

# Interannual and decadal variability of the oceanic carbon sink in the North Atlantic subpolar gyre

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## ABSTRACT

The evaluation of interannual and decadal variations of air-sea CO<sub>2</sub> fluxes represents important step for understanding the changes in the global carbon cycle. In this study we analyse the variations of sea surface dissolved inorganic carbon (DIC) and total alkalinity (TA) in the North Atlantic over the period 1993–2003 (SURATLANT Program). The analysis focuses on the subpolar gyre (53°N–62°N/45°W–20°W). Large interannual variability of DIC and air-sea CO<sub>2</sub> fluxes is observed mostly during summer. In the extreme case, this region was a CO<sub>2</sub> source in 2003 explained by a dramatic warming and the absence of late-summer bloom. At the decadal scale, DIC and TA concentrations appeared stable indicating a complex balance between primary production, vertical mixing, horizontal transport and anthropogenic CO<sub>2</sub>. We also found that winter  $f$ CO<sub>2</sub> has increased at a rate of +2.8 μatm yr<sup>-1</sup> between 1993 and 2003, due to strong surface warming (1.5 °C over 10 yr) particularly since winter 1995 when the North Atlantic Oscillation index moved into a negative phase. This resulted in a decrease of carbon uptake in the North Atlantic subpolar gyre, a trend also suggested for the period 1972–1989 but not captured by current class atmospheric inverse models.

## 1. Introduction

### 1.1. Global carbon cycle variability

The concentration of atmospheric CO<sub>2</sub> has been rising for decades due to anthropogenic activities (mainly fossil fuel burning, cement production and land-use changes). Currently, approximately 7 Pg C are released to the atmosphere each year (Marland et al., 2005); about half of this is captured and stored by the ocean and terrestrial biosphere. However, the partitioning between ocean and terrestrial carbon sinks and the mechanisms that control the pathways of anthropogenic carbon ('the fate of fossil fuels') are still uncertain (see a review by Sabine et al., 2003). In order to better predict the evolution of the global carbon cycle and its coupling with climate change quantifying and understanding interannual and decadal variability of the carbon sinks represent an important step. Recent estimates based on atmospheric observations (CO<sub>2</sub> and O<sub>2</sub>) suggest that changes occurred between 1990 and 2003 in both the terrestrial and ocean carbon sinks (Manning and Keeling, 2005). Over this period, the

increase of the net ocean carbon uptake is relatively low compared to the uncertainties (1.9–2.2 (± 0.6) Pg C yr<sup>-1</sup>). Estimating and understanding such variation at global scale from oceanic observations is at present impossible. Therefore, focusing on regional analyses over a sufficiently long period to observe the carbon ocean system (e.g. Keeling, 1991; Bates, 2001; Wong et al., 2002; Dore et al., 2003; Keeling et al., 2004) remains highly relevant to detect changes in ocean carbon cycle. In particular, long time-series help to identify both processes that control trends and/or rapid variations. Regional investigations also help to develop and correct parametrizations which are used in ocean modelling to predict and understand future changes in biogeochemical cycles and their associated impacts on climate.

### 1.2. The North Atlantic carbon sink

Recent studies and different approaches have been developed to estimate the oceanic sinks/sources at global and regional scales: synthesis of surface ocean observations  $p$ CO<sub>2</sub>, forward and inverse ocean models, and atmospheric inversions. Here we recall the results obtained in the North Atlantic. On the ocean observations side, it has been well identified that the North Atlantic subpolar gyre (NASG) acts as a strong sink (Takahashi et al., 1993). The air-sea CO<sub>2</sub> fluxes have been derived from a  $\Delta p$ CO<sub>2</sub> climatology for a reference year 1995 (Takahashi et al., 2002).

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In this climatology, the North Atlantic, north of 50°N, represents an annual sink of  $-0.31$  to  $-0.36$  Pg C yr<sup>-1</sup> depending on the gas transfer coefficient used in the air-sea CO<sub>2</sub> calculation. Recently, Gloor et al. (2003) employed an inverse ocean model and suggested that the North Atlantic carbon sink (north of 53°N) is around  $-0.15$  Pg C yr<sup>-1</sup>, about half the estimate derived from *p*CO<sub>2</sub> observations, forward ocean models (Gloor et al., 2003) and atmospheric inversions (Gurney et al., 2004). Although atmospheric inverse models (hereafter, AIMs) have difficulties in separating the ocean and terrestrial carbon sinks in the North Atlantic bordered by American, European continents and Greenland, results appear consistent with the *p*CO<sub>2</sub> climatology which is used as an a priori information to constraint the inversions. Bousquet et al. (2000) performed AIMs over almost two decades (80's and 90's) and calculated significant interannual variability of the air-sea CO<sub>2</sub> fluxes in the North Atlantic, north of 20°N: for this large region the oceanic carbon sink varied between  $-0.6$  and  $-1.1$  Pg C yr<sup>-1</sup> (mean  $-0.80 \pm 0.15$  Pg C yr<sup>-1</sup> for the period 1984–1998); more importantly for our present analysis, the AIMs suggest that large and rapid variations, up to  $\pm 0.4$  Pg C yr<sup>-1</sup> can occur over relatively short periods, 2–5 yr. However, AIMs do not explain the origin of the variability and for this we must utilize ocean observations.

Gruber et al. (2002) used monthly ocean carbon data obtained at Bermuda time-series station during 1982–2000 to investigate the interannual variability of the air-sea CO<sub>2</sub> fluxes in the North Atlantic. They observed significant air-sea CO<sub>2</sub> fluxes anomalies explained mainly by variations of temperature and mixed-layer depth, both likely related to the North Atlantic Oscillation (NAO). They also compared the time-series analysis detailed at local scale (Bermuda, near 32°N–64°W) with the fluxes deduced by the AIMs at the large-scale, 20°N–80°N (Bousquet et al., 2000). Although such local versus large-scale comparison represents an optimistic attempt, the interannual variability,  $\pm 0.3$  Pg C yr<sup>-1</sup>, of the ocean carbon sink deduced from ocean observations and extrapolated to the North Atlantic is very close to the one deduced by the AIMs. The interannual variability is important as it represents more than 50% of the net carbon sink in the North Atlantic. This has to be confirmed with long-term observations in the regions north of the subtropical gyre.

If the interannual variability appears coherent between AIMs and data extrapolation, this appears less promising on decadal timescale. Based on a synthesis of seasonal *p*CO<sub>2</sub> data (50°N–70°N/80°W–10°W) for the period 1982–1998, Lefèvre et al. (2004) showed that oceanic *p*CO<sub>2</sub> increased at a rate faster than in the atmosphere, especially in summer. This results in a decrease of the oceanic carbon sink at high latitudes in the North Atlantic. This trend has been also inferred for the 1970s and 1980s in the eastern subpolar gyre through a reconstruction of wintertime *p*CO<sub>2</sub> (Omar and Olsen, 2006). These authors suggested that the sea surface *p*CO<sub>2</sub> growth rate could be as high as  $3 \mu\text{atm yr}^{-1}$ , much faster than in the atmosphere, implying a significant change of the carbon sink over 20 yr. However, such

a decrease of the carbon sink in the North Atlantic is at present not captured in the atmospheric inversions (Baker et al., 2006).

