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Changes in the partial pressure of carbon dioxide in the Mauritanian-Cape Verde upwelling region between 2005 and 2012.

By

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ABSTRACT

Coastal upwelling along the eastern margins of major ocean basins represent regions of large economic importance due to the high biological productivity. However, the physical forcing of upwelling processes that favor the production in these areas are being affected by global warming, which will modify the intensity of the upwelling and, consequently, the carbon dioxide cycle. For this reason, the role of observations in addressing any climate change impacts on the global carbon cycle in areas of upwelling is of great importance. Monthly high resolution surface experimental data for temperature and partial pressure of carbon dioxide in the Mauritanian-Cape Verde upwelling region from 2005 to 2012 are shown. This data set provides direct evidence of seasonal and interannual changes in the physical and biochemical processes. They confirmed an upwelling intensification and an increase in the CO_2 outgassing of 1 Tg a year in one of the four most important upwelling regions of the planet due to wind increase, even when primary production seems to also be reinforced. This increase in CO_2 intake together with the observed decrease in sea surface temperature at the location of the Mauritanian Cape Blanc, 21ºN, produced a pH decrease of -0.003 ± 0.001 per year.

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1. INTRODUCTION

The excess of CO_2 in the atmosphere, largely responsible of Global Climate Change, has prompted research on the role of the oceans in the carbon cycle. In recent decades data from different oceans have been taken as thoroughly as possible, with the aim to assess how the oceans act as sources or sinks within the carbon cycle. To achieve this goal, observations representative of the distribution of CO_2 fluxes between the ocean and atmosphere are necessary. In this regard, automated instruments have been installed on opportunity ships for sampling the ocean as much as possible, data is being collected at scientific cruises and long-term moorings have been deployed in various sites of the oceans (i.e., Astor et al., 2005: Lüger et al., 2004, 2006; González-Dávila et al., 2005; 2009; Schuster et al., 2009; Ullman et al., 2009; Watson et al., 2009; Padín et al., 2010; Gruber et al., 2002; Dore et al., 2003; Santana-Casiano et al., 2007; Bates et al., 2014). With the amount of data already gathered (http://www.socat.info/), climatologies that present average fluxes between the atmosphere and the ocean have been developed, so areas acting as a source or sink are now identified (Key et al., 2004; Takahashi et al., 2009). However, the low spatial resolution of these databases makes it lose relevant variability at relatively low spatial scales. This occurs in coastal areas, specially in upwelling regions, which are not adequately represented in large databases. Upwelling zones present a dynamic that raises water from relatively deep areas, which are rich in nutrients and CO_2. Nutrients promote primary production, which consumes CO_2, a process that would generate a CO_2 flux into the ocean. On the other hand, the upwelling also brings up CO_2 from deep seawater, which finally generates uncertainty about the actual role of upwelling areas as a source or sink of CO_2 (Michaels *et al.*, 2001). Indeed, previous researches indicate that upwelling areas act as a source or sink of CO_2 depending on their location (Cai *et al.*, 2006; Chen et al, 2013), where upwelling areas at low latitudes mainly act as a source of CO_2 (Feely *et al.*, 2002; Astor *et al.*, 2005; Friederich *et al.*, 2008; Santana-Casiano *et al.*, 2009; González-Dávila *et al.*, 2009) and those at mid-latitudes act as a sink of CO_2 (Frankignoulle and Borges, 2001; Hales *et al.*, 2005; Borges *et al.*, 2002; 2005; Santana-Casiano *et al.*, 2009; González-Dávila *et al.*, 2009). Several anthropogenic interactive effects are strongly influencing the general picture for the most representative Eastern Boundary Upwelling Systems (EBUS), and include upper ocean warming, ocean acidification and ocean deoxygenation (Gruber, 2011; Feely et al., 2008; Keeling et al., 2010). Moreover, evidence for an increase in winds that favor upwelling (Bakun, 1990; Demarcq, 2009; Oerder et al. 2015) support the possibility of a change in the current role of these highly productive areas. Recently, eddy-resolving regional ocean models have shown how upwelling intensification can be followed by major impact on the system's biological productivity and in the CO_2 outgassing (Lachkar and Gruber, 2013; Oerder et al., 2015). Wind observations and reanalysis products are controversial regarding the Bakun intensification hypothesis (Bakun 1990). Using different winds database for the Canary region, Barton et al. (2013) concluded that there was no evidence for a general increase in the upwelling intensity off northwest Africa. Marcello et al. (2011) found an intensification of the upwelling system in the same area during a 20-year period while the alongshore wind stress remained almost stable. Cropper et al. (2014) found that coastal summer wind speed increased, resulting in an increase in upwelling-favorable wind speeds north of 20ºN and an increase in downwelling-favorable winds south of 20ºN. Santos et al (2005; 2012) showed differences in Sea Surface Temperature, SST, between coast and ocean depending on the upwelling index, UI intensity, and that SST trends were not homogeneous either along latitude or longitude. Varela et al. (2015) also showed opposite results world wide when different wind databases were used and

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when the same wind database was considered depending on the length of data, season evaluated, and selected area. For the Mauritanian region, when wind stress data were used (Varela et al., 2015), a more persistent increasing trend in upwelling-favourable winds north of 21ºN and a decreasing trend south of 19ºN were determined.

Starting in June 2005, the QUIMA-voluntary opportunity ship line visited the Mauritanian-Cape Verde upwelling region northwest of Africa on a monthly basis (Fig. 1 and Supplementary Table 1S) producing for the first time a high resolution SST and partial pressure of CO_2, fCO_2, database. This database has been considered to show the variations in the CO_2 system under changes in the upwelling conditions in the Canary Ecosystem from 27ºN to 10ºN for the period 2005 to 2012.

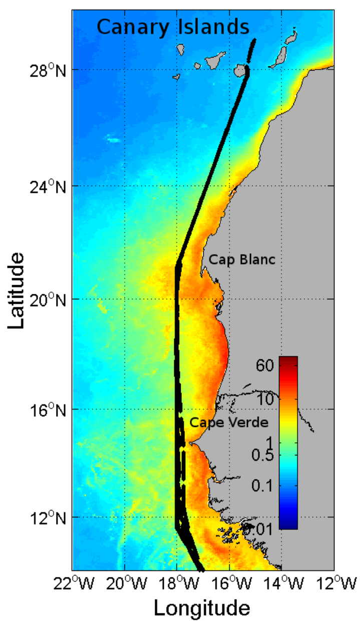

Fig. 1. Ship track in the area from 28ºN (Gran Canaria, The Canary Islands) to 10ºN (black dots). The locations of Cap Blanc and Cape Verde are indicated. Monthly Ocean Color (oceancolor.gsfc.nasa.gov) data for average chlorophyl *a* concentration (mg m^{-3}) were included in a MatlabTM routine and annually averaged, in order to draw the map for the area. The map has been generated using Matlab 7.12 R2011a.

