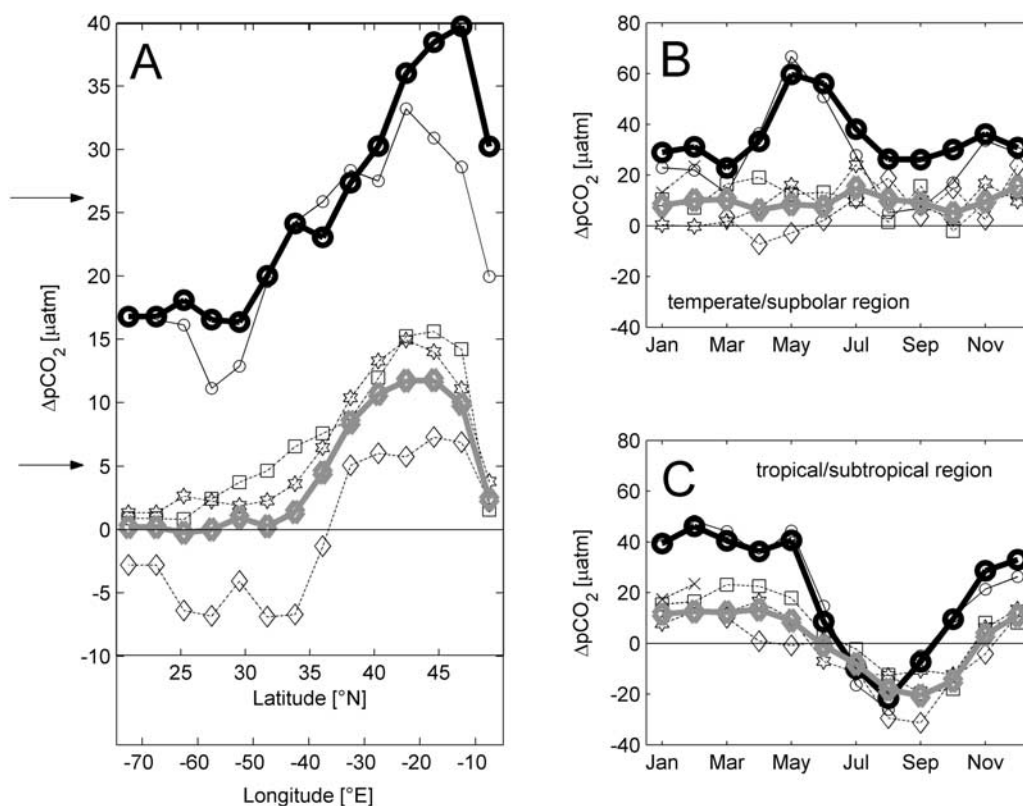


Figure 4. Annual and monthly mean $\Delta p\text{CO}_2$ (μatm). (a) Annual means versus latitude and longitude of each grid box shown in Figure 1, and monthly means averaged over (b) the temperate/subpolar region and (c) the tropical/subtropical regions. Regions and color/symbol coding is the same as for Figure 3. The horizontal arrows to the left of Figure 4a indicate the annual means for 1994/1995 at 26 μatm and for 2002/2005 at 5 μatm .

averaged gas exchange equation [Wanninkhof *et al.*, 2002; Watson and Orr, 2003]:

$$\bar{K} \times \bar{s} \times \overline{\Delta p\text{CO}_2}$$

where \bar{K} and \bar{s} are the mean gas transfer velocity and solubility for each grid box and month, calculated from NCEP/NCAR, $2.5^{\circ} \times 2.5^{\circ} \times 6$ -hourly reanalysis data [Kalnay *et al.*, 1996], averaged onto the same time-space grid as $\Delta p\text{CO}_2$. The Wanninkhof gas transfer parameterization for short-term winds [Wanninkhof, 1992] was used, $K = 0.31 (Sc/660)^{-0.5} U^2$, where U is the wind speed at 10m height, and Sc the Schmidt number for CO₂ in seawater. $\overline{\Delta p\text{CO}_2}$ is the value for that grid box and month obtained by the interpolation techniques described above. Using this time- and area-averaged gas exchange equation ignores small biases that may occur owing to covariance of K , s and $\Delta p\text{CO}_2$. However, the use of wind data from the whole grid box and time period is superior to alternatives using only monthly mean wind speeds, or only wind speeds measured when the ship was actually transiting the grid box [Lüger *et al.*, 2006; Wanninkhof *et al.*, 2002], because it more correctly accounts for the large nonlinearity in the gas transfer velocity K , due to episodic high winds. Annually averaged air-to-sea fluxes versus latitude for July 1994 to

June 1995 and for March to February in 2002/2003, 2003/2004, and 2004/2005 are shown in Figure 5a.