In the North Atlantic, it is expected that the air-sea CO<sub>2</sub> flux varies at interannual and decadal scales modulated by large-scale climatic events such as the NAO, through thermodynamics, wind speed, biological processes, freshening and ocean circulation changes (Häkkinen and Rhines, 2004; Curry and Mauritzen, 2005). In order to separate these processes, including anthropogenic carbon signal, it is relevant to go a step further than previous analysis based on *p*CO<sub>2</sub> data.

In this study, we present and discuss new carbon dioxide observations, including dissolved inorganic carbon (DIC) and total alkalinity (TA), obtained during 1993–2003 in the NASG. We describe the evolution of seawater fugacity (*f*CO<sub>2</sub>) and air-sea CO<sub>2</sub> gas exchange and compare our analysis with previous studies that attempted to detect the decadal change of the oceanic carbon sink in this region.

## 2. Methods and data selection

In July 1993, the SURATLANT program started collection of regular water samples three to four times a year, using one of three merchant vessels (*MV Skogafoss*, *MV Godafoss* and *MV Selfoss*) travelling between Iceland and the Newfoundland (Fig. 1). The ships did not follow exactly the same track depending on weather conditions but this has no impact for the seasonal and interannual analysis presented in this study. During the cruises (one cruise is typically 1 week) seawater was pumped from a depth of 3–5 m depending on the ship. Sea surface temperature (SST) and sea surface salinity (SSS) were recorded continuously by a ThermoSalinoGraph (TSG; Sea-Bird Electronics, Inc., USA, model 21) and discrete salinity samples were also regularly collected for the calibration of the TSG. SST and SSS accuracies were estimated to be  $\pm 0.01$  °C and  $\pm 0.01$  psu, respectively. It is important to note that SST was not measured at the intake and corrections, up to 0.5 °C, have been applied to the TSG temperature records after comparison with expendable bathythermograph (XBT) data.

During the periods 1993–1997 and 2001–2003, about 30 samples of DIC, TA and nutrients (Silicates, Phosphates) were collected during each crossing. To extinguish the biological activity, these bottles were poisoned with a saturated HgCl<sub>2</sub> solution. The carbon samples were measured at laboratory at Lamont Doherty Earth Observatory (LDEO; USA) between 1993 and 1997, and at Laboratoire de Biogéochimie et Chimie Marine (LBCM/IPSL) (now Laboratoire d'Océanographie et du Climat: Expérimentations et Approches Numériques (LOCEAN/IPSL)) in France since 2001. During 1993–1997, only DIC was measured using a coulometric method (Chipman et al., 1993), whereas since 2001, DIC and TA were both obtained using a potentiometric titration derived from the method developed by Edmond (1970) using a closed cell. The calculation of the equivalent point was estimated using a non-linear regression

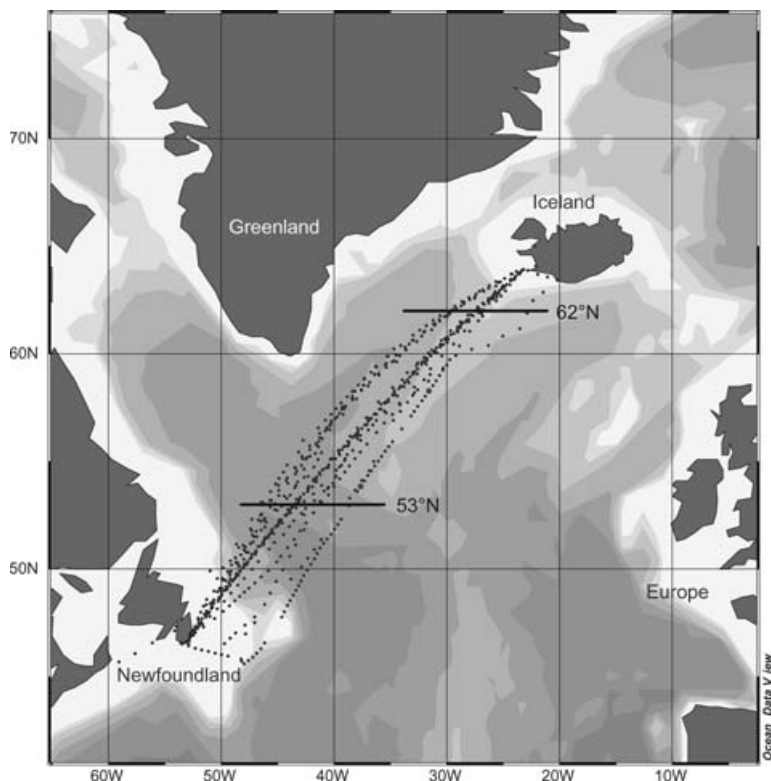


Fig. 1. Seawater surface sampling of carbon properties during the SURATLANT program (Iceland to Newfoundland) over the periods 1993–1997 and 2001–2003. This study is focused on the open ocean region (53°N–62°N/45°W–20°W) as indicated by black lines.

method (DOE, 1994). For calibration, we used Certified Reference Material (CRM) provided by Prof A. Dickson (Scripps Institution of Oceanography, San Diego, USA). The accuracy of DIC and TA are estimated to be  $\pm 2 \mu\text{mol kg}^{-1}$ .

To characterize oceanic  $f\text{CO}_2$  we used observed values of DIC, TA, SST, SSS in conjunction with CO2SYS (Lewis and Wallace, 1998). We selected the dissociations constants of Hanson (1973) and Mehrbach et al. (1973) refitted by Dickson and Millero (1987). The choice of another set of constants would change the absolute value of  $f\text{CO}_2$  (by not more than  $13 \mu\text{atm}$ ) but would not change our view concerning the  $f\text{CO}_2$  temporal variability, both at seasonal and decadal scales. The seasonality of nutrients being significant in high latitudes, this was taken into account for both phosphates and silicates in the  $f\text{CO}_2$  calculations.