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2. EXPERIMENTAL

2.1 Region evaluated.

The VOS line crosses the East Atlantic Ocean from the north of Europe (English Channel) to South Africa, calling Gran Canaria, the Canary Islands, with a periodicity of two months, which provides monthly data (southward or northward sections). In this work, the area between Gran Canaria at 27ºN and 10 ºN has been selected in order to study the Mauritanean-Cape Verde upwelling region. In its south route (Fig. 1), the ship leaves Gran Canaria, and goes straight to 100 Km off Cap Blanc, at 21ºN 17º45'W. It then follows this longitude, passing at 100 km off Cape Verde until 12ºN, where it changes direction to Cape Town, reaching 10ºN 17ºW at 330 km out of the coast of Guinea. Between 22ºN and 20ºN, the ship reaches the 500 m isobath. South of 15ºN, the ship moves between 1000 and 500 m isobath. In its north route, the ship follow the same reverse track.

2.2 Experimental data

Experimental data were obtained under the EU projects Carboocean and Carbochange (www.CarboOcean.org, https://carbochange.b.uib.no/) and now also available at http://www.socat.info/. An autonomous instrument for the determination of the partial pressure of CO_2 developed by Craig Neill following NOAA recommendations was installed in opportunity ships operated by the MSC company during the 2005 to 2008 period and Maersk Company from 2010 to 2012 along the so called QUIMA-VOS line between the UK and Cape Town, from July 2005 to January 2013 (Supplementary Table S1). Temperature was measured at three locations along the sampling circuit: in the intake (SeaBird SBE38L), in the equilibrator (SeaBird thermosalinograph SBE21 and internal PT100 thermometer), and in the oxygen sensor (Optode 3835 Aanderaa™). Differences between equilibrator and intake were constant in time due to the high seawater flux used but varied among ships due to the different locations of the equipment. Values varied between 0.06ºC when the equipment was placed close to the intake to 0.35ºC, when the equipment was one floor above, inside the engine room. The SST was also obtained from the NOAA_OI_SST-V2 data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA (http://www.esrl.noaa.gov/psd). These data had a spatial resolution of 1º latitude and 1º longitude and monthly averages were used. The correlation between our experimental SST data and satellite one was better than ± 1ºC, and reduced to ± 0.4ºC after removing the most affected upwelling regions (19-22ºN and 14-16ºN) , related to the high variability imposed by the upwelling.

The CO_2 molar fraction, $x$$CO_2$, in seawater was obtained every 150 s, while atmospheric $x$$CO_2$ data were taken every 200 min. The seawater intake was located at a 10 m depth. The system was calibrated every three hours, by measuring four different standard gases with mixing ratios of 0.0, 250 ppm, 380 ppm and 490 ppm of CO_2 in the air, provided by NOAA and traceable to the World Meteorological Organisation scale. The precision of the system is greater than 0.5 µatm and the accuracy estimated with respect to the standard gases is of 1 µatm. The fugacity of CO_2, $f$$CO_2$ (µatm), was calculated from $x$$CO_2$ after correcting for temperature differences between intake and equilibrator, according to the expressions for the seawater given by DOE (1994).

In order to compute a second carbonate system variable, the surface total alkalinity was computed from sea surface salinity, SSS, and SST (Lee et al., 2006). pH_T at the in situ temperature was computed from $f$$CO_2$ and A_T and with average annual surface ocean total phosphate and total silicate concentrations of 0.5 and 4.8 µmol kg^{-1}, respectively, from the World Ocean Atlas 2009, using the carbonic acid acidity constants by Merbach et al (1973) refitted by Dickson and Millero (1987).

Air-sea CO_2 fluxes, FCO_2 (mmol m^{-2} d^{-1}), were evaluated as

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$$FCO_2 = 0.24 * k * s * (fCO_2^{sw} - fCO_2^{atm}) \quad (1)$$

where 0.24 is the scale factor, *k* is the gas transfer velocity, *s* is the CO_2 solubility, fCO_2^{sw} is the seawater fugacity of CO_2 and fCO_2^{atm} is the atmospheric fugacity of CO_2. In order to evaluate ΔfCO_2 ($\Delta fCO_2 = fCO_2^{sw} - fCO_2^{atm}$), fCO_2^{atm} data were linearly interpolated to the fCO_2^{sw} time vector. A positive value for FCO_2 corresponds with a CO_2 outgassing from the ocean. *k* (cm h^{-1}) was evaluated with the parametrization (Wannikhoff, 1992):

$$k = 0.31 * W^2 * (Sc/660)^{-1/2} \quad (2)$$

where *W* is the wind speed at 10 m above the sea surface (m s^{-1}) and *Sc* is the Schmidt number.

The variables involved in estimating FCO_2 data (i.e. fCO_2^{sw}, fCO_2^{atm}, SST and SSS) were fitted to sinusoidal expressions (Lüger et al.,2004) for a given latitude as:

$$X(lat)^* = a_0 + a_1(t - 2005) + a_2 sin(2\pi t) + a_3 cos(2\pi t) + a_4 sin(4\pi t) + a_5 cos(4\pi t) \quad (3)$$

where a_i are the fitting coefficients, *t* is the sampling time expressed as year fraction and *X* represents any of the four variables. This procedure allowed us to re-construct the series of experimental data for periods not properly sampled. The variables were decomposed into an interannual term $X(lat)_t^* = a_0 + a_1(t - 2005)$ plus a periodical term $X(lat)_p^* = a_2 sin(2\pi t) + a_3 cos(2\pi t) + a_4 sin(4\pi t) + a_5 cos(4\pi t)$, that is, $X(lat)^* = X(lat)_t^* + X(lat)_p^*$. The periodical term accounts for the high frequency seasonal variability, while the interannual one marks the year-to-year trend. First, observations were grouped in a natural year for a given latitude, as if they had been taken in a single year (no correction was done for interannual variability). The mean seasonal climatology data associated with the periodic coefficients (i.e. a_2, a_3, a_4, and a_5) throughout the sampling period were determined. Next, the interannual coefficients a_1 were calculated by fitting the residuals resulting from subtracting the periodical component, $X(lat)_p^*$, from the original variable