3. Results and Discussion

[11] Sea surface $p\text{CO}_2$ (Figure 3) increased from the mid-1990s to the 2000s everywhere along the route between the Caribbean and the UK. The annual mean sea surface $p\text{CO}_2$ increased by 37 μatm from 328 μatm in 1994/1995 to 365 μatm in 2002/2005, a mean increase of 4.4 $\mu\text{atm a}^{-1}$ if a linear trend is assumed. The seasonal cycle of sea surface $p\text{CO}_2$ also changed in both the temperate/subpolar region (Figure 3b), and the tropical/subtropical region (Figure 3c). In the former, seawater $p\text{CO}_2$ showed a strong minimum in spring and summer in the mid-1990s, due to biological carbon uptake reducing sea-surface $p\text{CO}_2$, a pattern expected in temperate seas [Takahashi *et al.*, 1993]. This seasonal cycle was however much reduced in the more recent measurements. The seasonal cycle in the subtropical/tropical regions (Figure 3c) has the reverse phase, with a maximum in summer and a minimum in winter. In these strongly stratified waters, there is less deep mixing in winter to bring nutrients to the surface to fuel biological activity, while the summer increase in temperature drives up sea surface $p\text{CO}_2$. Here too, the amplitude of the seasonal cycle decreased from the mid-1990s to the recent past.

