A variable and decreasing sink for atmospheric CO_2 in the North Atlantic

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Abstract

A time series of observations from merchant ships between the UK and the Caribbean is used to establish the variability of sea surface pCO_2 and air-to-sea flux from the mid-1990s to early 2000s. We show that the sink for atmospheric CO_2 exhibits important inter-annual variability, which is in phase across large regions from year to year. Additionally, there has been an inter-decadal decline, evident throughout the study region but especially significant in the northeast of the area covered, with the sink reducing >50% from the mid-nineties 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^{o} and 65^{o}N declined by ~0.24 Pg C yr^{-1} from 1994/1995 to 2002-2005. Declining rates of winter-time 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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Introduction

The world's oceans are an important sink for atmospheric CO_2. 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 CO_2 is driven by ΔpCO_2, the difference between atmospheric and sea surface partial pressures of carbon dioxide (pCO_2). Sea surface pCO_2 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 CO_2 uptake is highest in temperate and subpolar waters where seasonal deep mixing and sub-surface 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 CO_2 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 CO_2 before mixing and sinking to depth in winter-time, and to efficient biological uptake of nutrients and carbon.

There are indications of substantial variability in the uptake of CO_2 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 CO_2 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.

Methods

The measurements

Direct, quasi-continuous autonomous measurements of SST and pCO_2 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 re-started 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 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.

Some differences from the system of Cooper et al have since been incorporated, as follows: A peristaltic pump now regulates the seawater flow to the equilibrator at approximately 3 litres 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 re-calibrated 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 ^{o}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 ~ 5^{o}C prior to the infra-red 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.

Routine measurement of CO_2 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 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 pCO_2 differences. Instead the air-side pCO2 was derived from monthly averages of mixing ratios from [*GLOBALVIEW* CO_2, 2006] for both the 1994/95 period and the 2002/05 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 pCO_2.

Data reduction

Calculation of sea surface pCO_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 xCO_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 xCO_2 in dry air, since a Li7000, used since 2002, does not internally correct for water vapor dilution. True xCO_2 was calculated by correcting this for detector drift, applying a linear interpolation between secondary gas standard concentrations. Equilibrator pCO_2 was found by correcting the true xCO_2 to 100% humidity at equilibrator temperature and pressure, using the saturated water vapour pressure appropriate to sea water given by [*Cooper, et al.*, 1998]: $pH_2O = 0.981 \exp(14.32602 - 5306.83 / (SST\,[Kelvin])$. The in situ sea surface pCO_2 was then calculated by correcting the equilibrator pCO_2 for the difference ΔT between in situ and equilibrator temperature, applying the relationship given by [*Takahashi, et al.*, 1993]: $pCO_2(insitu) = pCO_2(equ) \exp(-0.0423\,\Delta T)$.

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 pCO_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 where 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 2006JC003941_fs03ab) by repeating the analysis with a narrower, 5° wide band centered on the line. This results in better co-location 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.

Atmospheric pCO_2 values were calculated from the monthly, latitudinal atmospheric xCO_2 values given by [*GLOBALVIEW-CO_2*, 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 pCO_2 values by using NCEP/NCAR re-analysis estimates of barometric pressure and SST (6-hourly and 2.5° x 2.5° resolution, [*Kalnay, et al.*, 1996], also averaged onto the same time- space grid). The ΔpCO_2 was then calculated as atmospheric pCO_2 minus sea surface pCO_2 (note a positive ΔpCO_2 therefore depicts an uptake of CO_2 by the ocean surface). A Hovmüller plot of the gridded ΔpCO_2 is shown in Figure 2, together with the color-coded values and position of the 1^o x 1^o-binned data. Similar plots for SST and sea surface pCO2 are included in the Auxiliary Material (Figures 2006JC003941_fs01 and 2006JC003941_fs02). The gridded sea surface pCO_2 and ΔpCO_2 were then further averaged into two regions:

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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 pCO_2 along the route for the different periods, while Figures 3B and 3C show the annual pCO_2 cycle in the temperate/ subpolar region and the subtropical/tropical region respectively. Figures 4A, B, C show the equivalent plots for ΔpCO_2.

Flux calculations.

Air-to-sea fluxes of CO_2 were calculated from the ΔpCO_2 values obtained above, using the time and area averaged gas exchange equation [*Wanninkhof, et al.*, 2002; *Watson and Orr*, 2003]:

$$\overline{K} \times \overline{s} \times \overline{\Delta pCO_2}$$

where $\overline{K}$ and $\overline{s}$ are the mean gas transfer velocity and solubility for each grid box and month, calculated from NCEP/NCAR, 2.5° x 2.5° x 6-hourly re-analysis data [*Kalnay, et al.*, 1996], averaged onto the same time- space grid as ΔpCO_2. The Wanninkhof gas transfer parameterization for short-term winds [*Wanninkhof*, 1992] was used, $K = 0.31\left(Sc/660\right)^{-0.5} U^2$, where U is the wind speed at 10m height, and Sc the Schmidt number for CO_2 in sea water. $\overline{\Delta pCO_2}$ 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 due to covariance of K, s and ΔpCO_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 non-linearity 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.