X(*lat*). Fixing these five coefficients (a_1-a_5), new distributions for $f\mathrm{CO_2}^{sw*}$, $f\mathrm{CO_2}^{atm*}$, *temp** and *salinity** were constructed with a daily resolution based on the curve fits given for each variable as in Eq. (3), providing the coefficient a_0. The mean residual on the determination of those four variables with respect to the experimental values were ± 3.7 µatm, ± 1.5 µatm, ± 0.22 ºC, and ± 0.05 for $f\mathrm{CO_2}^{sw*}$, $f\mathrm{CO_2}^{atm*}$, *temp** and *salinity**, respectively. When the monthly satellite SST values were considered, the new *temp** function averaged for each month produced values within ± 0.47ºC, confirming that this procedure was able to fit non-sampled periods. It was assumed that the same procedure was valid for non-sampled $f\mathrm{CO_2}$. Finally, daily $\mathrm{FCO_2}^*$ time series between 10 and 27ºN with a latitudinal resolution of 0.5° were calculated with a standard error of estimation of 0.5 mmol m^{-2} d^{-1} (15% of error) that produced mean residuals (experimental $\mathrm{FCO_2}$ - $\mathrm{FCO_2}^*$) of 0.4 mmol m^{-2} d^{-1} and Pearson correlation coefficients between experimental and computed $\mathrm{FCO_2}^*$ of $r > 0.6$, $p < 0.01$.

Chlorophyll-a was calculated from measurements made by the Moderate Resolution Imaging Spectroradiometer (MODIS) aboard NASA's Aqua satellite. Monthly averages with spatial resolution of 9 km supplied by Ocean Color (oceancolor.gsfc.nasa.gov) were used.

Wind data were downloaded from the NCEP CFSR database at http://rda.ucar.edu/pub/cfsr.html developed by NOAA and retrieved from the NOAA National Operational Model Archive and Distribution System and maintained by the NOAA National Climatic Data Center. The spatial resolution is approximately 0.3 × 0.3° and the temporal resolution is 6 hours. The reference height of the wind data is 10 m.

Rainfall data were collected by the Precipitation Radar installed on the Tropical Rainfall Measuring Mission (TRMM) satellite (http://precip.gsfc.nasa.gov). Monthly averages with a spatial resolution of 0.5º×0.5º (product 3A12, version 07) were used

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(Supplementary Fig. S1) in order to explain changes in seasonal surface salinity distributions.

3. RESULTS AND DISCUSSION

3.1 Physical propeties

The variability of the Mauritanian-Cape Verde upwelling was analyzed in terms of the upwelling index (Nykjaer and Van Camp, 1994) (Fig. 2) using satellite wind data.

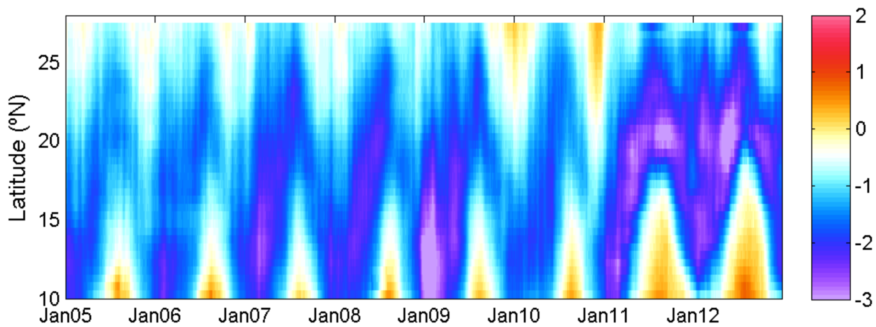

Fig. 2. Time series of upwelling index ($m^2 s^{-1}$) in the Mauritanian-Cape Verde upwelling region along the ship track computed following Nykjaer and Van Camp (1994).

Results clearly distinguish two main subareas in the upwelling system. 1) North of 20ºN, the upwelling conditions were favorable throughout the year, although the highest upwellings were observed from March to September with a northward shift from 20º to 22ºN. 2) South of 20ºN, a marked seasonality was observed. South of 15ºN, in the Cape Verde area, upwelling conditions were favorable during autumn and winter with the maximum intensity observed during January and February due to the replacement of the trade winds during the summer by the monsoon winds, which advect warm water northward along the shore (Nykjaer and Van Camp, 1994). Our results (Fig. 2) are quite consistent with previous research (Nykjaer and Van Camp, 1994; Marcello et al., 2011; Santos et al., 2005; 2012) but include the years 2010 to 2012 where UI at around 20-21ºN

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presented a shift of the upwelling regime intensity from high to strong. The analysis of upwelling trends along this area has been controversial since it is highly dependent on the selected region (Santos et al., 2012). The inter-annual evolution of UI over the period 2005 to 2012 (Fig. 3, green line) determined by averaging monthly values on an annual base followed that showed by Santos et al. (2012), indicating an increase in the UI (mean confidence interval of 9 $m^2 s^{-1}$).