As mentioned previously, TA was not measured during the first part of the experiment (1993–1997). However, as TA is strongly related to salinity at large-scale (Millero et al., 1998) we can use this relationship to create companion TA data to the DIC measurements obtained in 1993–1997 and calculate sea surface  $f\text{CO}_2$  for each sample. To support this assumption we explored relationship between TA and salinity based on measurements obtained at different seasons for years 2001–2002. This is shown on Fig. 2 for the full range of salinity measured along the tracks (SSS between 31 and 35.3). In general, the measurements show a strong relation between TA and salinity. The corresponding TA/SSS relation is indicated below (eq. 1), where TA is expressed

in  $\mu\text{mol kg}^{-1}$  and SSS in practical salinity scale:

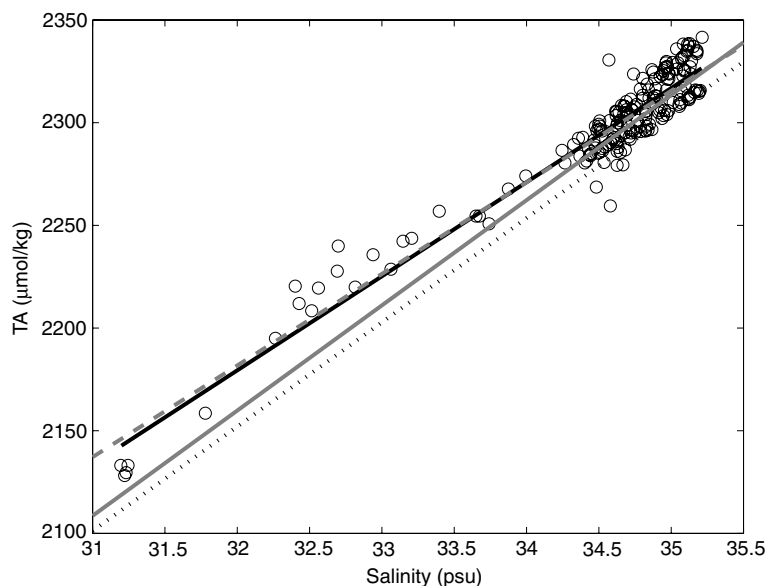
$$\begin{aligned} \text{TA} &= 45.808 \times \text{SSS} + 713.5, \quad r^2 = 0.92, \\ \text{RMSD} &= \pm 10.3 \mu\text{mol/kg}. \end{aligned} \quad (1)$$

This equation is highly consistent with those obtained during the transient tracer in the oceans/North Atlantic Study experiment (TTO/NAS) for the period August–September 1981. The surface water TA values obtained during TTO/NAS (Brewer et al., 1986a,b) in the area 47°N–65°N/6°W–59°W are described by eq. (2):

$$\begin{aligned} \text{TA} &= 44.603 \times \text{SSS} + 754.4, \quad r^2 = 0.94, \\ \text{RMSD} &= \pm 7.6 \mu\text{mol/kg} \end{aligned} \quad (2)$$

These relationships at high latitudes are very close to that determined by Millero et al. (1998) based on surface TA data obtained over the entire Atlantic Ocean. They are also very close to the relationship deduced by Lüger et al. (2004) based on recent observations in mid-latitudes of the North Atlantic. These relationships are summarized in Fig. 2. This comparison suggests that TA/SSS relation, such as the one calculated with our data (eq. 1), is remarkably coherent at seasonal and decadal scales (1981 vs. 2001–2002), as well as for both regional and large scales in the Atlantic Ocean. In the following we will use relationship (1) to simulate surface TA variability for the period 1993–1997 and from all DIC/TA pairs we will calculate  $f\text{CO}_2$  for each sample and cruise.

Fig. 2. Plot of total alkalinity (TA in  $\mu\text{mol kg}^{-1}$ ) versus salinity from all samples measured in the North Atlantic Ocean (Iceland to Newfoundland) for the period 2001–2002. The black line identifies the relationship derived from SURATLANT data (this study). The dashed grey line (almost superposed on the black line) represents the relationship derived from August–September 1981 data for the same area (TTO/NAS, Brewer et al., 1986a,b). The grey line corresponds to the relationship determined by Millero et al. (1998) for the Atlantic Ocean, and the dotted line represents relationship determined for the North Atlantic basin ( $35^{\circ}\text{N}$ – $50^{\circ}\text{N}/10^{\circ}\text{W}$ – $70^{\circ}\text{W}$ ) by Luger et al. (2004).



The data obtained during the SURATLANT cruises identify different water masses from the coastal waters near Iceland in the north, to coastal zone off Newfoundland. For the purpose of this study, an analysis of the ocean carbon interannual variability, we have selected data in the region where both hydrological and carbon properties are homogeneous, that is, where meso-scale processes do not appear to influence long-term variability. Figure 3 shows two transects during the same year in summer (August 2001) and winter (December 2001). For each season the measurements clearly indicate the presence of strong gradients of SST, SSS, DIC and TA south of  $53^{\circ}\text{N}$  when crossing the Labrador Current and approaching Newfoundland. Influence of coastal waters is also identified north of  $62^{\circ}\text{N}$  near Iceland. Between  $53^{\circ}\text{N}$  and  $62^{\circ}\text{N}$ , the central waters in the subpolar gyre, sea surface properties are much more homogeneous, although eddies have been identified occasionally at latitude  $53^{\circ}\text{N}$ – $55^{\circ}\text{N}$ . Another feature seen on these data is the opposed seasonality of SST and DIC/ $f\text{CO}_2$ , whereas for salinity and TA the seasonality is low. This indicates that at seasonal scale seawater  $f\text{CO}_2$  is mostly controlled by DIC, and partly modulated by SST in the central region. In the region south of  $50^{\circ}\text{N}$  the  $f\text{CO}_2$  seasonality is opposite in sign with high values in summer caused by surface warming and low TA. In this study focused on interannual and decadal variability, we analysed in detail the measurements obtained in the open ocean area,  $53^{\circ}\text{N}$ – $62^{\circ}\text{N}/45^{\circ}\text{W}$ – $20^{\circ}\text{W}$  (indicated by arrows in Fig. 3) and for each cruise we averaged all data in this region. In doing so we expect that interannual variations may be attributed to large-scale forcing only, without considering small-scale processes or meso-scale features. The averaging procedure over the subpolar region will also permit comparison of our results with previous analyses and climatology.

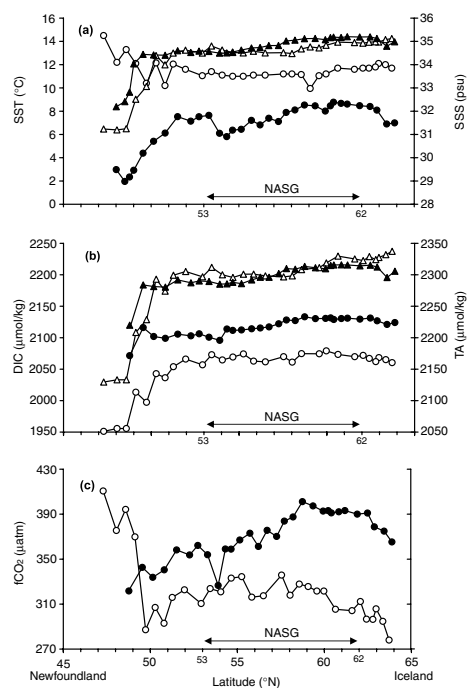


Fig. 3. Seasonal variations of sea surface temperature (dots), salinity (triangles) (a), DIC (dots) and TA (triangles) (b) and  $f\text{CO}_2$  (c), along the same track between Iceland and the Newfoundland, for summer (August 2001, open symbols) and winter (December 2001, filled symbols). The horizontal arrows indicate the open ocean region of the NASG.