Results and Discussion

Sea surface pCO_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 pCO_2 increased by 37 μatm from 328 μatm in 1994/95 to 365 μatm in 2002/05, a mean increase of 4.4 μatm $year^{-1}$ if a linear trend is assumed. The seasonal cycle of sea surface pCO_2 also changed in both the temperate/subpolar region (Figure 3B), and the tropical/subtropical region (Figure 3C). In the former, seawater pCO_2 showed a strong minimum in spring and summer in the mid-nineties, due to biological carbon uptake reducing sea-surface pCO_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 pCO_2. Here too, the amplitude of the seasonal cycle decreased from the mid-nineties to the recent past.

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The effect of changes in SST (shown in Auxiliary Material 2006JC003941_fs04) was investigated as a possible cause of the pCO_2 trends, as follows. Assuming no change in salinity, alkalinity, and total CO_2 concentration, sea-surface pCO_2 increases by 4.23% $^oC^{-1}$ [*Takahashi, et al.*, 1993]. In Figure 3 (thin lines with open circles) we include the effect of re-calculating the mid-nineties sea surface pCO_2, accounting for the difference in temperature from 1994/95 to 2002/05 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 pCO_2 between the mid-nineties 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.

Atmospheric pCO_2 also increased from the mid-1990s to the early 2000s, by a mean of 1.8 μatm year^{-1} between 20 and 50^o N [*GLOVALVIEW-CO2*, 2006]. The resulting ΔpCO_2 (atmospheric pCO_2 – sea surface pCO_2, Figure 4A) reduced by 21 μatm, from 26 μatm in the mid-1990s to 5 μatm in the early 2000s, or by 2.5 μatm year^{-1} if a linear trend is assumed. The seasonal cycles of ΔpCO_2 also changed, with the seasonal amplitude being reduced in both the temperate/subpolar region (Figure 4B) and the tropical/subtropical region (Figure 4C).

The calculated uptake of CO_2 from the atmosphere is lower across the entire route in the recent years than in the mid-nineties (Figure 5). On average, the uptake decreased by 1.2 mol m^{-2} year^{-1} (range from 0.54 to 2.1 mol m^{-2} year^{-1}) from the mid-nineties to 2002/05.

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A statistical analysis of the significance of this decrease was made as follows. In each 10^o x 5^o grid box, air-to-sea flux and ΔpCO_2 were used to test the null hypothesis that the 1994-1995 data are from the same population as sampled by the three 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 ΔpCO_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 ΔpCO_2. Thus in the temperate/subpolar region, the mid-nineties ΔpCO_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 ΔpCO_2. Hence we conclude there is inter-decadal decline in addition to the inter-annual 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 inter-decadal change, the mean decrease in flux across the region (1.23 mol m^{-2} yr^{-1}) is 6.5 times the average of the standard deviations of the annual fluxes in 2002/5.

The inter-annual variability tends to be in phase across the region, with for instance, fluxes and ΔpCO_2 lowest at all locations in 2002/3 and increasing monotonically at most locations through the subsequent two years. This observation, and the inter-decadal decline, both point to the control of the air-sea flux by large-scale effects with multi-annual time scales, such as the North Atlantic Oscillation and similar climate indices.

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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 re-calculating the mid-nineties ΔpCO2 and fluxes after adjusting surface pCO_2 for the difference in temperature from 1994/95 to 2002/05 as described above for Figure 3. The thermodynamic effect of temperature on ΔpCO_2, and hence on fluxes, accounts for ~30% of the difference between the mid-nineties and the recent data in the temperate/subpolar region, but has much less effect in the subtropical region.

To estimate the effect of changes in wind speed (shown in Auxiliary Material 2006JC003941_fs05), we re-calculated the 2002/05 fluxes by using the 2002/05 ΔpCO_2 and 2002/05 SST with the 1994/95 wind speeds. The gas transfer velocities K_j were those calculated in the equivalent month for the year 1994-95. Thus each point is given by $\frac{1}{36}\sum_{1}^{n=36}\overline{K_j} \times \overline{s_i} \times \overline{\Delta pCO_{2i}}$ 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 5Aa (black squares) are the fluxes from the pCO_2 climatology of [*Takahashi et al.* 2002] referenced to 1995 (the data used were obtained from http://www.ldeo.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 1994/95 data is good, but since our

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1994/1995 observations are included in the climatological data base, these two estimates are not fully independent.

To estimate the effect of changes in barometric pressure (shown in Auxiliary Material 2006JC003941_fs06), we re-calculated the 1994/95 fluxes by using the 1994/95 SST, 1994/95 wind speed, and ΔpCO2 resulting from 1994/95 sea surface pCO_2 minus atmospheric pCO_2 calculated using the 2002/05 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 2006JC003941_fs06). The effect in the 1994/95 fluxes is small and not significant (results not shown).