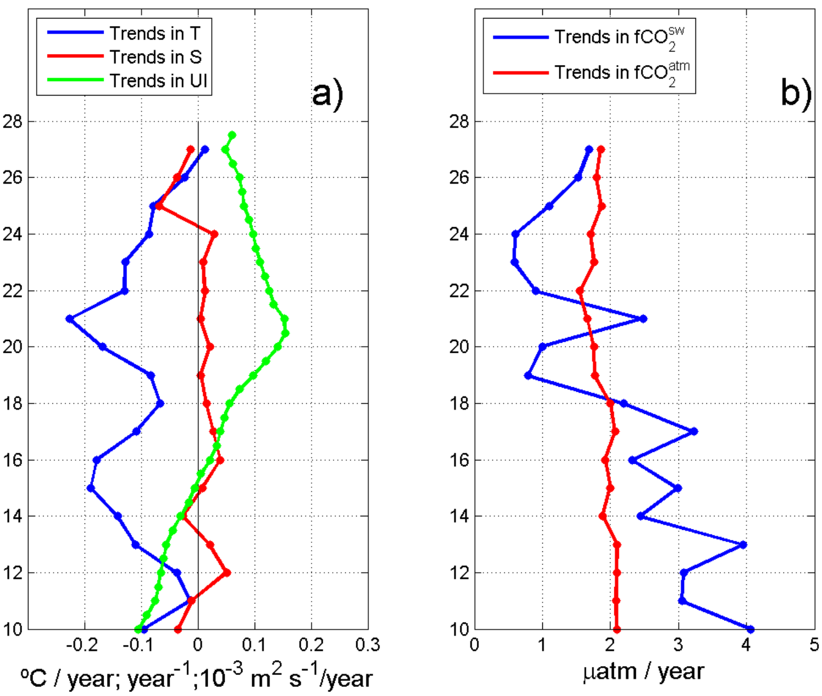
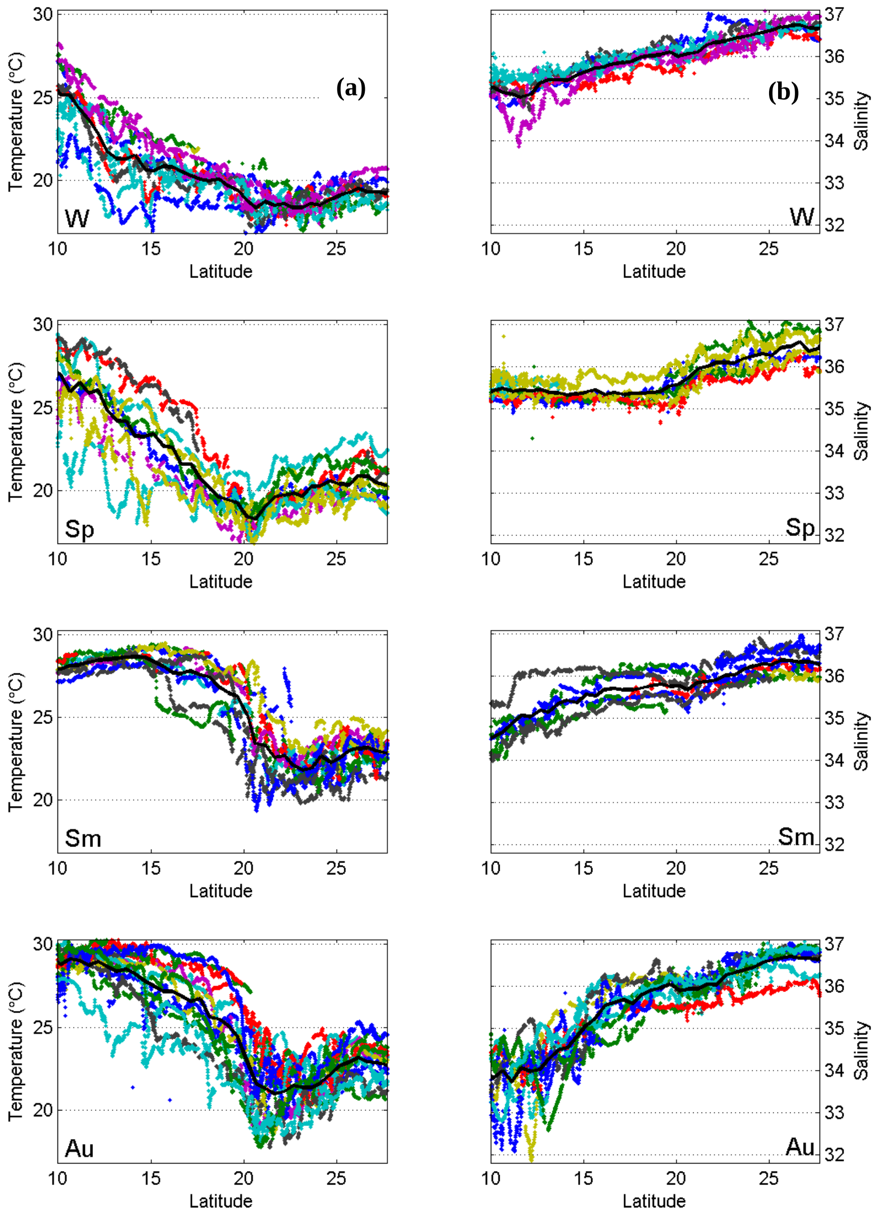


Fig. 3. Latitudinal distribution of the interannual trends for the Upwelling Index (UI) and for the four experimental variables along the QUIMA-VOS line integrated over every degree. The a) pannel presents the trends for Upwelling index (mean confidence interval of 9 m^2s^{-1}), SST (ºC yr^{-1}, confidence interval 0.13ºC) and SSS (yr^{-1}, confidence interval 0.06) and the b) pannel the trends for fCO_2^{sw} and fCO_2^{atm} (confidence intervals 4.23 and 0.44 µatm).

The upwelling index (except for the area south of 15ºN) confirmed the stronger upwelling observed since 1995-1996 in this region after a more than a 10-year (from at least 1982 to 1995) period of weaker upwelling (Santos et al., 2012). Local zonal differences between ocean and coastal SST trends determined by using satellite data by Santos et al. (2005) for the period 1982 to 2000, extended by Santos et al. (2012) until 2010 and in this study until 2012 (data not shown) confirmed the intensification of the upwelling regime along the African coast. This has been described as a decadal scale shift of the upwelling regime intensity (Marcello et al., 2011; Santos et al., 2012). To the south of 15ºN, the annual UI values (Fig. 2 and 3) indicate that the SST close to the coast is becoming warmer. They serve as an indication of decadal variability of the summer monsoon winds and associated northward advection of warm water along the coast (Santos et al., 2012). The highest upwelling intensity along the VOS line was located at the capes, Cap Blanc and Cape Verde. From satellite chlorophyll-*a* data, especially off Cap Blanc, giant filaments with chlorophyll concentrations above 1 mg m^{-3} persist year-round, spreading from the coast several hundred kilometers offshore (Fig. 1). North of Cap Blanc the upwelled water originates from the North Atlantic Central Water, and mixes with South Atlantic Central Water, SACW, towards the south (Mittelstaedt, 1983). South of Cap Blanc, the upwelling of nutrient rich SACW promotes phytoplankton growth between Cap Blanc and Cape Verde. Towards 12°N, upwelling is also fed by the North Equatorial Under Current (Hagen and Schemainda, 1984). Moreover, the entire northwest African coast is also influenced by the African desert dust transport by the mid-tropospheric Harmattan winds originating from the central Sahara, which supplements the levels of micronutrients (such as iron) to the adjacent marine ecosystem (Mittelstaedt, 1983; Neuer et al., 2004; Swap et al., 1996).