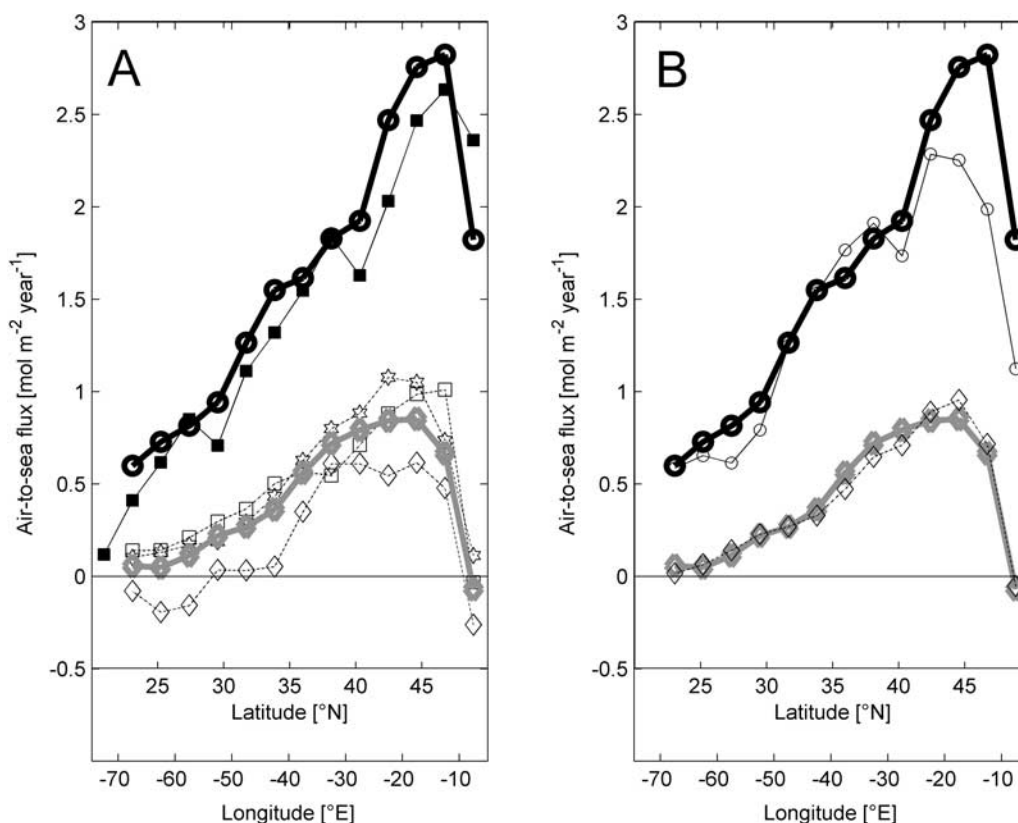


Figure 5. Annual mean air-to-sea fluxes ($\text{mol m}^{-2} \text{a}^{-1}$) versus latitude and longitude for each grid box shown in Figure 1. (a) Line patterns are according to Figures 3a and 4a, with the addition of the black squares indicating fluxes calculated from the 1995 climatology of *Takahashi et al.* [2002] obtained from <http://www.ldeo.columbia.edu/res/pi/CO2/>. (b) The annual averages of 1994/1995 and 2002/2005 are repeated, compared with 2002/2005 fluxes recalculated using 1994/1995 wind speeds to calculate the gas transfer velocities as outlined in the text (thin black line with diamonds), and the 1994/1995 fluxes with $\Delta p\text{CO}_2$ are adjusted to account for SST change from 1994/1995 to 2002/2005 (thin black lines with circles).

[12] The effect of changes in SST (shown in auxiliary material Figure S4) was investigated as a possible cause of the $p\text{CO}_2$ trends, as follows. Assuming no change in salinity, alkalinity, and total CO_2 concentration, sea-surface $p\text{CO}_2$ increases by $4.23\% \text{ } ^\circ\text{C}^{-1}$ [*Takahashi et al.*, 1993]. In Figure 3 (thin lines with open circles) we include the effect of recalculating the mid-1990s sea surface $p\text{CO}_2$, accounting for the difference in temperature from 1994/1995 to 2002/2005 according to this relationship. On the annual average (Figure 3a), the effect of SST has a significant effect only in the temperate/subpolar region, where it is able to account for about 20% of the difference in sea surface $p\text{CO}_2$ between the mid-1990s and the recent data. Most of this effect is concentrated in mid-late summer (Figure 3b). In the tropical/subtropical region (Figure 3c), the thermodynamic effect of SST change is barely significant.

[13] Atmospheric $p\text{CO}_2$ also increased from the mid-1990s to the early 2000s, by a mean of $1.8 \mu\text{atm a}^{-1}$ between 20°N and 50°N [*GLOBALVIEW-CO₂*, 2006]. The resulting $\Delta p\text{CO}_2$ (atmospheric $p\text{CO}_2$ – sea surface $p\text{CO}_2$, Figure 4a) reduced by $21 \mu\text{atm}$, from $26 \mu\text{atm}$ in the mid-1990s to $5 \mu\text{atm}$ in the early 2000s, or by $2.5 \mu\text{atm a}^{-1}$ if a linear trend is assumed. The seasonal cycles of $\Delta p\text{CO}_2$ also

changed, with the seasonal amplitude being reduced in both the temperate/subpolar region (Figure 4b) and the tropical/subtropical region (Figure 4c).

[14] The calculated uptake of CO_2 from the atmosphere is lower across the entire route in the recent years than in the mid-1990s (Figure 5). On average, the uptake decreased by $1.2 \text{ mol m}^{-2} \text{ a}^{-1}$ (range from 0.54 to $2.1 \text{ mol m}^{-2} \text{ a}^{-1}$) from the mid-1990s to 2002/2005. A statistical analysis of the significance of this decrease was made as follows. In each $10^\circ \times 5^\circ$ grid box, air-to-sea flux and $\Delta p\text{CO}_2$ were used to test the null hypothesis that the 1994–1995 data are from the same population as sampled by the 3 years of 2002–2005 data (thus $n = 4$), using a two-tailed t-test. Considering annual averages, the hypothesis is rejected at $p = 0.1$ for fluxes and at 0.2 for $\Delta p\text{CO}_2$ everywhere on the band. At $p = 0.05$, it is rejected at all longitudes east of 55°W and accepted at the remaining grid boxes for fluxes; it is rejected at all longitudes east of 35°W , and half of those west of it, for $\Delta p\text{CO}_2$. Thus in the temperate/subpolar region, the mid-1990s $\Delta p\text{CO}_2$ and fluxes both fall outside the populations sampled by the 2002–2005 data with 95% confidence. Over the route as a whole, this statement holds with 90% confidence for fluxes and with 80% confidence

for $\Delta p\text{CO}_2$. Hence we conclude there is interdecadal decline in addition to the interannual variability sampled to date by the early 2000s data, and that this is particularly significant in the temperate/subpolar region of the route. As another illustration of the statistical significance of the interdecadal change, the mean decrease in flux across the region ($1.23 \text{ mol m}^{-2} \text{ a}^{-1}$) is 6.5 times the average of the standard deviations of the annual fluxes in 2002/2005.