Our observations can be compared with other sources of information on the secular variation of sea surface pCO_2. In the North Atlantic subpolar gyre, [*Lefèvre, et al.*, 2004] observed a mean increase of 1.8 μatm $year^{-1}$ between 1982 and 1998. In the eastern subpolar gyre, [*Omar and Olsen*, 2006] reconstructed a mean increase of 3.0 μatm $year^{-1}$ between 1972 and 1989, whilst in the western subpolar gyre, utilized a shipping route from Iceland to Newfoundland [*Corbière, et al.*, 2007] calculate, from DIC and alkalinity data, an increase winter-time sea surface pCO_2 of 3.0 μatm $year^{-1}$ 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 pCO_2 increase of 3.6 μatm $year^{-1}$ from 1995 to 2002 in the east, but a

change approximately tracking the atmosphere (1.7 μatm year^{-1}) in the west [*Lüger, et al.*, 2004; *Lüger, et al.*, 2006]. Measurements at the Bermuda Atlantic Time Series (BATS) station at 31°40'N, 64°E, also show surface pCO_2 increasing in parallel the atmosphere in the long term average [*Bates, et al.*, 1996], but inter-annual 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 pCO_2 increase of 1.3 ± 0.2 μatm year^{-1} for the 35-year period 1970-2004, indistinguishable from the rate of increase in atmospheric pCO_2. However, near Station ALOHA, [*Keeling, et al.*, 2004] observed an increase of sea surface pCO_2 of 1.4 ± 0.2 μatm year^{-1} from 1988 to 1996, but a higher increase of 3.2 ± 0.4 μatm year^{-1} from 1997 to 2002 probably related to changes in the Pacific Decadal Oscillation.

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 pCO_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) 2002/05; (3) 2002/03; (4) and (5) 2002, and (6) 2000/01. Earlier reference times are for the year 1994/1995. No earlier measurements are available on the route of Lüger et al., so

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(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 re-analysis averages over the appropriate periods.

While no clear relationship emerges that is applicable across the whole region to relate either sea surface pCO_2 or fluxes to SST anomalies, these comparisons confirm a concerted change across large sub-regions. Sea surface pCO_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) whilst pCO_2 tracked the atmosphere and there was no change or a somewhat opposite trend in the north-western subtropics (points 5 and 6 in Figure 6).

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 CO_2 uptake from the atmosphere in those regions and weaken the seasonal cycle of CO_2 fluxes. In the north-western 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 CO_2 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 winter-time NAO index declined

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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 - 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.

The annual decrease of the North Atlantic uptake of atmospheric CO_2, estimated from results plotted in Figure 6c is ~ 1.1 mol m^{-2} yr^{-1} from the mid-nineties to 2002-2004. This applies to an area of 1.8×10^{13} m^2 of the North Atlantic between 20^oN and 65^oN, excluding the western subtropics. This equates with a reduction of ~0.24 Pg C yr^{-1} in the uptake, a value on which we can assign an error bar of $\pm$ 0.1 Pg yr^{-1} if we take the standard deviation of points 1-4 in Figure 6 as indicative of the uncertainty. For comparison, climatological data [*Takahashi, et al.*, 2002] give an integrated sink for this region of ~0.4 Pg yr^{-1}. For the whole North Atlantic, atmospheric inversion models

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suggest large variations (up to 0.4 Pg yr^{-1}, [*Bousquet, et al.*, 1999]) but with large uncertainties, while extrapolation of the inter-annual variation at the BATS site [*Gruber, et al.*, 2002] was used to suggest variability of 0.3 Pg yr^{-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 CO_2, with interannual variability considerably less than 0.1 Pg C yr^{-1}.

During the last decade there has been a sharp decrease in the intensity of the sub-polar gyre circulation [*Häkkinen and Rhine*, 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 CO_2 uptake by the region [*Watson, et al.*, 1995], so we might predict from first principles that this would be accompanied by a decrease in CO_2 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 CO_2 [*Sarmiento and LeQuéré*, 1996].

Reduction in the activity of the subpolar gyre led to its contraction from the mid-nineties onwards, with expansion northward of the temperate and subtropical waters especially on

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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 1994/95. 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 pCO_2 we observe also means that the Revelle buffer factor for the surface water will have increased (for instance by about 5% for a 40 μatm increase such as we observe, if the alkalinity remains constant), helping to reduce the capacity of the water to take up CO_2 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 CO_2 is rising, an uptake sufficient for the surface to track the atmospheric rise at southerly latitudes will cause pCO_2 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.

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 CO_2 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

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the North Atlantic general circulation, coupled to variation in atmospheric forcings as embodied in the NAO index.

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Figure captions

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 centre of the band from which data were selected, and the grid along it marks the 10^o x 5^o areas used for averaging data. The thick green line depicts the border between the northeast temperate/subpolar and the southwest tropical/subtropical region.

Figure 2: Hovmüller plots of ΔpCO_2 [µatm] (defined as the atmosphere minus sea surface), for 1994/95 (top) and 2002/05 (bottom), calculated as described in the text.

Figure 3: Annual and monthly mean sea surface pCO_2 [µatm]. Annual means versus latitude or longitude of each grid box shown in Figure 1 (A), and monthly means averaged over the temperate/subpolar region (B) and the tropical/subtropical region (C). For the annual averages (A), the thick black line indicates averages of 1994/95, the thick grey line averages of 2002/05. The thin line with circles are the 1994/95 averages recalculated assuming constant alkalinity and total CO_2 content, but accounting for the change in SST between 1994/95 and 2002/05. The thin lines with other markers give the average for individual years (from March – February, diamonds for 2002/03, stars for 2003/04, squares for 2004/05). The horizontal arrows to the left of A indicate the annual means for 1994/95 at 328 µatm and for 2002/05 at 365 µatm. For the monthly means in the temperate/subpolar region (B; grid boxes east of 30^oW), the thick black line, the thick grey line, and the thin line with circles are the same as in A); 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.