The area is also affected by the migration of the Inter-Tropical Convergence Zone (ITCZ), related to maximum precipitation rates. To have a significant satellite precipitation record in our region of interest, precipitation data were integrated longitudinally between 25.25ºW and 9.75ºW. Time series for the latitudinal distribution of integrated precipitation (Supplementary Fig. 1S) identified the average position of the ITCZ related to maximum precipitation rates. The ITCZ was located at its southernmost position (2ºN) during winter, reaching its northernmost position (14-16ºN) around summer. The ITCZ reached our area of interest (>10°N) from late spring to late summer.

The latitudinal distributions of experimental surface temperature and salinity along the vessel track are shown in Fig. 4, grouped by seasons. In situ temperature at 27°N shows temperatures in the range of 18 to 24°C with the minimum in winter and maximum in late summer-early autumn. The annual temperature range was somewhat higher at 20°N, with summer maximum of around 26°C and minimum in spring of about 17ºC. At 10°N, temperatures were the highest throughout the year (>25°C), with minimum values in winter and maximum in late spring and late autumn. The low values observed during the end of summer are related to the arriving of the ITZC at those latitudes. The thermal distribution shows a temperature increase as we move to the Equator and a notable cooling at the upwelled waters off Mauritania. The temperature generally decreased from 10ºN to about 20ºN to 21ºN, where the ship meets the Mauritanian upwelling. From there to the north, the temperature rises as the ship leaves the upwelling area on its way to the Canary Islands. Only during winter time and the begining of the spring, the upwelling of cold water from Cape Verde area was detected. Salinity minimum values were normally located at 10ºN, increasing to maximum values at the Canaries' latitude. The minimum values of salinity were exceptionally low during autumn from 10ºN to 16ºN by both the freshwater input from rivers that increase their outflow during this season (Nicholson, 1981) and by the northward shift of the ITCZ during this part of the year.



286 Fig. 4. Experimental series of a) SST and b) SSS data in the Mauritanian - Cape Verde coastal
287 region grouped by seasons: winter (W), spring (Sp), summer (Sm) and autumn (Au). The averaged
288 values for all cruises in Table S1, are shown in black for each season including the 95%
289 confidence limits.
290

291 Anomaly fields for temperature and salinity (data not shown) were calculated as
292 the difference between the observations and the mean values at each season for individual

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latitudes. For temperature, the largest anomalies in winter and spring were located south of 18°N, with values of ±2ºC, related to the seasonal cycle of the Cape Verde upwelling. During summer the pattern changed and the largest anomalies were detected in the upwelling area at 18-22°N, with values of ±5ºC when the upwelling index for the Mauritanian area was highest (Fig. 2). In autumn the temperature anomalies were shifted slightly to the north, 20-24°N, with values of ±3ºC related to the observed pulses in upwelling favorable winds that affected the surface seawater properties. On the other hand, salinity anomalies showed a very homogeneous pattern in all latitudes for winter, spring and summer, with values generally within ±0.5. However, during autumn important anomalies south of 18°N were observed, with values in the range of ±1.5. In this region, the upwelling development, the river discharge and the rainy season controlled the observed distribution (Yoo and Carton, 1990).

3.2 Carbon dioxide variability

The latitudinal distribution of the experimental fCO_2^{sw} data (Fig. 5a) grouped by seasons, showed they were always above the fCO_2^{atm}, with the highest values between 18 and 23ºN for all seasons due to the variability imposed by the upwelling off Mauritania. During winter, when the Cape Verde upwelling develops (Fig. 2), the 12-15ºN region also presented higher fCO_2^{sw} values than those in the atmosphere. fCO_2^{sw} data showed a latitudinal shift along the sea1sons following that observed in the upwelling index: i.e., in winter, the largest values were located between 19º and 24ºN; in spring, they were located between 16º and 22ºN; during summer and autumn, the largest fCO_2^{sw} values were recorded in the range 20º to 23ºN. fCO_2^{sw} normalized to the mean SST of 22ºC for the region ($NfCO_2^{sw}$, Fig. 5b) reinforced the variability indicating that upwelling is the major factor contributing to the fCO_2 variability.

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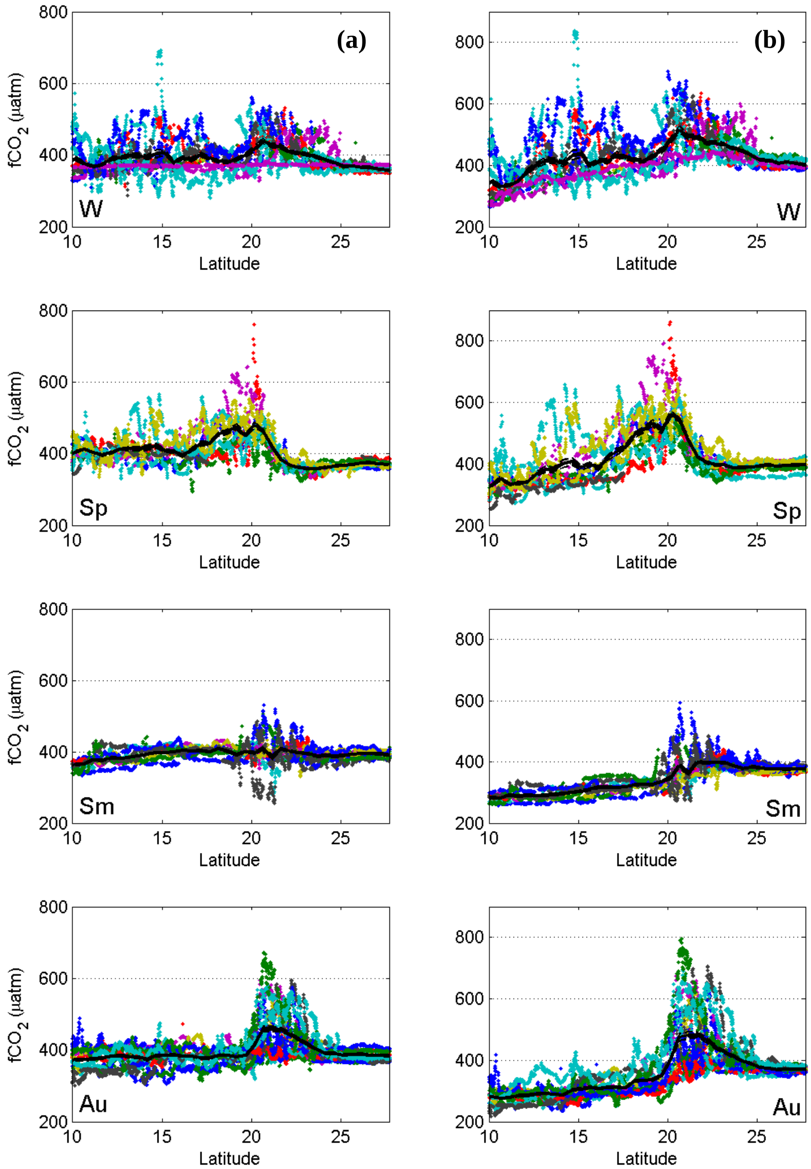

Fig 5. Experimental series of fugacity of CO_2 data in the Mauritanian-Cape Verde coastal region grouped by seasons: winter (W), spring (Sp), summer (Sm) and autumn (Au). a) fCO_2^{sw} latitudinal distribution. b) Normalized fCO_2^{sw} values to a constant temperature of 22ºC. The averaged values for all cruises in Table S1, are shown in black for each season including the 95% confidence limits.