[15] The interannual variability tends to be in phase across the region, with for instance, fluxes and $\Delta p\text{CO}_2$ lowest at all locations in 2002/2003 and increasing monotonically at most locations through the subsequent 2 years. This observation, and the interdecadal decline, both point to the control of the air-sea flux by large-scale effects with multiannual timescales, such as the North Atlantic Oscillation and similar climate indices.

[16] The effects of changes in SST and surface wind speeds on the fluxes were investigated as possible causes of the trends observed. In the temperate/subpolar region in particular, there has been an increase in SST between the two periods being considered. In Figures 4 and 5b we include the effect of recalculating the mid-1990s $\Delta p\text{CO}_2$ and fluxes after adjusting surface $p\text{CO}_2$ for the difference in temperature from 1994/95 to 2002/2005 as described above for Figure 3. The thermodynamic effect of temperature on $\Delta p\text{CO}_2$, and hence on fluxes, accounts for $\sim 30\%$ of the difference between the mid-1990s and the recent data in the temperate/subpolar region, but has much less effect in the subtropical region.

[17] To estimate the effect of changes in wind speed (shown in auxiliary material Figure S5), we recalculated the 2002/2005 fluxes by using the 2002/2005 $\Delta p\text{CO}_2$ and 2002/2005 SST with the 1994/1995 wind speeds. The gas transfer velocities K_j were those calculated in the equivalent month for the year 1994–1995. Thus each point is given by $\frac{1}{36} \sum_{j=1}^{n=36} K_j \times \bar{s}_i \times \overline{\Delta p\text{CO}_{2i}}$ where i runs from 1 to 36 while j runs 1–12, 1–12:1–12. The results, indicated as a thin black line with diamonds in Figure 5b, show little effect on the annually averaged air-to-sea fluxes. Also shown for comparison, in Figure 5a (black squares) are the fluxes from the $p\text{CO}_2$ climatology of Takahashi *et al.* [2002] referenced to 1995 (the data used were obtained from <http://www.ideo.columbia.edu/res/pi/CO2/> and supersede those in the original paper). Each of these points was calculated by averaging points in the 4-by-5 degrees grid of Takahashi that fell within each of our grid boxes shown in Figure 1. The agreement with our 1994/1995 data is good, but since our 1994/1995 observations are included in the climatological database, these two estimates are not fully independent.

[18] To estimate the effect of changes in barometric pressure (shown in auxiliary material Figure S6), we recalculated the 1994/1995 fluxes by using the 1994/1995 SST, 1994/1995 wind speed, and $\Delta p\text{CO}_2$ resulting from 1994/1995 sea surface $p\text{CO}_2$ minus atmospheric $p\text{CO}_2$ calculated using the 2002/2005 barometric pressure. Barometric pressure changes from the mid-1990s to the early 2000s were within the interannual variability, i.e., not significant, except in spring in the subtropical/tropical region (auxiliary material Figure S6). The effect in the 1994/1995 fluxes is small and not significant (results not shown).