### 3. Results

#### 3.1. Variations of hydrological and carbon parameters

The seasonal cycle of SST is well marked (Fig. 4a) suggesting that the seasonality will be also captured for carbon

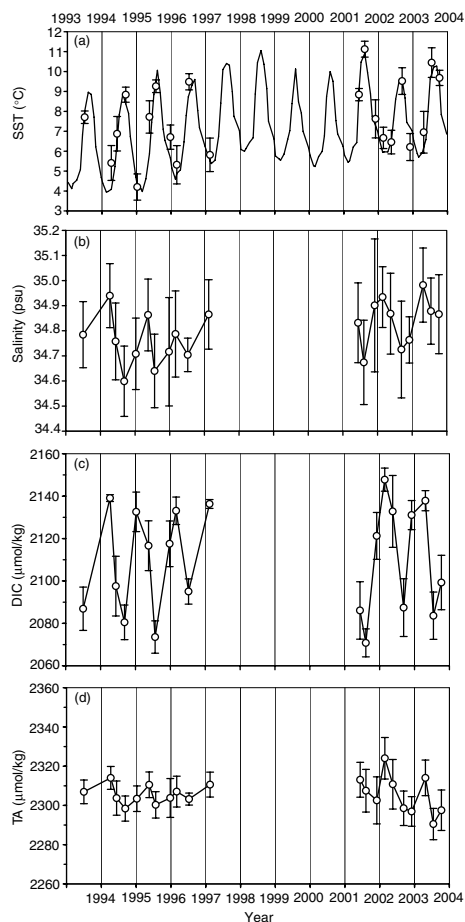


Fig. 4. Interannual variability of sea surface temperature (a), salinity (b), DIC (c), TA (d) over the period 1993–2003 from data averaged in the NASG ( $53^{\circ}\text{N}$ – $62^{\circ}\text{N}/45^{\circ}\text{W}$ – $20^{\circ}\text{W}$ ) (see Fig. 1). Open symbols indicate in situ measurements. Vertical bars indicate the standard deviation around the mean. In Fig. 4a the continuous line indicates the monthly SST for the same region (updated products from Reynolds and Smith, 1994, <http://iridl.ldeo.columbia.edu/SOURCES/.IGOSS/.nmc/>).

parameters. The comparison between in situ observations and monthly products (Reynolds and Smith, 1994) also reveals coherent SST values and warm/cold seasonal phasing. In addition, both in situ and climatological products reveal a gradual warming of about  $1.5^{\circ}\text{C}$  over 10 yr, modulated by a relatively stable period during 1999–2000. Over the investigated period, 1993–2003, the SST minimum was  $4.2^{\circ}\text{C}$  ( $\pm 0.6$ ) in winter 1995 and the maximum was  $11.1^{\circ}\text{C}$  ( $\pm 0.3$ ) in late August 2001. The recent years 2001–2003 were clearly warmer when compared with 1993–1996; this decadal SST variation may significantly impact on sea surface  $f\text{CO}_2$  and air-sea  $\text{CO}_2$  fluxes anomalies.

As opposed to SST, the seasonal cycle for SSS is not clearly observed from these data (Fig. 4b) because in this region the interannual variability can be as high as the salinity seasonal cycle (Reverdin et al., 2002). These authors also identified detectable changes during 2–3 yr periods with both positive and

negative salinity anomalies; an increase of salinity in 1995–1997 (Fig. 4b), followed by a decrease in 1998–1999 (Reverdin et al., 2002). Unfortunately for this period no DIC or TA observations exist. Since 2001, during repeat DIC and TA measurements, the data indicates that SSS increased significantly, this signal was also detected by ARGO floats ([www.coriolis.eu.org](http://www.coriolis.eu.org)).

The mean concentrations of DIC measured in 1993–1997 and 2001–2003 in the central subpolar gyre are presented in Fig. 4c. As expected from the SST data, the timing of the cruises captured the DIC seasonal cycle. The sea surface DIC concentrations are maximum in winter (December to April) and minimum in summer (July to September) due to the biological activity (Antoine et al., 2005). The mean DIC concentrations vary from  $2070.3 \pm 5.2 \mu\text{mol kg}^{-1}$  in August 2001 to  $2140.0 \pm 5.3 \mu\text{mol kg}^{-1}$  in February 2002. Depending on the year the observed seasonal amplitude of DIC varies between 40 and  $80 \mu\text{mol kg}^{-1}$ . Although one would expect to detect a regular increase of DIC due to anthropogenic  $\text{CO}_2$  invasion, no decadal trend has been deduced from these observations. The expected anthropogenic trend, between 10 and  $20 \mu\text{mol kg}^{-1}$  over the last decade, may be counterbalanced by natural processes (mixing and biological activity) and/or simply masked in this data set by the large variability in the seasonal signal in this region.

The TA seasonality (Fig. 4d) is much less pronounced than for DIC. For the period 1993–1997 it reflects directly the salinity as we applied the TA/salinity relationship described above. For the period 2001–2003 the TA data show detectable seasonality of about  $10$ – $15 \mu\text{mol kg}^{-1}$  with higher concentrations in late winter, up to  $2327.1 \pm 10.3 \mu\text{mol kg}^{-1}$  in 2002 compared to late summer, as low as  $2289.5 \pm 5.5 \mu\text{mol kg}^{-1}$  in 2003. Again, no clear decadal evolution can be identified for TA from 1993 to 2003. However, we note that TA concentrations decreased in recent years and this may impact on sea surface  $f\text{CO}_2$  calculations. This is opposed to salinity which suggests that other processes than dilution may explain the slight decrease of TA.

### 3.2. Variations of oceanic $f\text{CO}_2$

As opposed to DIC and TA, the calculated  $f\text{CO}_2$  showed a gradual increase during the observational period (Fig. 5). The spatial average  $f\text{CO}_2$  in the region also presents very contrasting seasonality depending of the year. Large seasonality, around  $60 \mu\text{atm}$ , was observed in 1993, 1994 and 2001, whereas it was less than  $20 \mu\text{atm}$  in 1996 and 2003. During each year the  $f\text{CO}_2$  minimum observed in summer is dependent on the phasing between the period of the cruise (one week) and the phytoplankton bloom events. In this region, two blooms generally occur, in June and September. This is clearly identified with Chlorophyll-a concentrations (Antoine et al., 2005). This is also identified in the nutrients climatology (Louanchi and Najjar, 2001) as well as reflected in the  $f\text{CO}_2$  climatology of Takahashi et al. (2002, also shown in Fig. 5 for reference year 1995). Both the period and intensity of the blooms certainly explain why we observed large

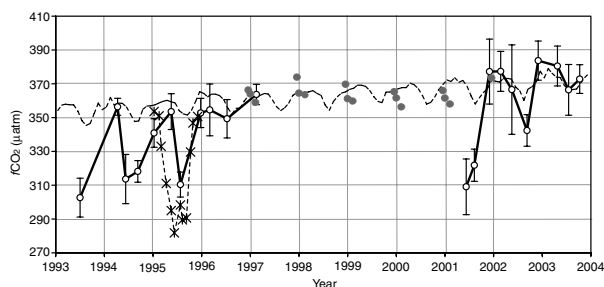


Fig. 5. Interannual variability of sea surface and atmospheric  $f\text{CO}_2$  during 1993–2003 in the North Atlantic subpolar gyre ( $53^\circ\text{N}$ – $62^\circ\text{N}$ ). Open symbols indicate ocean  $f\text{CO}_2$  averaged between  $53^\circ\text{N}$  and  $62^\circ\text{N}$ . Vertical bars indicate the standard-deviation around the mean. Black stars indicate the oceanic  $f\text{CO}_2$  climatology for the year 1995 (Takahashi et al., 2002). Grey dots indicate oceanic  $f\text{CO}_2$  extrapolated for winter months (December to February) over the period 1997–2001. Thin dashed line indicates the monthly atmospheric  $f\text{CO}_2$  data deduced from concentrations observed at Mace Head (Ireland).

change in the DIC and  $f\text{CO}_2$  seasonalities from year to year. This high variability makes it very difficult to derive decadal changes and/or trends from summer data only.