According to Takahashi et al. (1993), fCO_2^{sw} increases with temperature at a rate that is 4.3% µatm ºC^{-1} (around 16 µatm ºC^{-1} at this area) in a thermodinamically controlled

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system. At 27ºN, the rate, as SST increases, was only of 7.45 µatm ºC^{-1} due first to biological uptake and second to the CO_2 outflux. At 20ºN the rate became negative with a value of -10.9 µatm ºC^{-1}, clearly indicating the important injection of cool and CO_2 rich seawater at the upwelling area, neither being compensated by the solubility nor the biological carbon pumps. At 10ºN, and as a result of the seasonal upwelling, the rate was still negative but of only -4.3 µatm ºC^{-1}. When NfCO_2^{sw} was related with SST at the latitudes 19º to 21ºN in the upwelling vicinity of Cap Blanc, an inverse relationship of 70-100 µatm ºC^{-1} was found during winter and spring, while in summer and autumn the inverse relationship was reduced to 12-18 µatm ºC^{-1}. While the upwelling indexes at those latitudes were quite constant throughout the year, the different rates observed should be related to biological consumption of the CO_2 excess. During winter and spring the injection of CO_2 in the upwelling is not decreased by the biological activity in the area. At the end of spring and during summer the Chl-*a* content reached its maximum and most of the CO_2 was consumed and/or exported and, therefore, the rate was strongly reduced.

Figure 3 depicts the observed interannual trends (a_1 coefficient in Eq. 3) for the four experimental recorded detrended parameters, together with the UI trend. Confidence intervals of the computed mean annual values for SST, SSS, fCO_2^{atm}, fCO_2^{sw} were 0.13ºC, 0.06, 0.44 µatm and 4.23 µatm, respectively. There was a clear SST trend whereby seawater along the VOS line track was getting cooler with maximum cooling rates at the location of Cap Blanc (21ºN) and Cape Verde upwellings (15ºN) with rates higher than -0.2ºC yr^{-1}. Data from the first three years (2005 to 2008) at 21ºN showed lower temperatures with higher cooling rates that reached -0.7ºC yr^{-1}, although three years of data are not representative. The area crossed by the VOS line along 17º45'W from 22ºN to 10ºN is located inside the 1000 m isobath that is well inside the mean frontal activity in the Canary region of about 200 km width (Wang et al., 2015). The different changes

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in temperature in the coastal slope and offshore waters are related to the different origins of the waters upwelled from depths of about 100 m to the surface (Mittelstaedt, 1983) that spread off the coastal area. The offshore water SST is less variable owing to longer residence time in the ocean surface. These effects and the fact that the VOS line keeps a track line that crossed the upwelling cells at a distance to the coast that varies among cells, contributes to the observed spatial variability. There was no attempt to compare latitudinal and longitudinal effects on the observed values. Our experimental data, however, does not show any positive annual based SST rates in the upwell affected area, and only when the ship approached the Canary Islands, the trends became less negative, reaching a value of +0.02ºC yr^{-1} at 27ºN, similar to those obtained for oceanic Atlantic water (Bates et al., 2014).

fCO_2^{atm} for the area presented the interannual increase of about 2 ± 0.3 µatm y^{-1} observed in atmospheric stations, while fCO_2^{sw} presented a heterogeneous distribution. South of 18ºN the rate of increase was always higher than that in the atmosphere reaching a maximum value of 4.1 ± 0.4 µatm y^{-1} at 10ºN. At 27°N, fCO_2^{sw} increased at a rate of 1.7 ± 0.2 µatm y^{-1} similar to that determined at the ESTOC time series site (González-Dávila et al., 2010) located at 29º10' N 15º30'W. In the Cap Blanc area, fCO_2^{sw} increased at an averate rate of 2.5 ± 0.4 µatm y^{-1} with the highest values in the period 2005 to 2008 (a rate of 4.6 ± 0.5 µatm y^{-1} was computed with only those years). Around Cap Blanc, fCO_2^{sw} always presented lower rates of increase than in the atmosphere with values well below 1 µatm y^{-1}. The observed decrease in SST and the trends in fCO_2^{sw} can only be explained by a reinforced upwelling. North of 18ºN, the lowest rate of increase in fCO_2^{sw} compared to fCO_2^{atm}, together with a decrease in temperature, indicated that upwelling is also favoring an increase in the net community production around the Mauritanian upwelling, consuming and/or exporting the CO_2 rich upwelled waters favored by the lateral transport of the Mauritanian current (Lachkar and Gruber, 2013; Varela et al., 2015). The upwelling intensification effects observed in the trends of our experimental data support the recent wind stress trends (Crooper et al., 2014; Varela et al., 2015; Santos et al., 2012) of increased upwelling-favorable winds, at least for the period 2005-2012 in the Canary upwelling region (Fig. 2 and 3). The intensification of the upwelling results in a change in the measured upwelled water properties due to either higher upwelling velocities or deeper source upwelled waters. However, what remains unclear from these records is to what extent those changes reflect upwelling variations due to climate change forcing versus natural decadal variability in the upwelling areas occurring over interannual timescales.