Figure 4: Annual and monthly mean ΔpCO_2 [µatm]. Annual means versus latitude and longitude of each grid box shown in Figure 1 (A), and monthly means averaged over the temperate/subpolar region (B) and the tropical/subtropical region (C). Regions and color/symbol coding is the same as for Figure 3. The horizontal arrows to the left of A indicate the annual means for 1994/95 at 26 µatm and for 2002/05 at 5 µatm.

Figure 5: Annually mean air-to-sea fluxes [mol m^{-2} yr^{-1}] versus latitude and longitude for each grid box shown in Figure 1. Line patterns in A (left) is according to Figure 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/. In B, the annual averages of 1994/95 and 2002/05 are repeated, compared with 2002/05 fluxes re-calculated using 1994/95 wind speeds to calculate the gas transfer velocities as outlined in the text (thin black line with diamonds); and the 1994/95 fluxes with ΔpCO_2 adjusted to account for SST change from 1994.95 to 2002/05 (thin black lines with circles).

Figure 6: Summary of changes in annual sea surface pCO_2 [µatm] and calculated fluxes [mol m^{-2} yr^{-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*]; (6) [*Gruber et al., 2002*]. Temperature change was calculated using NCEP-NCAR re-analysis averages for the appropriate periods. CO_2 measurements in the early 2000s were made: (1) and (2) 2002/05; (3) 2002/03; (4) and (5) 2002; (6) 2000/01. Earlier reference times are for the year 1994/1995; measurements were not being made by Lüger et al., during that earlier period, so (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 CO_2 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.