In winter however,  $f\text{CO}_2$  is always high, because at these latitudes deep mixing with enriched  $\text{CO}_2$  subsurface waters dominates the cooling effect and biological activity is low. During this season, the concentration of DIC is high and stable for several weeks to months (Takahashi et al., 1993) and the same is true for  $f\text{CO}_2$  (Takahashi et al., 2002). Taking this into account, we believe that winter  $f\text{CO}_2$  data are not dramatically affected by sampling bias and that they contain a better description of long-term trends. In order to detect a trend over 1993–2003, we propose to extrapolate between the period that was not sampled for the carbon parameters (1997–2000) during winter months (December–February). For this we have explored MLR's to fit the  $f\text{CO}_2$  data with other parameters (latitude, longitude, SST, salinity) and we found that a simple relation with temperature (eq. 3) was adequate:

$$f\text{CO}_2 = 9.95 \times \text{SST} + 303.97, \quad r^2 = 0.51, \quad (3)$$

RMSD =  $\pm 17.4 \mu\text{atm}$ .

We applied this relation using monthly SST products (as shown in Fig. 4a, Reynolds and Smith, 1994) for the months of December, January and February in 1997–2001. The extrapolated  $f\text{CO}_2$  based on eq. (3) compared well with the original data in winter 1997 and 2001 (Fig. 5). For the period 1998–2001, the extrapolated  $f\text{CO}_2$  in winter are close to the atmospheric values. Based on this we suggest that sea surface  $f\text{CO}_2$  has regularly increased from about  $350 \mu\text{atm}$  during winters 1994–1996 to  $380 \mu\text{atm}$  during the winter 2003. The ocean  $f\text{CO}_2$  in winter was lower than atmospheric values in 1994–1996, reaching equilibrium in 1997 and was higher than atmospheric values in 2002–2003. Therefore, air-sea  $\text{CO}_2$  fluxes in winter have recently moved from a sink to a source in this region.

### 3.3. Air-sea $\text{CO}_2$ fluxes

We computed the sea-air  $\text{CO}_2$  flux following the expression:

$$F = ks(\Delta f\text{CO}_2)^{\text{oc-atm}}, \quad (4)$$

where  $k$  is the gas transfer coefficient which scales as the square of the wind-speed (Wanninkhof, 1992),  $s$  is the solubility of the  $\text{CO}_2$  in seawater which is a function of temperature and salinity (Weiss, 1974) and  $(\Delta f\text{CO}_2)^{\text{oc-atm}}$  is the difference between ocean and the overlying atmospheric  $f\text{CO}_2$ .  $(\Delta f\text{CO}_2)^{\text{oc-atm}}$  was computed using the average sea surface  $f\text{CO}_2$  values during each cruise (as shown in Fig. 5) and the monitoring atmospheric  $x\text{CO}_2$  data recorded at Mace-Head station in Ireland (M. Ramonet, personal communication). The atmospheric  $x\text{CO}_2$  values were converted to fugacity at 100% humidity using the polynomial of vapour pressure established by Weiss and Price (1980). For the wind-speed we used the monthly mean wind-speed from NCEP reanalysis averaged in the region  $53^\circ\text{N}$ – $62^\circ\text{N}$ . The calculated air-sea  $\text{CO}_2$  fluxes are presented in Fig. 6 for each cruise as well as for winter season in 1997–2001 using extrapolated  $f\text{CO}_2$  based on equation (3). During the period 1993–1997, the seasonal fluxes varied from  $-12 \text{ mmol m}^{-2} \text{ d}^{-1}$  (a  $\text{CO}_2$  sink in June 1994) to about  $+1 \text{ mmol m}^{-2} \text{ d}^{-1}$  (a  $\text{CO}_2$  source in February 1997). In recent years the  $\text{CO}_2$  fluxes varied from  $-11 \text{ mmol m}^{-2} \text{ d}^{-1}$  (June 2001) up to  $+3 \text{ mmol m}^{-2} \text{ d}^{-1}$  (February 2002). For the year 2003 the situation was dramatically different. In particular, during April 2003 the ocean was a relatively large  $\text{CO}_2$  source, whereas during July 2003 the ocean was near equilibrium and in late summer 2003 the ocean was again a  $\text{CO}_2$  source of about  $+1 \text{ mmol m}^{-2} \text{ d}^{-1}$ .

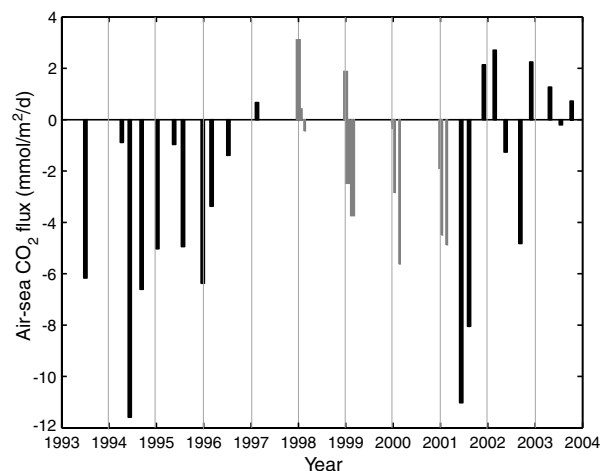


Fig. 6. Air-sea  $\text{CO}_2$  flux ( $\text{mmol m}^{-2} \text{ d}^{-1}$ ) estimated in the North Atlantic subpolar gyre for the period 1993–2003. Black bars represent fluxes estimated from in-situ data ( $f\text{CO}_2$  calculated from DIC and TA); grey bars correspond to fluxes determined from extrapolated winter  $f\text{CO}_2$ .

