

# Decadal variability of the air-sea CO<sub>2</sub> fluxes in the Subtropical waters of the Eastern North Atlantic based on empirical algorithms

Padin<sup>1</sup>, X.A., Molinés<sup>2</sup>, de la Paz<sup>1</sup>, M., J.-M., Ríos<sup>1</sup>, A.F. and Pérez<sup>1</sup>, F.F.

<sup>1</sup> Grupo de Oceanología, Instituto de Investigaciones Maríñas (CSIC), Eduardo Cabello 6, 36208 Vigo (Spain)  
<sup>2</sup> Laboratoire Ecoulements Géophysiques et Industriels, BP 53X 38041 Grenoble-cedex (France)

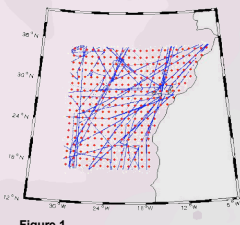
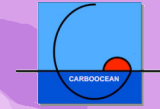


Figure 1.

**INTRODUCTION:** The best procedure for achieving an accurate estimation of seawater CO<sub>2</sub> fugacity (fCO<sub>2</sub><sup>sw</sup>) and of the capacity of ocean to absorb CO<sub>2</sub> is from of sampling networks. Furthermore robust empirical algorithms make the most of the information that the *in situ* recordings provide for extending the observed fCO<sub>2</sub><sup>sw</sup> relationships both in temporal and spatial scale. The purpose of this paper is to construct an empirical algorithm for estimating the long-term trend of the fCO<sub>2</sub><sup>sw</sup> and FCO<sub>2</sub> over the subtropical waters of the Eastern North Atlantic Ocean.

**DATA:** Underway measurements of fCO<sub>2</sub><sup>sw</sup>, sea surface temperature (SST), sea surface salinity (SSS) and other ancillary variables located between 34°N – 17°N and 30°W and the African continent excluding shelf areas around the coast with a depth cut-off of 500 m (Fig. 1) were downloaded from the CarboOcean webpage ([www.carboocean.org](http://www.carboocean.org)). This dataset was completed from the co-location of different products of NCEP/NCAR (<http://www.cdc.noaa.gov>) and DRAKKAR (<http://www.ifremer.fr/lp/drakkar/>) projects with the NAO index (Jones et al., 1997). At least the final dataset were averaged on monthly 1° x 1° grid for homogenizing the data in both space and time (Fig. 1).

**ALGORITHM ESTIMATION (Escheme 1):** Every fCO<sub>2</sub><sup>sw</sup> value was referenced to their respective months during the year 2000 correcting the CO<sub>2</sub> increase in the atmosphere from the measurement date in the meteorological station of Izaña located at 28°N (Canary Island, Spain) belonging to NOAA's Earth System Research Laboratory network. Subsequently the thermodynamic influence on fCO<sub>2</sub><sup>sw</sup> measurements was removed by normalising the fCO<sub>2</sub><sup>sw</sup> data to 23°C according to Takahashi et al. (1993). This new variable (fCO<sub>2</sub><sup>sw</sup>) was modelled from SST, mixing layer depth (MLD) and the NAO index (Jones et al., 1997) for the first time from a multiple linear regression (MLR) analysis using the statistic program STATISTICA. The thermodynamic and the atmospheric CO<sub>2</sub> correction were undone for computing the modelled fCO<sub>2</sub><sup>sw</sup> values. The *rms* error and the coefficient of determination (*r*<sup>2</sup>) of the fitting was ±9.5 μatm and 0.87, respectively. The partial contribution to the empirical algorithm pointed out SST as the main forcing explaining 81% of the fCO<sub>2</sub><sup>sw</sup> variability whereas both MLD and NAO only explained 3%.

**FCO<sub>2</sub> FLUXES:** The CO<sub>2</sub> exchange between the ocean and the atmosphere (FCO<sub>2</sub>; mol m<sup>-2</sup> yr<sup>-1</sup>) was calculated according to:  $FCO_2 = a k S \Delta fCO_2$ , where *a* is the unit conversion factor, *S* (mol kg<sup>-1</sup> atm<sup>-1</sup>) is the CO<sub>2</sub> solubility in seawater (Weiss et al., 1974), *k* (cm hr<sup>-1</sup>) is the CO<sub>2</sub> transfer velocity (Wanninkhof, 1992) and Δ*f*CO<sub>2</sub> (μatm) is the air-sea fCO<sub>2</sub> difference (i.e. fCO<sub>2</sub><sup>sw</sup> – fCO<sub>2</sub><sup>atm</sup>).