[19] Our observations can be compared with other sources of information on the secular variation of sea surface $p\text{CO}_2$. In the North Atlantic subpolar gyre, Lefèvre *et al.* [2004] observed a mean increase of $1.8 \mu\text{atm a}^{-1}$ between 1982 and 1998. In the eastern subpolar gyre, Omar and Olsen [2006] reconstructed a mean increase of $3.0 \mu\text{atm a}^{-1}$ between 1972 and 1989, while in the western subpolar gyre, utilizing a shipping route from Iceland to Newfoundland, Corbière *et al.* [2007] calculate, from DIC and alkalinity data, an increase wintertime sea surface $p\text{CO}_2$ of $3.0 \mu\text{atm a}^{-1}$ between 1994 and 2003, which they relate predominantly to increasing SST. In the temperate/subpolar regions, a year of measurements during 2002 on a commercial vessel operating between Europe and New York, compared with climatology referenced to 1995, showed a mean rate of sea surface $p\text{CO}_2$ increase of $3.6 \mu\text{atm a}^{-1}$ from 1995 to 2002 in the east, but a change approximately tracking the atmosphere ($1.7 \mu\text{atm a}^{-1}$) in the west [Lüger *et al.*, 2004, 2006]. Measurements at the Bermuda Atlantic Time Series (BATS) station at $31^\circ 43' \text{N}$, $-64^\circ 30' \text{E}$, also show surface $p\text{CO}_2$ increasing in parallel the atmosphere in the long-term average [Bates *et al.*, 1996], but interannual changes there have been correlated to the North Atlantic Oscillation (NAO) [Gruber *et al.*, 2002]. These authors speculated that the entire North Atlantic sink might vary in concert with the NAO. Observations in the North Pacific also suggest a link between climate indices and CO_2 uptake. For the North Pacific as a whole [Takahashi *et al.*, 2006] report a mean rate of $p\text{CO}_2$ increase of $1.3 \pm 0.2 \mu\text{atm a}^{-1}$ for the 35-yr period 1970–2004, indistinguishable from the rate of increase in atmospheric $p\text{CO}_2$. However, near Station ALOHA, Keeling *et al.* [2004] observed an increase of sea surface $p\text{CO}_2$ of $1.4 \pm 0.2 \mu\text{atm a}^{-1}$ from 1988 to 1996, but a higher increase of $3.2 \pm 0.4 \mu\text{atm a}^{-1}$ from 1997 to 2002 probably related to changes in the Pacific Decadal Oscillation.

[20] Figure 6 summarizes changes from the mid-1990s to early 2000s in the North Atlantic along five sections of shipping routes and at the BATS station (locations are shown in Figure 6a). Figure 6b plots the change between these two periods of annual average sea surface $p\text{CO}_2$ against change in SST, while Figure 6c shows change in estimated air-to-sea flux against the same variable. Data sources are: (1) and (2) this paper; (3) Corbière *et al.* [2007]; (4) and (5) Lüger *et al.* [2004, 2006]; (6) Gruber *et al.* [2002]. Measurements in the early 2000s were made in the following periods: (1) and (2) 2002/2005; (3) 2002/2003; (4) and (5) 2002, and (6) 2000/2001. Earlier reference times are for the year 1994/1995. No earlier measurements are available on the route of Lüger *et al.*, so (4) and (5) are referred to climatological fluxes [Takahashi *et al.*, 2002]. The thick black line in the inset map marks the approximate boundary between the region of decline and that of no change or some increase in the flux. SST changes have been derived from NCEP/NCAR reanalysis averages over the appropriate periods.

[21] While no clear relationship emerges that is applicable across the whole region to relate either sea surface $p\text{CO}_2$ or fluxes to SST anomalies, these comparisons confirm a concerted change across large subregions. Sea surface $p\text{CO}_2$ increased and air-to-sea fluxes declined from the mid-1990s to early 2000s in all the northern/eastern regions

and in the western tropics (points 1 to 4 in Figure 6) while pCO₂ tracked the atmosphere and there was no change or a somewhat opposite trend in the northwestern subtropics (points 5 and 6 in Figure 6).

[22] The NAO has an effect on SST, wind speed and winter mixed layer depth [Marshall *et al.*, 2001]. A fall in NAO index is associated with positive temperature anomalies, reduced storm activity and hence a weaker seasonal cycle in mixed layer depth in the subpolar gyre, and might be expected to decrease the CO₂ uptake from the atmosphere in those regions and weaken the seasonal cycle of CO₂ fluxes. In the northwestern subtropical North Atlantic, a fall in NAO index is associated with negative anomalies in SST, where the Gulf Stream shifts northward

in response to a positive NAO [Marshall *et al.*, 2001], and might be expected to correlate with anomalies in the CO₂ uptake in the opposite sense there. Though the records plotted in Figure 6 are too short to rigorously test the hypothesis of NAO control of the sink, the wintertime NAO index declined markedly from the early 1990s to the 2002–2005 (<http://www.cru.uea.ac.uk/cru/data/nao.htm>), so a connection between positive NAO and higher uptake is consistent. Such a trend seems to be observable in the atmospheric inverse analyses of Patra *et al.* [2005], covering the period 1988–2001. These authors calculated a flux into the northern North Atlantic with a strong positive correlation to the wintertime NAO ($r = 0.71$), for the region north of 50°N. The correlation was much weaker ($r = 0.14$) in the latitude band south of this, but this may reflect the fact that the in situ observations indicate that only the eastern part of this region is varying in phase with the NAO. The general decline in the North Atlantic sink in this region does not seem to be evident in their atmospherically derived fluxes however, though a direct comparison is difficult because their analysis finishes in the year 2002. Also, the strongest correlation Patra *et al.* find of the flux with the NAO in a region between 30°N and 50°N is a negative one, when the flux is lagged by 7 months from the wintertime NAO, and this also does not seem to be supported by the in situ data summarized in Figure 6.