## 4. Discussion

### 4.1. The 2003 flux anomaly

The oceanic  $\text{CO}_2$  source anomaly observed during spring–summer 2003 is clearly due to relatively high oceanic  $f\text{CO}_2$  rather than changes in the wind-speed that enters the calculation of the gas transfer coefficient (eq. 4). Many processes could explain why  $f\text{CO}_2$  was so high during this period. We identified that both solubility changes due to warming and biological processes were responsible for the increase of  $f\text{CO}_2$  leading to a continuous ocean  $\text{CO}_2$  source in 2003. First we note that, although the sea surface warming was not as high as in 2001 (Fig. 4a), the SST anomaly was well above  $1^\circ\text{C}$  over a large portion of the North Atlantic in summer 2003. This synoptic situation was also associated with the extreme weather conditions experienced in Europe which also had a strong impact on the terrestrial carbon sink (Ciais et al., 2005). In contrast with 2001 when ocean  $f\text{CO}_2$  was around  $320\ \mu\text{atm}$  during summer (Fig. 5) we have estimated values up to  $380\ \mu\text{atm}$  in summer 2003. We must look to other processes than warming, to explain the large differences of  $f\text{CO}_2$  between the warm years 2001 and 2003. Observations of inorganic carbon parameters help to understand this intriguing situation. During spring–summer 2003 both DIC and TA concentrations present particular anomalies. In April 2003, the DIC concentrations were high ( $2138\ \mu\text{mol kg}^{-1}$ ). This was explained by a late bloom that occurred in May–June 2003 (Fig. 7). Without any strong productivity before April, the oceanic  $f\text{CO}_2$  remained above equilibrium from February to April 2003 (Fig. 5). From April to July, the DIC concentrations decreased from  $2138$  to  $2085\ \mu\text{mol kg}^{-1}$  and TA decreased

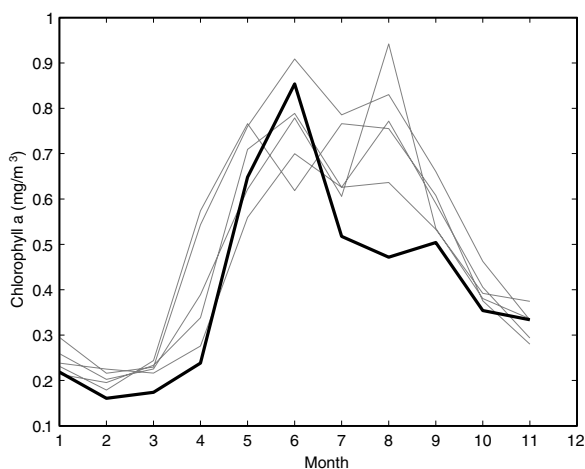


Fig. 7. Annual cycles of Chlorophyll-a concentrations ( $\text{mg m}^{-3}$ ) derived from SeaWiFS in the NASG ( $53^\circ\text{N}$ – $62^\circ\text{N}/45^\circ\text{W}$ – $20^\circ\text{W}$ ) for different years, 1998–2003. Months of December are not represented (no data were available). Grey lines indicate average monthly Chlorophyll-a concentrations for 1998–2002 (years marked with two blooms). The black line highlights the year 2003 (year with only one bloom) where we observed a dramatic change of air-sea  $\text{CO}_2$  fluxes.

from  $2314$  to  $2290\ \mu\text{mol kg}^{-1}$ . The variations of DIC were likely controlled by a relatively strong phytoplanktonic bloom in May–June 2003 (Fig. 7). At the same time, the SST increased from  $6.9$  to  $11^\circ\text{C}$  corresponding to an increase of  $f\text{CO}_2$  of about  $80\ \mu\text{atm}$  (at constant DIC and TA). The seasonal warming effect and biological production combine to produce a relatively small change for  $f\text{CO}_2$ . This contrasts to the situation of previous years (summer 1993, 1994, 1995 and 2001, Fig. 5), or compared to the  $p\text{CO}_2$  climatology. All previous studies indicate that oceanic  $f\text{CO}_2$  is well below the equilibrium during summer in the NASG and hence this region is believed to be a permanent and strong sink during summer (Lefèvre et al., 1999; Takahashi et al., 2002). Our observations in 2003 indicate that a late spring bloom could balance the solubility changes due to warming leading to low variations of  $f\text{CO}_2$  during the season.

The  $\text{CO}_2$  source anomaly in spring–summer 2003 was maintained until October. Between July and October the variations of DIC and TA concentrations were low and SST did not change significantly, all leading to small  $f\text{CO}_2$  variations. The origin of the small variations observed in DIC could be explained by a large anomaly of the biological activity clearly identified during late summer 2003 (Fig. 7). Compared to previous years, the average of sea surface Chlorophyll-a concentrations were particularly low in August. Explaining why the secondary bloom did not occur in August 2003 is beyond the scope of the present analysis. At that stage we can relate this blooming anomaly to the particularly low winds during at least two weeks at the end of July. Both the exceptional warming of air masses and the warming in SST would increase the stratification, leading to shallowing of the mixed-layer and limitation of supply of nutrients into the euphotic zone. In this case, the absence of a bloom in August 2003 (Fig. 7) and consequently no large DIC drawdown in late-summer could explain the relatively high DIC concentrations in October and hence the  $\text{CO}_2$  source anomaly.

The anomaly of the summer carbon sink in 2003 was also observed in 1996. In July 1996, DIC concentrations were relatively high (Fig. 4c) as well as  $f\text{CO}_2$  (Fig. 5). Consequently the summer sink in 1996 was not as strong as previous years, less than  $-2\ \text{mmol m}^{-2}\ \text{d}^{-1}$  (Fig. 6). Unfortunately, we have no direct or satellite observations to detect the phasing and level of the bloom in 1996. A possible explanation is that during 1996 the NAO index moved into a negative phase leading to weaker winds, reduced vertical mixing, less nutrients input in the euphotic zone, lower primary productivity and consequently a modest seasonal decrease of DIC in July. This situation in the subpolar gyre is opposed to the one that occurs in the subtropical region where during negative NAO the amplitude of the seasonal DIC cycle is stronger (Gruber et al., 2002). This suggests that extrapolation of interannual variability deduced from local air-sea  $\text{CO}_2$  fluxes monitored at BATS to the whole North Atlantic basin may create erroneous results.

Comparing observed and modelled responses, it is interesting to note that results from 13 atmospheric inverse models (AIMs)

suggest that over the period 1988–2002, the largest interannual variability of the air-sea  $\text{CO}_2$  fluxes in the North Atlantic occurred in 1996 (TransCOM3, Baker et al., 2006). However, the direction of the anomaly is opposite to our observations and with those deduced in the subtropical region (Gruber et al., 2002). During the negative NAO in 1996, the AIMs estimate a large positive anomaly of the carbon sink in the region  $15^\circ\text{N}$ – $50^\circ\text{N}$  when BATS data (Bermuda Atlantic Time Series) indicate stronger carbon sink. North of  $50^\circ\text{N}$  the AIMs estimate a stronger sink while our data suggested the sink was reduced. These contrasting results call for a more comprehensive data synthesis of  $f\text{CO}_2$  and ocean carbon systems and detailed comparisons between air-sea  $\text{CO}_2$  fluxes deduced from oceanic observations with those derived from AIMs.