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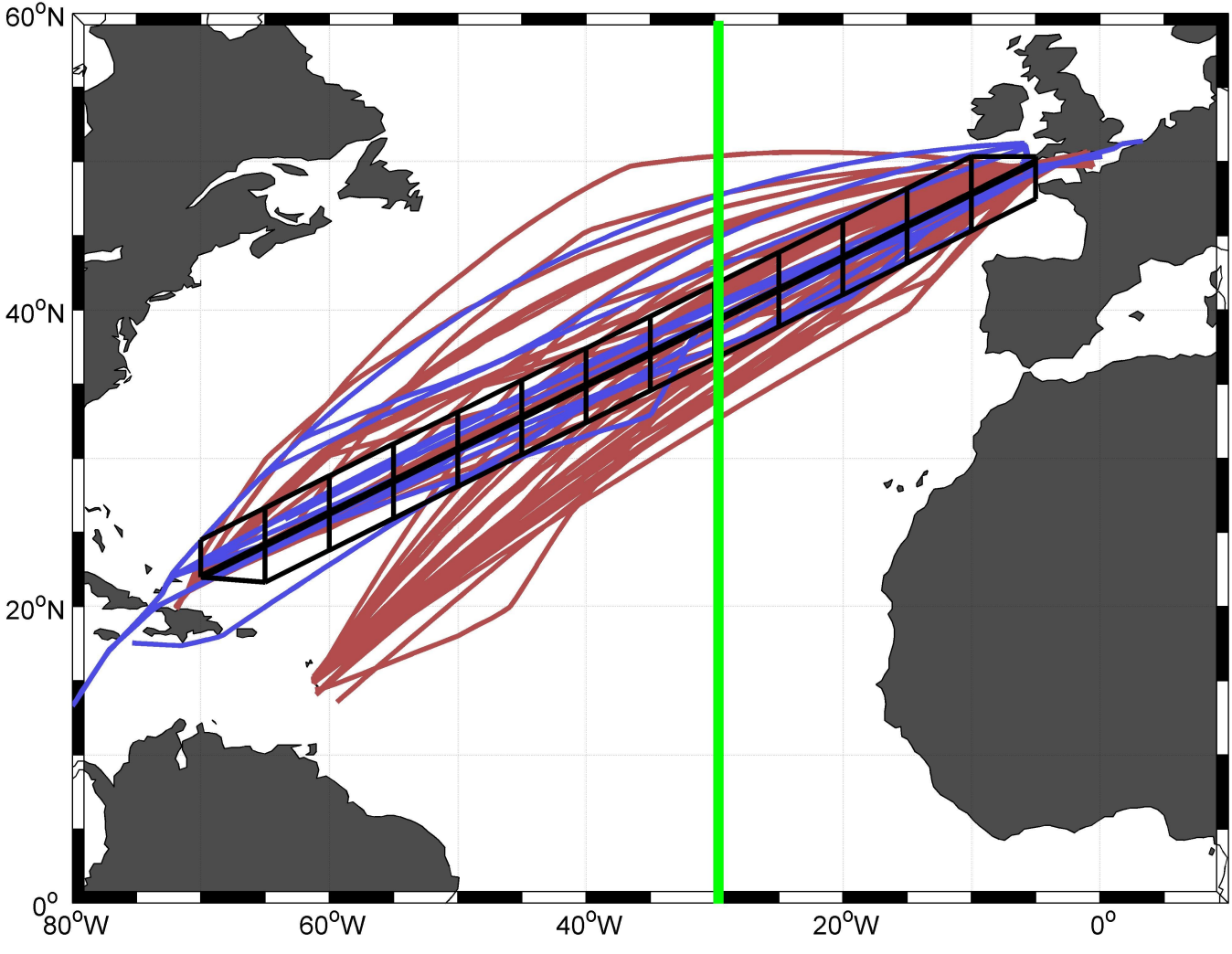
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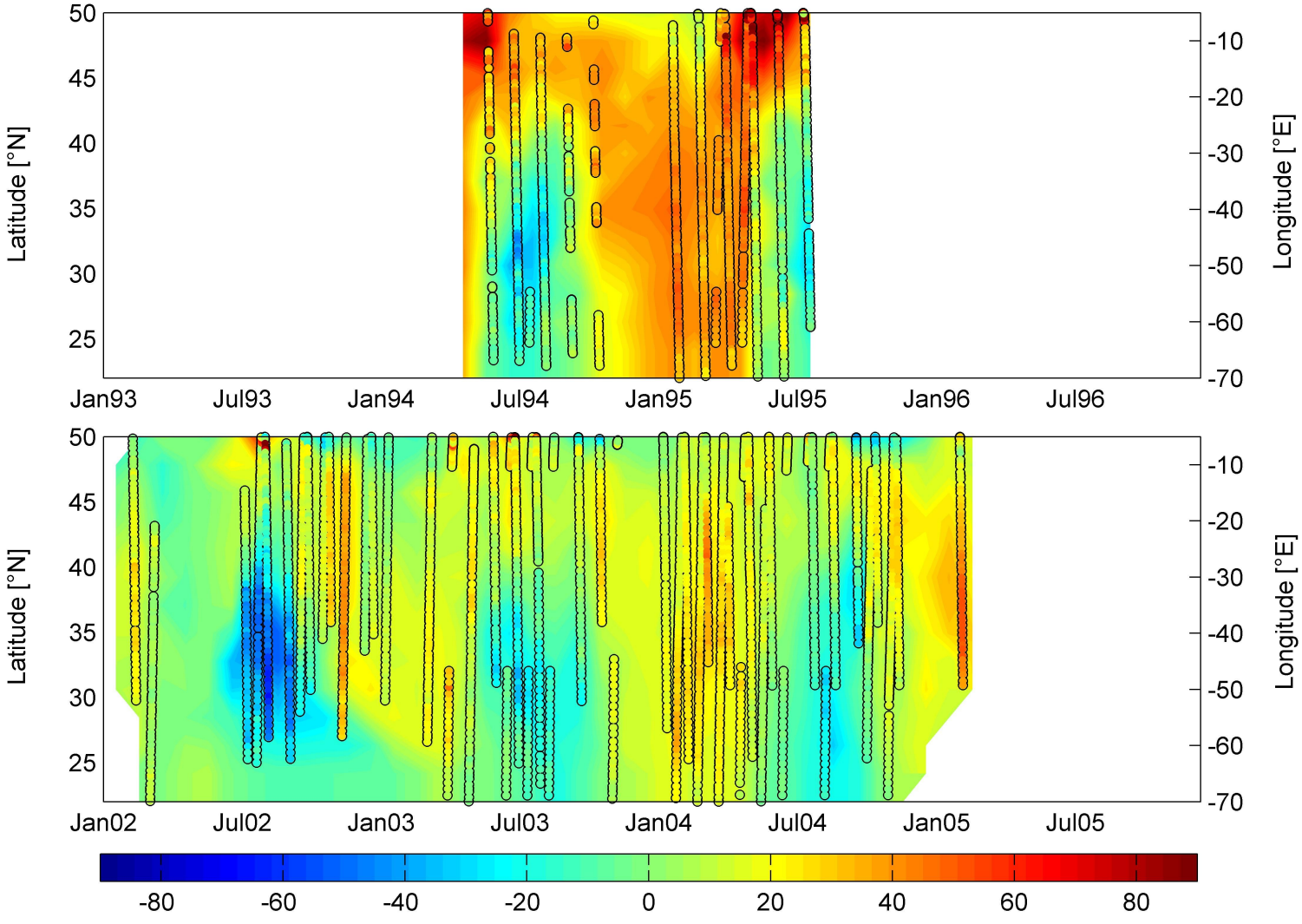
80°W
60°W
40°W
20°W
0°