[23] The annual decrease of the North Atlantic uptake of atmospheric CO₂, estimated from results plotted in Figure 6c is $\sim 1.1 \text{ mol m}^{-2} \text{ a}^{-1}$ from the mid-1990s to 2002–2004. This applies to an area of $1.8 \times 10^{13} \text{ m}^2$ of the North Atlantic between 20°N and 65°N, excluding the western subtropics. This equates with a reduction of $\sim 0.24 \text{ Pg C a}^{-1}$ in the uptake, a value on which we can assign an error bar of $\pm 0.1 \text{ Pg a}^{-1}$ if we take the standard deviation of points 1–4 in Figure 6 as indicative of the uncertainty. For comparison, climatological data [Takahashi

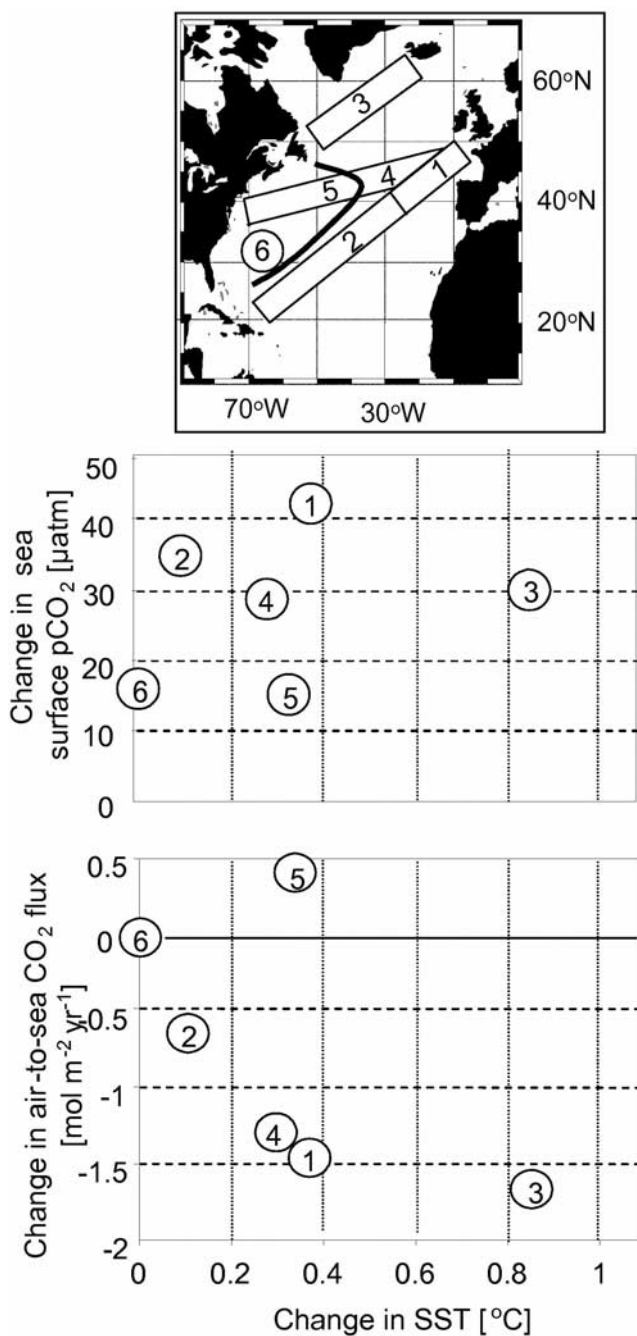


Figure 6. Summary of changes in annual sea surface pCO₂ (µatm) and calculated fluxes (mol m⁻² a⁻¹), versus change in annual mean SST, from mid-1990s to early 2000s. Figure 6a shows the locations of the studies, along five sections of shipping routes and at the BATS station. Data sources are: (1) and (2), this paper; (3), Corbière *et al.* [2007]; (4) and (5), Lüger *et al.* [2004, 2006]; and (6), Gruber *et al.* [2002]. Temperature change was calculated using NCEP-NCAR reanalysis averages for the appropriate periods. CO₂ measurements in the early 2000s were made: (1) and (2), 2002/2005; (3), 2002/2003; (4) and (5), 2002; and (6), 2000/2001. Earlier reference times are for the year 1994/1995; measurements were not being made by Lüger *et al.*, during that earlier period, so sources (4) and (5) are referred to climatological fluxes [Takahashi *et al.*, 2002]. The change in air-to-sea flux and SST are those observed from the mid-1990s to the earlier 2000s for each study; a positive change in air-to-sea flux depicts an increase in the uptake of CO₂ by the sea surface, and a positive change in SST depicts a warming. The thick black line in the inset map marks the approximate boundary between the region of decline in flux and that of no change or some increase in the flux.

et al., 2002] give an integrated sink for this region of $\sim 0.4 \text{ Pg a}^{-1}$. For the whole North Atlantic, atmospheric inversion models suggest large variations (up to 0.4 Pg a^{-1} [Bousquet *et al.*, 1999]) but with large uncertainties, while extrapolation of the interannual variation at the BATS site [Gruber *et al.*, 2002] was used to suggest variability of 0.3 Pg a^{-1} . By contrast, “ocean-only” carbon models [Buitenhuis *et al.*, 2006; Le Quéré *et al.*, 2000] currently model an increasing sink through this period due to the increasing atmospheric CO₂, with interannual variability considerably less than 0.1 Pg C a^{-1} .