## 4.2. Decadal change of the carbon sink

### 4.2.1. The period 1993–2003

For the recent period, 1993–2003, large interannual variations of the carbon sink have been observed in summer (1996, 2003), using DIC anomalies and satellite Chlorophyll-*a* data, we inferred these were mainly due to seasonal changes of primary production and maybe related to changes in wind speed and NAO. Therefore, in order to investigate the decadal variability we have first selected observations obtained during winter. Based on winter data (December–February) and those reconstructed for the period 1997–2000 (eq. 3), the  $f\text{CO}_2^{\text{oc}}$  growth rate is estimated to be  $+2.8 \mu\text{atm/yr}$  on average (Fig. 8). This is higher than the mean atmospheric growth rate of  $+1.8 \mu\text{atm yr}^{-1}$  for the period 1993–2003 from Mace Head (M. Ramonet, personal communication). The difference in the growth rates implies a decrease of the carbon sink, a signal not captured in AIMs (Bousquet et al.,

2000; Baker et al., 2006). Moreover, the AIMs suggest an opposite scenario for which the ocean carbon sink at high latitudes in the North Atlantic increased for the period 1988–2002 (Baker et al., 2006).

To explain the observed changes in the carbon sink, we refer to SST variations and changes of biological productivity to understand the evolution of oceanic  $f\text{CO}_2$  at decadal timescales. In addition, at this scale we also have to take into account the anthropogenic  $\text{CO}_2$  increase. This increase has been well documented in the North Atlantic, at BATS stations in the subtropical region (Bates, 2001), but also at higher latitudes (e.g. Friis et al., 2005). For the period 1981–1999, the accumulation of anthropogenic  $\text{CO}_2$  should result in an increase of DIC of about  $10$ – $25 \mu\text{mol kg}^{-1}$  near  $55^\circ\text{N}$ – $30^\circ\text{W}$  (Friis et al., 2005). However we did not observe such a trend for DIC during the recent period, 1993–2003 (Fig. 4c). In addition, using August 1981 TTO/NAS observations (Brewer et al., 1986b), we estimated an average surface DIC concentration of  $2068.1 \pm 13.4 \mu\text{mol kg}^{-1}$  in the subpolar gyre. This value is lower but not dramatically different than summer observations in 1993–2003 (Figs. 3b, 4c). This suggests that the DIC increase due to anthropogenic uptake is balanced by processes that decrease DIC over the same period and over a relatively large area (recall that Fig. 4c shows the average of DIC measurements for each cruise, e.g. not a local information as obtained at time-series stations).

One candidate to explain the DIC decrease is biological activity. Using remote sensing observations it is possible to compare Chl-*a* and primary productivity between the 1980s and the beginning of the 2000s. For example Gregg et al (2003) indicated a large-scale decrease of primary production in the North Atlantic basin. North of  $30^\circ\text{N}$  the decrease was  $-0.3 \text{ Pg C yr}^{-1}$  on average. However, a detailed inspection of the maps produced by Gregg et al. (2003, their fig. 3) also reveals that the decadal

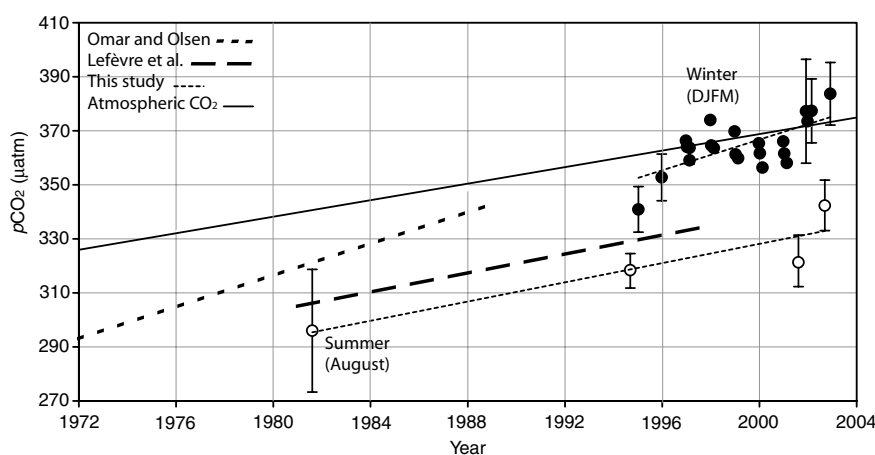


Fig. 8. Evolution of winter  $p\text{CO}_2^{\text{oc}}$  (December–February) (black dots) and summer  $p\text{CO}_2^{\text{oc}}$  (August–September) in the NASG (open symbols) (1981, TTO/NAS data; 1993–2003, SURATLANT data). The linear regressions for summer and winter are shown with dashed lines. Dotted line identifies the trend deduced from reconstructed wintertime  $p\text{CO}_2^{\text{oc}}$  for 1972–1989 (Omar and Olsen, 2006). The long-dashed line indicates the  $p\text{CO}_2^{\text{oc}}$  trend deduced from August observations for the period 1982–1998 (Lefèvre et al., 2004). For reference, the long-term atmospheric  $p\text{CO}_2^{\text{atm}}$  (December–March) in the northern hemisphere is also shown.



variation of the primary production in the North Atlantic is not homogeneous: between 30°N and 45°N the primary production was lower for recent years, but north of 45°N, the region of interest in our analysis, the primary production appeared to be higher in the late nineties. Another analysis based on satellite observations was recently produced by Antoine et al. (2005). Their analysis shows that the largest increase of Chl-a between the 1980s and the late 1990s in the North Atlantic Ocean occurred at high latitude during spring and summer. This is in agreement with the regional distribution of the primary production changes deduced by Gregg et al. (2003). Another approach, based on in situ observations was described by Sameoto (2004) who used the Continuous Plankton Recorder data, including the Phytoplankton Colour Index (PCI) to derive regional variability. This analysis indicates that the PCI increased regularly between 1991 and 2001 on a line between Iceland and Newfoundland (the same track and ship used in SURATLANT). These three independent analyses suggest that the primary production increased since about 10 yr in the region investigated here (53°N–62°N). If this is true, this would translate in a decrease in DIC. The absence of a positive trend for DIC from 1993 to 2003 could be explained by a balance between primary production and anthropogenic CO<sub>2</sub> increase.

As both DIC and TA were relatively stable over 1993–2003, the long-term variation of ocean  $f\text{CO}_2$  is likely controlled by the rapid warming experienced in this region since the decrease of the NAO. Since 1993 the increase in SST was about 1.5°C over 10 yr, with significant warming in winter 1998, 2001, 2002 and 2003 (Fig. 4a). To quantify the impact of the SST on  $f\text{CO}_2^{\text{oc}}$ , we calculated  $f\text{CO}_2^{\text{oc}}$  each year (1994–2003) at a constant temperature for each month using reference SST of year 1993. The mean difference between  $f\text{CO}_2^{\text{oc}}$  and  $f\text{CO}_2^{\text{oc}}(T=\text{constant})$  increases with time at a rate of 2.6  $\mu\text{atm yr}^{-1}$ , suggesting that sea surface warming explain almost entirely the  $f\text{CO}_2^{\text{oc}}$  trend of 2.8  $\mu\text{atm yr}^{-1}$ .