Because of the upwelling intensity is changing, other variables will also be affected. $pH_{T,is}$ at 21 ± 0.25ºN was computed from fCO_2 and alkalinity pairs of data. Alkalinity was computed from regional correlations with SST and SSS (Lee et al., 2006) which could under-represent seasonal and interannual variations in upwelling areas. However, pH computed from fCO_2 values are relatively insensitive to errors in $A_{T,}$ and fCO_2 controls the magnitude and variability of pH (a 60 µmol kg^{-1} change in A_T will affect a 0.1% in pH, that is, about 0.01 pH units). Figure 6 depitcs the computed $pH_{T,is}(A_T, fCO_2)$ data and the harmonic fitting Eq. (3) providing seasonal variability and interannual trend. Considering the small systematic biases in interannual dynamics, it is determined a decrease in pH at a rate of -0.003 ± 0.001 per year (Fig. 6). This decrease is on the highest rate values determined in several time series stations (Bates et al., 2014), where oceanic SST has only slightly increased in the last decades. However, at the Mauritanian upwelling area and at the location where our VOS line approached this region, SST decreased at a rate of -0.22 ± 0.06ºC y^{-1} (Fig. 3). Solely, this decrease in temperature would increase the pH by a rate of +0.004 yr^{-1} and the fCO_2 would decrease by 4 µatm yr^{-}

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[1] The net effect of the increase in the amount of rich CO_2/low pH upwelled waters in the Mauritanian upwelling would be, therefore, a decrease in the pH of over -0.007±0.002 units y^{-1} and an increase in fCO_2 of +6.5 ± 0.7 µatm y^{-1} (with periods where those rates could reach values of 0.015 y^{-1} in pH and 10.5 µatm y^{-1} in fCO_2 as recorded during 2005-2008). Those values are greatly compensated by the important decrease in the SST resulting in the observed rates of -0.003 ± 0.001 pH units and +2.5 ± 0.4 µatm of fCO_2 per year.

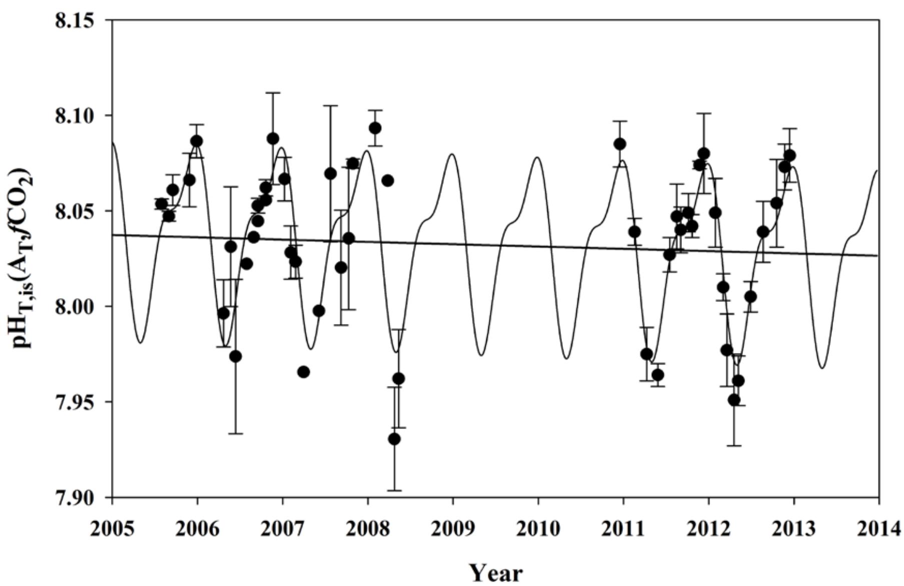

Fig. 6. pH at *in situ* SST in total proton scale computed from total alkalinity (based on regional correlations with SST and SSS, Lee et al., 2006) and fCO_2 at 21 ± 0.25 °N. The error bar represents the standard deviation of the computed data for each cruise for the selected latitude. The black line shows the harmonic fitting Eq. (3) for the data and the corresponding linear trend.

3.3 Fluxes of CO_2

The annual air-sea CO_2 flux for the full domain was positive (Fig. 7a), with the area off Mauritania, between 18 and 22°N, acting as an active source of CO_2 to the atmosphere

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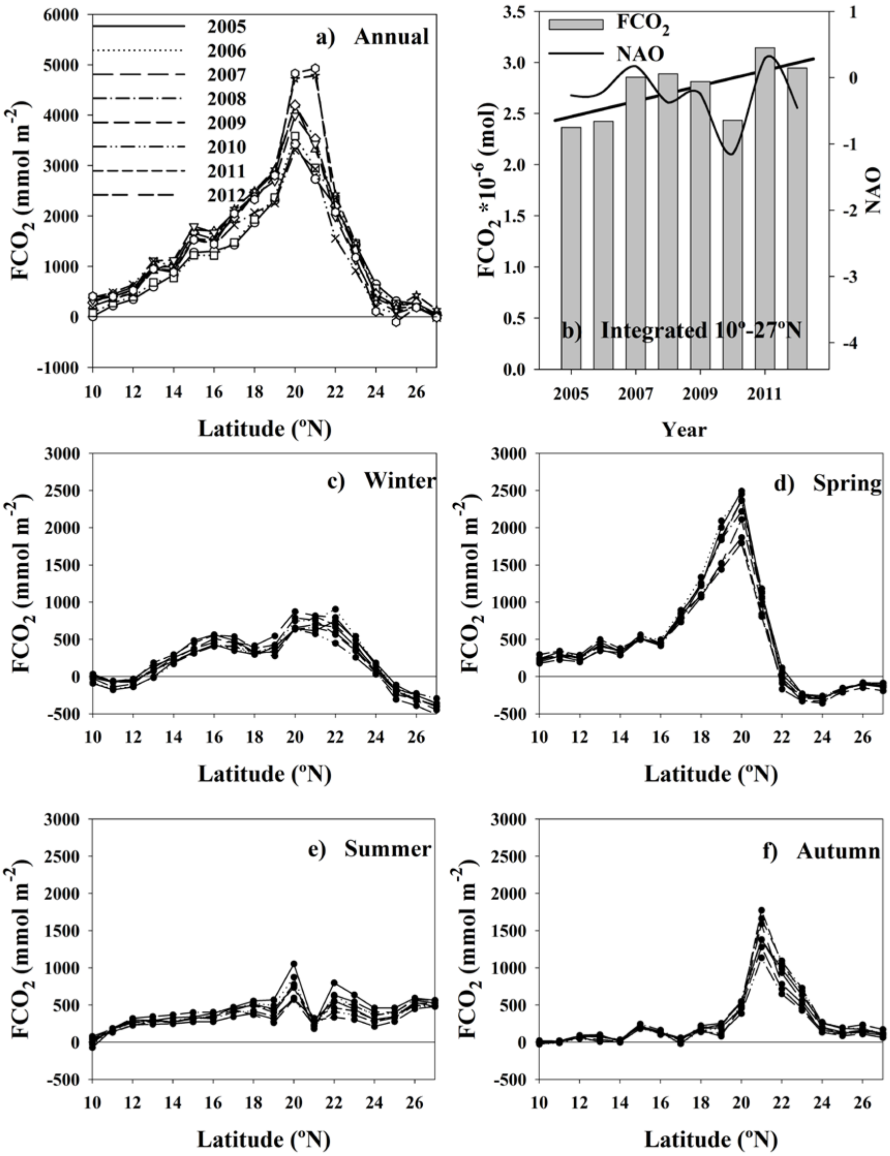