**EXTRAPOLATION:** The fCO<sub>2</sub><sup>sw</sup> and FCO<sub>2</sub> variability at long-term trend was analyzed extrapolating the observed relationships from 1980 to 2006. The fCO<sub>2</sub><sup>sw</sup> reconstruction was based on the robust consistency of the *in situ* SST fitting, main factor explaining the fCO<sub>2</sub><sup>sw</sup> variability, by the NCEP/NCAR model.

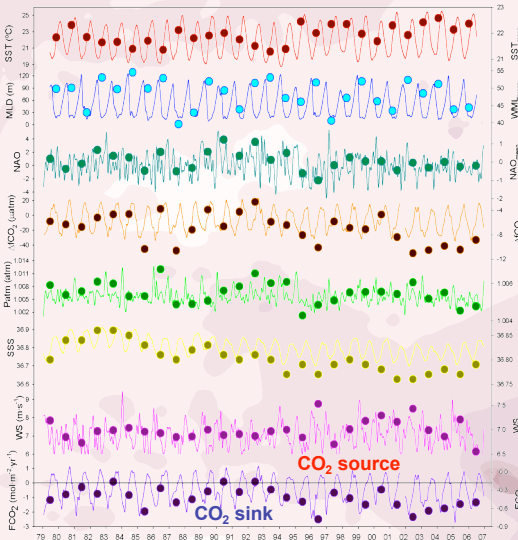


Figure 5.

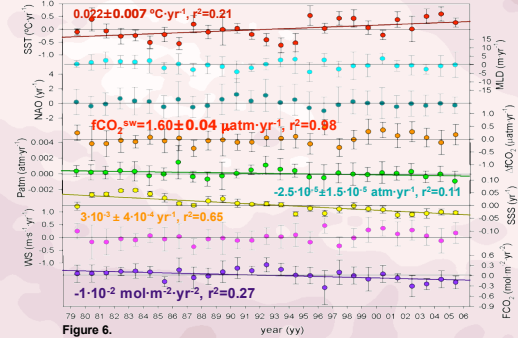


Figure 6.

year	air-sea CO <sub>2</sub> gradient (ΔfCO <sub>2</sub> )			air-sea CO <sub>2</sub> flux (FCO <sub>2</sub> )		
	NAO	MLD	SST	ΔfCO <sub>2</sub>	WS	MLD
0.60	0.47	8	5	0.86	0.65	0.72
winter	0.50	32	10	0.77	0.64	9
spring	0.77	67	6	0.88	0.75	9
summer	0.84	80	3	0.88	0.77	6
autumn	0.26	16	11	0.84	0.69	14

Table 1.

**RESULTS AND DISCUSSION:** The annual averages of every variable from 1980 to 2006 made evident some significant trends at decadal scale. So, SST showed fluctuations with a period of approximately 7 years and an amplitude of 1.5°C in addition to a unambiguous warming. The NAO index also reproduced the decadal cycles that seems to come early the SST oscillations in 5 years agreeing the delay of 3–5 years of the ocean responses to the NAO changes (Eden and Jung, 2001). The Δ*f*CO<sub>2</sub> mean throughout the time span showed a slight underaturation of subtropical waters of around -7±14 μatm. Attending to FCO<sub>2</sub>, the study region was described as a net soft sink of 0.5±0.8 mol m<sup>-2</sup> yr<sup>-1</sup> that was not statistically different of 0.3±0.3 mol m<sup>-2</sup> yr<sup>-1</sup> proposed by the recent climatological CO<sub>2</sub> atlas (Takahashi et al., 2009). The annual FCO<sub>2</sub> means were comprised between -0.16±0.78 and -0.74±0.94 mol m<sup>-2</sup> yr<sup>-1</sup> computed during the years 1992 and 2002, respectively. So, the ocean uptake in this area of 2.4 10<sup>6</sup> km<sup>2</sup> has taken up from -0.005 during the first 1990's to a maximum of 0.02 PgC yr<sup>-1</sup> during 2002 for a total absorption of 0.3 PgC from 1980 to 2006.