[24] During the last decade there has been a sharp decrease in the intensity of the subpolar gyre circulation [Häkkinen and Rhines, 2004], indicative of decreased formation of dense water in winter in northern regions, with ongoing freshening and warming of waters in the northern North Atlantic [Curry *et al.*, 2003; Dickson *et al.*, 2002] that would enhance the degree of stratification seen there. The decrease in the polar gyre is tied to reduced heat loss in the northern North Atlantic [Curry *et al.*, 2003; Dickson *et al.*, 2002], itself part of the pattern of declining NAO index during this period. There is a direct proportionality between rates of heat loss of the North Atlantic and the major component of the CO₂ uptake by the region [Watson *et al.*, 1995], so we might predict from first principles that this would be accompanied by a decrease in CO₂ uptake. There are also tentative indications of a slowing of the meridional overturning circulation [Bryden *et al.*, 2005] which, if correct, would further tend to decrease the uptake of CO₂ [Sarmiento and Le Quéré, 1996].

[25] Reduction in the activity of the subpolar gyre led to its contraction from the mid-1990s onward, with expansion northward of the temperate and subtropical waters especially on the eastern side of the Atlantic [Hátún *et al.*, 2005]. As a result, we might expect much of our study region to become more dominated by recirculated temperate and subtropical waters than was the case in 1994/1995. This recirculated water has resided for a comparatively long period at the surface and is more equilibrated with the atmosphere than during the periods of stronger subpolar gyre activity. The substantial rise in sea surface pCO₂ we observe also means that the Revelle buffer factor for the surface water will have increased (for instance by about 5% for a $40 \mu\text{atm}$ increase such as we observe, if the alkalinity remains constant), helping to reduce the capacity of the water to take up CO₂ from the atmosphere. Finally, as Olsen *et al.* [2006] discuss, in a region such as the North Atlantic in which the buffer factor increases as water is transported to the north and where the atmospheric CO₂ is rising, an uptake sufficient for the surface to track the atmospheric rise at southerly latitudes will cause pCO₂ to rise faster than the atmosphere further to the north. In conjunction with changes in transport and ventilation acting in the same direction, it may further amplify the increase observed, at least in the temperate and subpolar part of the study region.

[26] Therefore we conclude that the observed changes in surface temperature and ventilation of the North Atlantic offer a probable explanation for the reduction in the CO₂ sink now being observed there, exacerbated by changes in the buffer capacity of the surface water. Though these changes are in the same direction as those seen in coupled models of anthropogenically forced climate change and

probably include a component due to this cause, they are probably also related to natural, decadal-to-century length variations of the North Atlantic general circulation, coupled to variation in atmospheric forcings as embodied in the NAO index.

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