Fig. 7. Latitudinal distribution of seasonal and annual CO_2 fluxes, FCO_2 (mmol m^{-2}). Fluxes of CO_2 were computed using Wannikhoff (1992) parametrization and satellite winds with a resolution of 6 hours. a) Integrated year-to-year from 2005 to 2012 and b) latitudinally integrated for 2005 to 2012 together with annual values for NAO index. Latitudinal distribution of FCO_2 seasonally integrated from 2005 to 2012 are depicted for winter (c), spring (d), summer (e) and autumn (f).

with values close to 5 mol CO_2 m^{-2} (Fig. 7a). North of 24ºN, in the area not affected by the coastal upwelling, an average flux of +0.2 ± 0.1 mol CO_2 m^{-2} was determined.

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The ingassing observed during winter and spring of -185 ± 36 mmol CO_2 m^{-2} for the full period (Fig. 7) was surpassed by the outgassing during summer and autumn of 295 ± 150 mmol CO_2 m^{-2}. South of 24ºN, it was observed that during spring (Fig. 7d) the photosynthetic activity was not intense enough to uptake the CO_2 injected by the strongest upwelling in the surface waters and the area acted as a source of CO_2 with values reaching 3 mol CO_2 m^{-2} in 2012. During summer (Fig. 7e), primary producers and lateral advection of warm waters by the Mauritanian current could consume/export the CO_2 rich waters reaching values of 0.5 mol m^{-2}. During autumn (Fig. 7f), only the area between 20ºN and 23ºN acted as a source of 1-2 mol CO_2 m^{-2}, while the rest was almost in equilibrium. It was also detected that the late autumn-winter upwelling in the 14º to 17ºN region contributed to an increased outgassing with a second annual submaximum of about 0.7 mol CO_2 m^{-2} in winter (Fig. 7c). South of 14ºN, annual CO_2 fluxes decreased from about 1 mol m^{-2} at 14ºN to being roughly in equilibrium at 10°N.

The integrated CO_2 fluxes for the area 10º to 27ºN along the VOS line section for the years 2005 to 2012 (Fig. 7b) were between 2.3 and 3.1 10^6 mol, with an important interannual variability. FCO_2 increased during the studied period by 0.08 ± 0.03·10^6 mol yr^{-1}. The augment in FCO_2 is related to the observed increase in wind speed (Fig. 3, indicated as UI) north of 16ºN that far surpassed the effect of the smaller annual rate of increase in fCO_2^{sw} than in fCO_2^{atm} north of 19ºN with the exception at 21ºN (Fig. 3). South of 16ºN, the decrease in wind speed did not exceed the effect of the increment in ΔfCO_2 associated to the increase in downwelling indexes (Fig. 3; Santos et al., 2012), and FCO_2 was slightly ascending. The variability observed in the annual integrated CO_2 fluxes (Fig. 7b) was related with the basin-scale oscillations, the North Atlantic Oscillation (NAO) index and the East-Atlantic Pattern (EA) (http://www.cpc.ncep.noaa.gov/data/teledoc/telecontents.shtml). Cropper et al. (2014)

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found winter upwelling variability was strongly correlated with the winter NAO (r values ranged from 0.50 at 12–19ºN to 0.59 at 21–26ºN), due to the strength of the Azores semi-permanent high-pressure system, which modifies trade wind strengths. The annual integrated FCO_2 was related with the annual NAO index (Fig. 7b) with a similar r = 0.54, even when fluxes are not only controlled by wind strength. However, Fig. 7a clearly indicates that the Mauritanian upwelling area was the most important contributor to FCO_2. There was not a significant correlation coefficient with the winter NAO (r = 0.23). Also, the EA index, because represents the southward-shifted NAO-like oscillation, presented a lower significant value (r = 0.48), as it was observed by the upwelling index (Cropper et al., 2014). The correlation between fluxes and climate indexes describing the main mode of variability across the Atlantic sector may be directly related to the Azores High and its influence on the trade wind strength.

If the FCO_2 values are assumed to be valid for at least 100 km to both sides of the QUIMA-VOS line, the total flux of CO_2 being ejected to the atmosphere would reach a value of 30 Tg of carbon dioxide a year for the period 2005-2012, with a rate of increase of 1 Tg yr^{-1}. However, it should be considered that the export of the rich fCO_2 upwelled water with high nutrient concentration off the coastal areas would promote a decrease in surface fCO_2 values (as those observed north and south 21ºN) that will produce an ingassing of CO_2. This could balance the observed outgassing increase in a more global scale.

4. CONCLUSIONS

The Mauritanian-Cape Verde upwelling has been shown to be an important area sensitive to decadal and climate change forcing on upwelling processes, which strongly affects the CO_2 surface distribution, ocean acidification rates and air-sea CO_2 exchange.

The results for the period 2005 to 2012 confirm, firstly, the upwelling intensification at the Mauritanian-Cape Verde upwelling system by using experimental SST and carbon dioxide system variables. Secondly, that upwelling regions at low-mid latitudes are strong sources of CO_2 to the atmosphere and thirdly, that as a direct result, the pH is decreasing at a rate of -0.003 ± 0.001 per year and the amount of emitted CO_2 is increasing annualy at a rate of 1 Tg due to wind increase even when primary production seems to also be reinforced in the upwelling area. The extent to which those changes can be attributed to natural decadal variability in this EBUS over interannual timescales remains unclear and more years of monthly data should be recorded. Sustained volunteer observing lines are shown as one of the most significative contributors to the knowledge of how ocean surface waters are being affected by present and future climate change. The results from VOS lines can provide accurate data for changes in SST, FCO_2 and, consequently, upwelling intensification effects due to global change conditions under decadal natural variability.

Data availability.

All data are free available at the SOCAT data base, http://www.socat.info/ and at the Carboocean and Carbochange web pages www.CarboOcean.org, https://carbochange.b.uib.no/, respectively

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Author contributions

M.G.D. and J.M.S.C worked in the equipment installation, data collection and designed the study. F.M. processed the data, generated figures and results. All of them collaborated in the discussion of the data and the writing of the paper.

Competing interests

There is not any competing interest.

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