The long-term trend was assessed subtracting the seasonal cycle by monthly means. These seasonal residuals were averaged at annual scale and subsequently fitted to a least-squares regression linear (Fig. 6). The subtropical waters were warming over the time span in parallel to a clear freshening. The time series of fCO<sub>2</sub><sup>sw</sup> constructed from the empirical algorithm showed a year-to-year increase that is statistically lower than the fCO<sub>2</sub><sup>atm</sup> rise of 1.74±0.02 μatm yr<sup>-1</sup>. However the Δ*f*CO<sub>2</sub> showed a no significant trend like the one reported from the time series recorded in the ESTOC site (Santana-Casiano et al., 2007) and in contrast to the increase found in the subpolar waters (Schuster and Watson, 2007). On the other hand, the FCO<sub>2</sub> values pointed out an acceleration of the ocean uptake of -1.10<sup>-2</sup> mol m<sup>-2</sup> yr<sup>-2</sup> (*r*<sup>2</sup>=0.27) that represented an increase of 60% during the study period. This trend to absorb CO<sub>2</sub> that represented a little amount was opposed to the changes observed in the subpolar North Atlantic Ocean although do not contradict the reported reduction of the sink capacity of the North Atlantic Ocean.

As well as the geographical variability, the interannual rates depend much more on season (Padin et al., 2008). As particular feature, a maximum acceleration of the ocean absorption of 0.02±0.01 mol m<sup>-2</sup> yr<sup>-2</sup> that was also shown during the summer was highlighted in December coinciding with a notable rise of wind speed and a relaxation of the atmospheric pressure.

The contribution of the three inputs in the interannual Δ*f*CO<sub>2</sub> variability was analyzed from their seasonal residuals (Table 1). The NAO index that is significantly linked to biological and physical processes was clearly the main driver of the interannual Δ*f*CO<sub>2</sub> variability explaining a 47%, especially during spring and summer. Contrary, MLD was more relevant during autumn and winter although showed opposite correlations. So, negative correlations as winter pointed out the relationship between the fertilization associated to the mixing processes and the biological CO<sub>2</sub> drawdown whereas the direct correlation was reached during the breakdown of the summer stratification and the entrance of CO<sub>2</sub>-enriched subsurface waters.

The ocean uptake whose interannual fluctuations were explained in 86% was strongly controlled by the Δ*f*CO<sub>2</sub> and so, by the NAO index. This close link clearly demonstrated the direct correlation between the NAO index and the FCO<sub>2</sub> variability. Attending to the observed in the northern latitudes, these results confirm that the ocean uptake is not in phase throughout the North Atlantic Ocean under the same NAO scenario (Wetzel et al., 2005).

*in situ* fCO<sub>2</sub><sup>sw</sup>  
 normalization to year 2000  
 normalization to 23°C (Takahashi et al., 2003)  
*in situ* fCO<sub>2</sub><sup>sw</sup>  
 fCO<sub>2</sub><sup>sw</sup> = 362.8 ± 0.4 - 11.3 ± 0.2 (SST-23)  
 - 0.15 ± 0.01 · MLD + 2.0 ± 0.2 · NAO JONES  
 modelled fCO<sub>2</sub><sup>sw</sup>  
 normalization to 23°C (Takahashi et al., 2003)  
 normalization to year 2000  
 modelled fCO<sub>2</sub><sup>sw</sup>

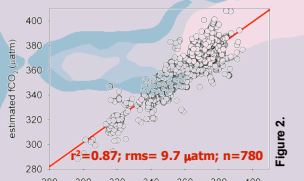


Figure 2.

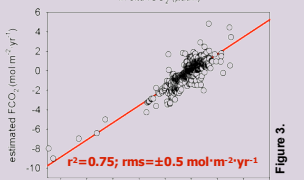


Figure 3.

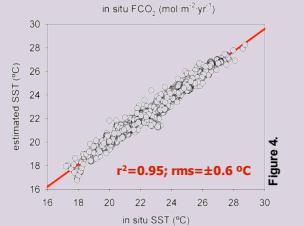


Figure 4.

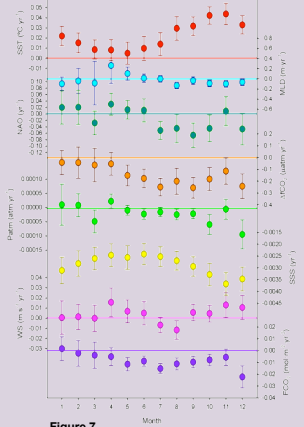


Figure 7.

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