The rapid warming may be explained by the transport of warmer waters in the Irminger Sea. When the circulation in the subpolar gyre is weak, as it was at the end of the 1990s (Häkkinen and Rhines, 2004), warmer waters from the south or east can be penetrate the surface of the Irminger Sea (Hátún et al., 2005). As DIC concentration of water coming from the south is lower than in the subpolar gyre, this may be another process that could counter-balance the CO<sub>2</sub> anthropogenic increase, explaining why DIC was relatively constant since 1993 (Fig. 4c) whereas  $f\text{CO}_2^{\text{oc}}$  increased regularly by warming. To quantify the effect of each process and separate the impact of transport, primary production and anthropogenic uptake, further studies are needed based on biogeochemical ocean models.

#### 4.2.2. Decadal changes for the last 30 years

Quantifying the changing pattern of oceanic carbon sources and sinks over multidecadal scale is an important issue for better un-

derstanding the coupling between climate change and the global carbon cycle. In this context, it is therefore very attractive to compare our results for the period 1993–2003 with other studies also based on oceanic observations. The rapid  $f\text{CO}_2^{\text{oc}}$  increase of about +2.8  $\mu\text{atm yr}^{-1}$  we deduced from winter observations in the NASG is close to that derived by Omar and Olsen (2006) for the period 1972–1989. These authors used a back-calculation method based on DIC and TA concentrations observed in the subpolar mode waters to reconstruct surface wintertime  $p\text{CO}_2^{\text{oc}}$ . With the help of transient tracers to determine the ages of the mode water, they found that the  $p\text{CO}_2^{\text{oc}}$  growth rate was 3.0  $\mu\text{atm yr}^{-1}$ , suggesting that during 1972–1989 the oceanic carbon sink decreased. This trend is very similar to the one we derived for 1993–2003 (Fig. 8). If the change of  $p\text{CO}_2^{\text{oc}}$  is assumed to be constant at multidecadal timescales, this comparison is in agreement with the indirect determination of the  $p\text{CO}_2^{\text{oc}}$  growth rate proposed by Omar and Olsen (2006).

In contrast, Lefèvre et al. (2004) used an important sea surface  $p\text{CO}_2$  dataset in the North Atlantic to investigate the decadal variations of this property for the period 1982–1998. They found that in the North Atlantic Drift Region (NADR, 44°–58°N, 42°–10°W) the annual mean oceanic growth rate was about 1.8  $\mu\text{atm yr}^{-1}$ , slightly higher than in the atmosphere (1.5  $\mu\text{atm yr}^{-1}$  for 1982–1998). Lefèvre et al. (2004) also suggested that the oceanic CO<sub>2</sub> growth rate is seasonally modulated, with higher growth rate in March–July (>2.0  $\mu\text{atm yr}^{-1}$ ) than November–February (<2  $\mu\text{atm yr}^{-1}$ ), but they recognize that winter season is much less constrained by observations than summer (N. Lefèvre, personal communication). This may explain the differences with our analysis. However, we cannot exclude the fact that the  $p\text{CO}_2^{\text{oc}}$  growth rate may depend on the period investigated (1982–1998 vs. 1993–2003).

Although we have identified significant interannual  $f\text{CO}_2^{\text{oc}}$  and DIC variability in summer (Section 4.1), that could create suspicious results for long-term investigations, we attempted to compare our recent summer observations (1993–2003) with those obtained in August–September 1981 during the TTO/NAS experiment (Takahashi et al., 1985, 1993). For this period and the same region (NASG) we estimated a mean  $p\text{CO}_2$  of  $296 \pm 23 \mu\text{atm}$ . This value is reported in Fig. 8 and clearly shows that on average  $p\text{CO}_2$  was lower in 1981 than during the 1990s. Based on few years sampled during the same month (August) the oceanic  $p\text{CO}_2$  growth rate from 1981 to 2002 is estimated around 1.8  $\mu\text{atm yr}^{-1}$ . This is in very good agreement with the value derived by Lefèvre et al. (2004) for August. This comparison suggests that the oceanic  $p\text{CO}_2$  growth rate in the NASG is lower in summer than in winter and perhaps relatively constant over multidecadal scale, at least for the period 1972–2003.

## 5. Concluding remarks

From 1993 to 2003, we observed substantial variability of the carbon sink in the subpolar gyre of the North Atlantic. During

1993–1997, the data present a clear seasonality in the open ocean region marked by a strong CO<sub>2</sub> sink in summer and near-equilibrium in winter. In recent years, 2001–2003, we observed a dramatic change of the source/sink seasonality. In the most extreme case, we observed that region to be a CO<sub>2</sub> atmospheric source during all seasons in 2003. This strong anomaly was controlled by sea surface warming and the absence of a secondary bloom during late-summer.

During the period 1993–2003, we also observed a reduction in the strength of the CO<sub>2</sub> sink. To explain this, observations of DIC, TA and *f*CO<sub>2</sub> were used to interpret this change. At regional scale, and specifically in the subpolar gyre, the decadal increase of primary production (Gregg et al., 2003; Antoine et al., 2005) would lead to larger DIC seasonality and an increase of the carbon sink. This view from satellite data is supported by in situ observations acquired with the Continuous Plankton Recorder (Sameoto, 2004). However, our observations show that DIC is relatively constant during 1993–2003. We interpret the reduction of the carbon sink as a complex balance between anthropogenic CO<sub>2</sub>, increase of primary production and/or possible changes in the water masses transport, combining to produce the relatively small observed DIC change. This suggests that the increase of oceanic *f*CO<sub>2</sub> is mainly controlled by the rapid warming observed in the subpolar gyre since the mid-1990s.

We have estimated decadal trends of oceanic *f*CO<sub>2</sub> for winter (December–February, +2.8 μatm yr<sup>-1</sup>) and summer (August–September, +1.8 μatm yr<sup>-1</sup>). Although the period is not the same as previous studies, these results are in good agreement with estimates based on winter *p*CO<sub>2</sub> reconstruction for 1972–1989 (Omar and Olsen, 2006) and close to the average values in August–September based on a *p*CO<sub>2</sub> synthesis between 1982 and 1998 (Lefèvre et al., 2004). This synthesis, shown in Fig. 8, suggests that the carbon sink has decreased since 1972 in the high latitude of the North Atlantic. This result contradicts to the trends deduced from atmospheric inverse transport models that calculate an increase of the carbon sink in 1988–2002 in the same region (Baker et al., 2006).

This analysis highlights the need for monitoring the CO<sub>2</sub> in the surface ocean and investigating in more details their interannual and decadal variabilities. This requires exploring long-term observations of both hydrological and carbon properties (not only *f*CO<sub>2</sub> but DIC and TA as well) and performing diagnostic analysis of coupled biogeochemical models in order to better separate the air-sea CO<sub>2</sub> fluxes anomalies associated with advective transport, vertical mixing, biological processes and the invasion of anthropogenic carbon in the ocean.

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