Latitude [°N]
50
45
40
35
30
25
Longitude [°E]
-10
-20
-30
-40
-50
-60
-70
Jan93
Jul93
Jan94
Jul94
Jan95
Jul95
Jan96
Jul96
Latitude [°N]
50
45
40
35
30
25
Longitude [°E]
-10
-20
-30
-40
-50
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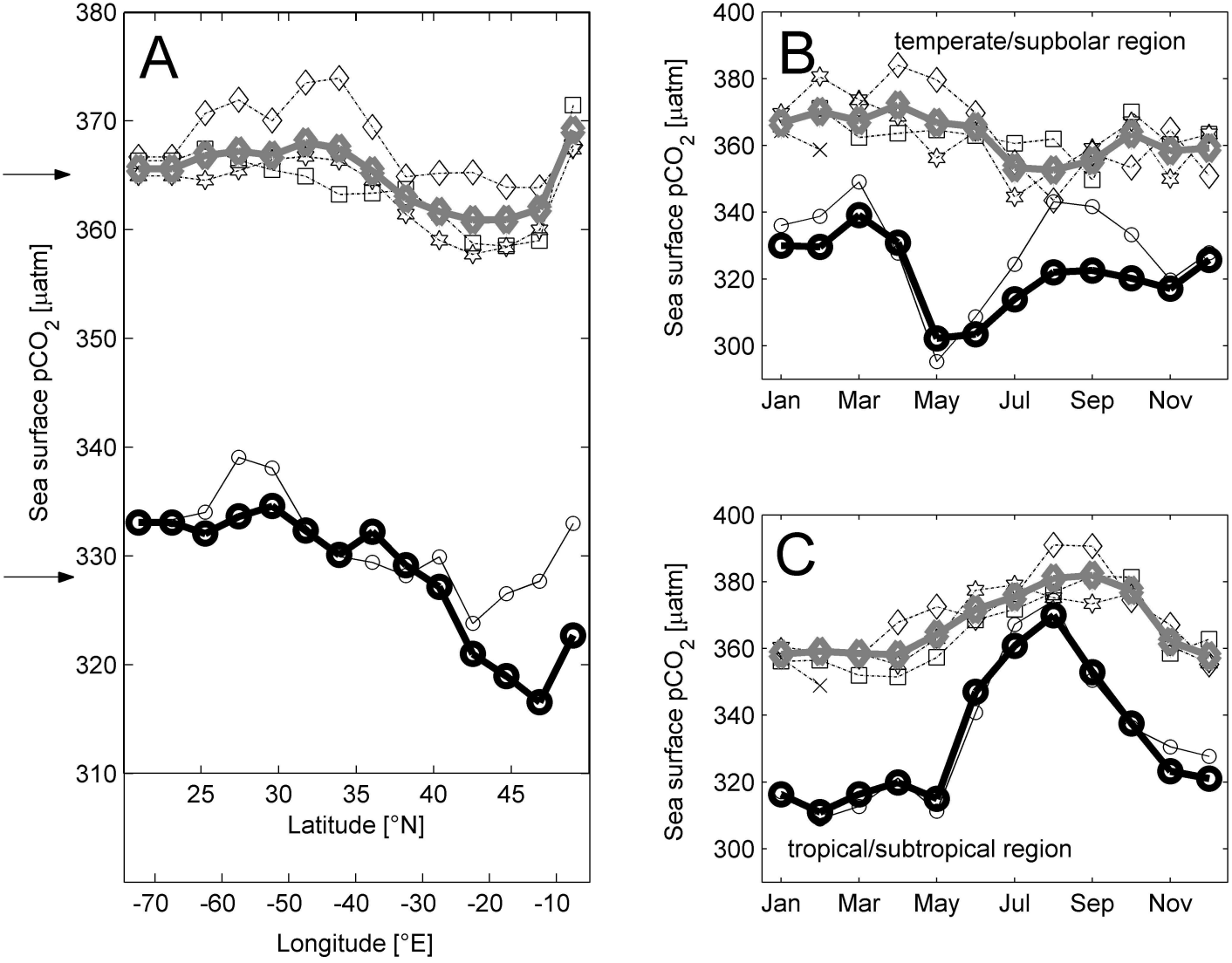
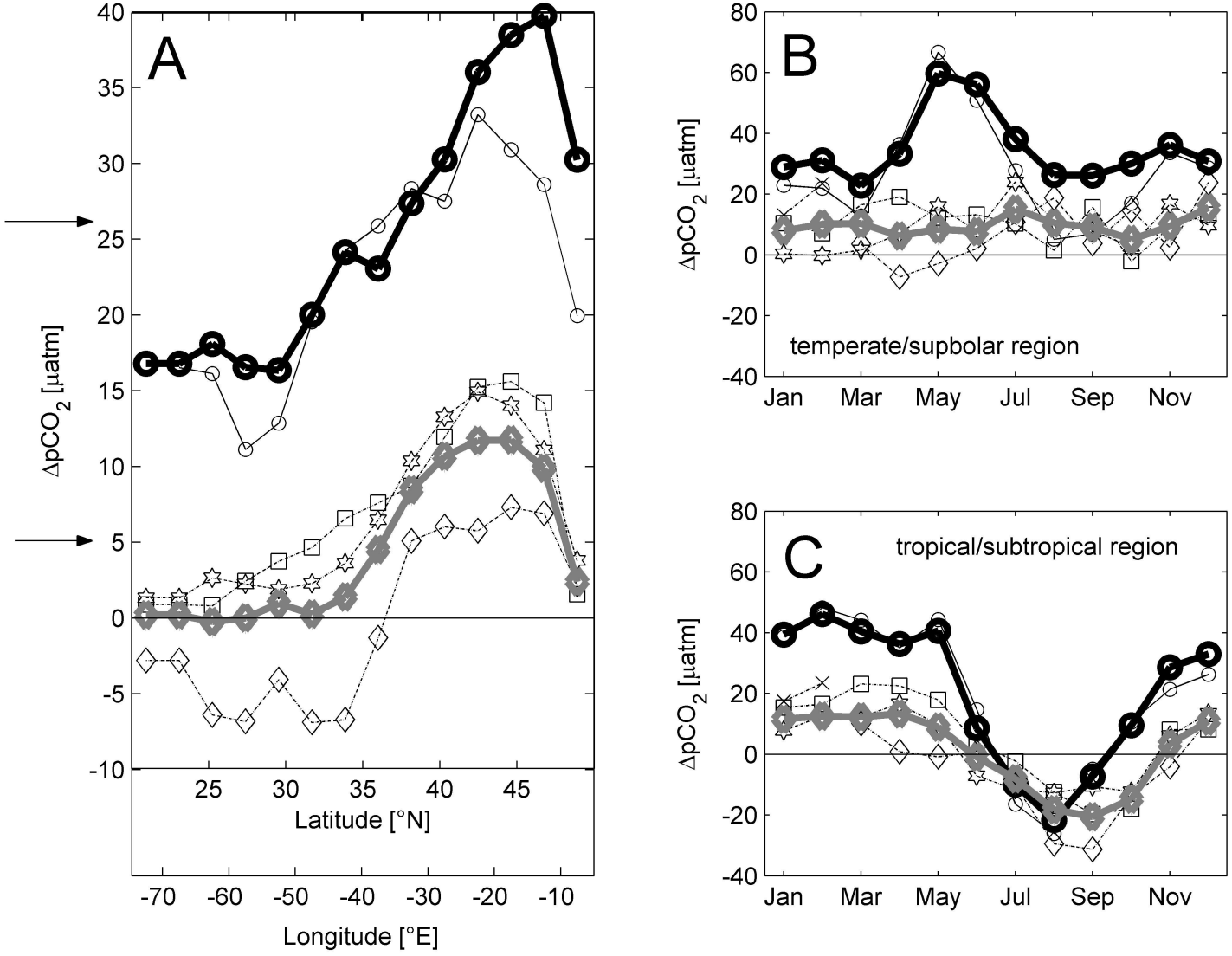
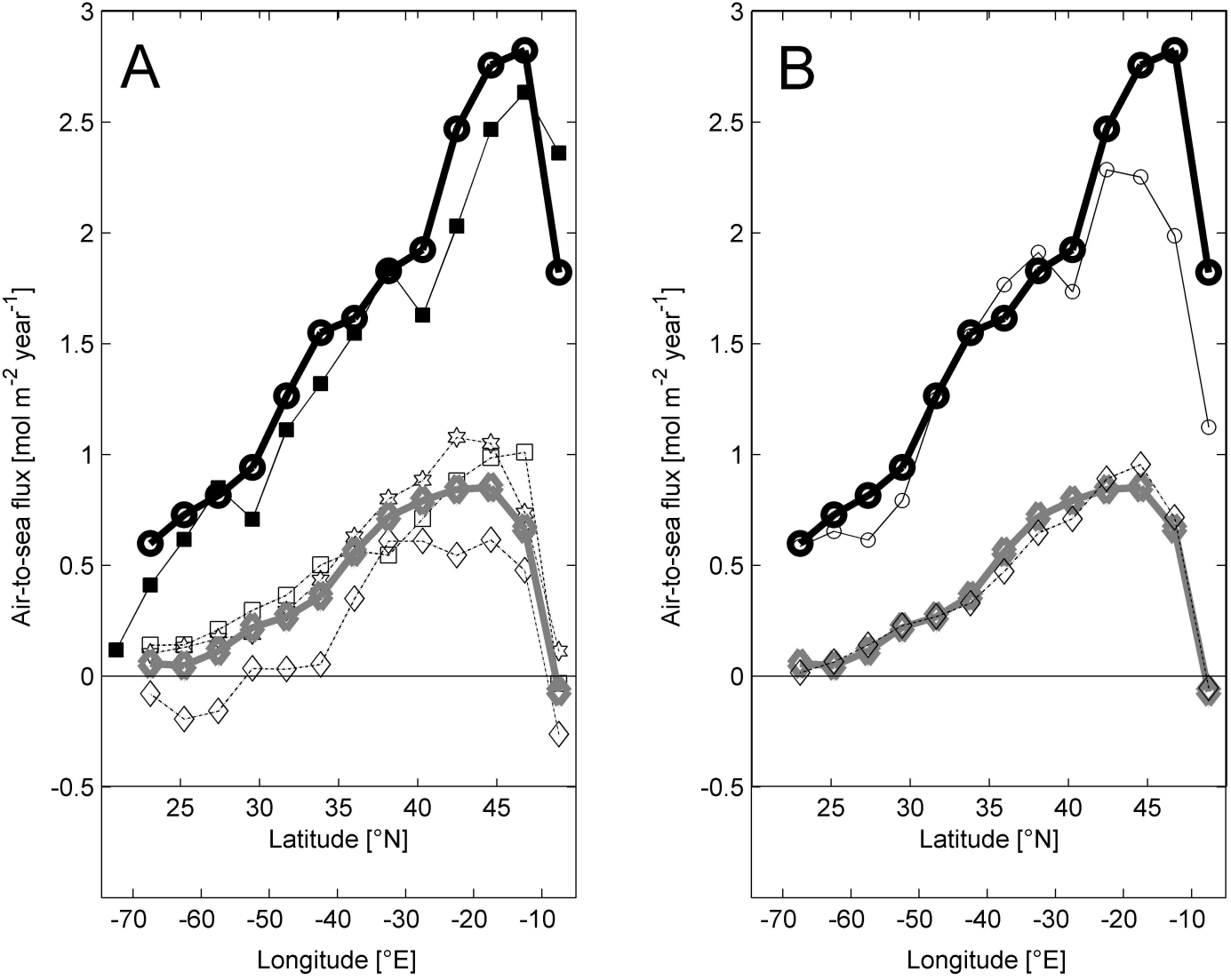
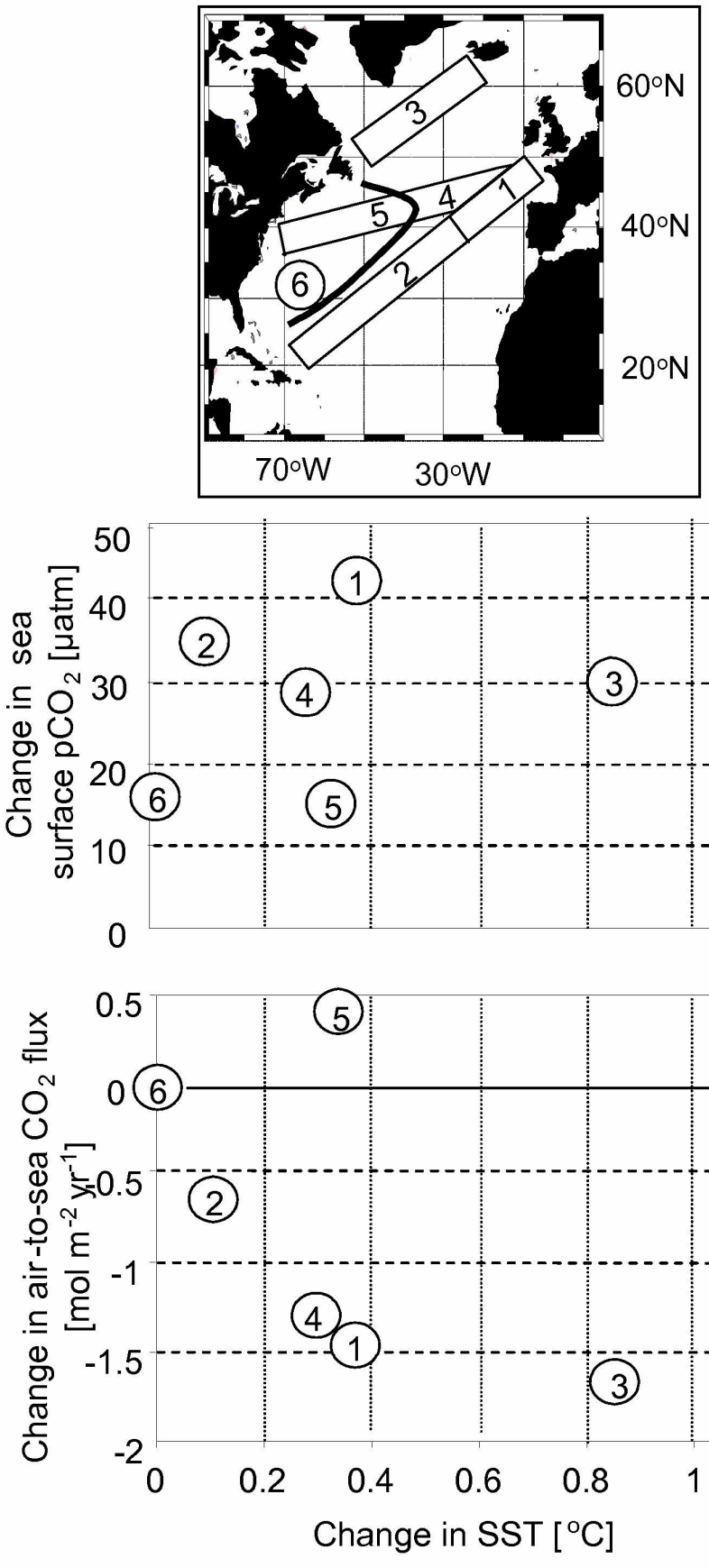

A
B
C
temperate/supbolar region
tropical/subtropical region
Sea surface pCO2 [µatm]
Latitude [°N]
Longitude [°E]
Jan
Mar
May
Jul
Sep
Nov


A
B
C
ΔpCO2 [µatm]
Latitude [°N]
Longitude [°E]
temperate/supbolar region
tropical/subtropical region
Jan
Mar
May
Jul
Sep
Nov


A
B
Air-to-sea flux [mol m-2 year-1]
3
2.5
2
1.5
1
0.5
0
-0.5
25
30
35
40
45
Latitude [°N]
-70
-60
-50
-40
-30
-20
-10
Longitude [°E]


60°N
40°N
20°N
70°W
30°W
1
2
3
4
5
6
Change in sea surface pCO2 [µatm]
50
40
30
20
10
0
Change in air-to-sea CO2 flux [mol m-2 yr-1]
0.5
0
-0.5
-1
-1.5
-2
0
0.2
0.4
0.6
0.8
1
Change in SST [°C]