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 ecological and economic importance due to the high biological productivity. The role of these regions in the global carbon cycle makes them essential in addressing climate change. The physical forcing of upwelling processes that favor the production in these areas are already being affected by global warming, which will modify the intensity of the upwelling and, consequently, the carbon dioxide cycle. Here, we present monthly high resolution surface experimental data for temperature and partial pressure of carbon dioxide in one of the four most important upwelling regions of the planet, the Mauritanian-Cape Verde upwelling region, from 2005 to 2012. This data set provides direct evidence of seasonal and interannual changes in the physical and biochemical processes. Specifically, we show an upwelling intensification and an increase of 0.6 Tg a year in CO$_2$ outgassing due to increased wind speed, despite increased primary productivity. This increase in CO$_2$ outgassing together with the observed decrease in sea surface temperature at the location of the Mauritanian Cape Blanc, 21°N, produced a pH decrease of $-0.003 \pm 0.001$ per year.
1. INTRODUCTION

The excess of CO$_2$ in the atmosphere, largely responsible for global climate change, has prompted research on the role of the oceans in the carbon cycle. The aim in recent decades has been to assess how the oceans act as sources or sinks within the carbon cycle. To achieve this goal, high spatial and temporal observations representative of the distribution of CO$_2$ fluxes between the ocean and atmosphere are necessary. Automated instruments on volunteer observing ships (VOS) serve to provide as many observations throughout the global ocean as possible, in addition to the data collected on scientific cruises and at long-term moorings (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, identifying areas acting as a source or sink (Key et al., 2004; Takahashi et al., 2009). However, the low spatial resolution of these databases limits the applicability especially in coastal areas. Upwelling regions are particularly under-represented in such large databases. Upwelling presents a dynamic process that raises nutrient and CO$_2$ rich water from relatively deep areas to the surface. The nutrients reaching the photic zone promote primary production, which consumes CO$_2$. This process generates a CO$_2$ flux into the ocean. On the other hand, the upwelling also brings up CO$_2$ from deep seawater, which generates uncertainty about the actual role of upwelling areas as a source or sink of CO$_2$ (Michaels et al., 2001). Indeed, upwelling areas may act as a source or sink of CO$_2$ depending on their location (Cai et al., 2006; Chen et al., 2013), where upwelling regions
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 mainly 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 strongly influence Eastern Boundary Upwelling Systems (EBUS), including upper ocean warming, ocean acidification and ocean deoxygenation (Gruber, 2011; Feely et al., 2008; Keeling et al., 2010). Moreover, evidence of increased wind speed that would favor upwelling (Bakun, 1990; Demarcq, 2009; Oerder et al., 2015) supports the possibility of a change in the dynamics of these highly productive areas. Recently, eddy-resolving regional ocean models have shown how upwelling intensification can cause a major impact on the system’s biological productivity and 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 wind databases 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 while 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 Sea Surface Temperature (SST) was not homogeneous either along latitude or longitude and depending on the upwelling index (UI intensity). Varela et al. (2015) demonstrated opposite results worldwide depending on the length of data, season evaluated, and selected area within the same wind dataset or between datasets. 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 21°N and a decreasing trend south of 19°N was determined.

Starting in June 2005, the QUIMA-VOS line visited the Mauritanian-Cape Verde upwelling region northwest of Africa on a monthly basis (Fig. 1 and Supplementary Table S1) producing for the first time a high resolution database of SST and partial pressure of CO₂ expressed as fugacity f/CO₂. This database shows the variations in the CO₂ system under changes in the upwelling conditions in the Canary Ecosystem from 27°N to 10°N for the period 2005 to 2012.

Fig. 1. Ship track in the area from 28°N (Gran Canaria, The Canary Islands) to 10°N (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. The map has been generated using Matlab 7.12 R2011a.
2.1 Study Region.

The VOS line crosses the East Atlantic Ocean from the north of Europe (English Channel) to South Africa, calling at 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 Mauritanian-Cape Verde upwelling region. In its route south (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 route north, the ship follows 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 CO₂ developed by Craig Neill following NOAA recommendations was installed in a VOS line. This was operated by the MSC company from 2005 to 2008 and the Maersk Company from 2010 to 2012. This VOS line (QUIMA-VOS) run 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™). After the
seawater pump, the intake is divided in two lines, one feeding the CO₂ system and the
other the oxygen sensor, the fluorometer and the seabird thermosalinometer. Differences
between equilibrator and intake were constant in time due to the high seawater flow but
varied among ships due to the different locations of the equipment. Values varied between
0.06°C when the equipment was placed close to the intake to 0.35°C, 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 1° latitude
and 1° longitude and monthly averages were used. The correlation between our
experimental SST data and satellite one was better than ± 1°C, and improved to ± 0.4°C
after removing the most affected upwelling regions (19-22°N and 14-16°N), related to the
high variability imposed by the upwelling.

The CO₂ molar fraction, xCO₂, in seawater was obtained every 150 s, while atmospheric
xCO₂ data were obtained every 180 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 in the ranges of 0.0, 250-290 ppm, 380-410 ppm and 490-530 ppm of
CO₂ 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 inside the standards range. For
xCO₂ values higher than the highest standard (532.04 ppm), the accuracy will be reduced,
even when linearity was observed in all cases inside the standards range. The fugacity of
CO₂, f/CO₂ (µatm), was calculated from xCO₂ after correcting for temperature differences
between intake and equilibrator, according to the expressions for the seawater given by
DOE (1994). Normalised f/CO₂ to the mean SST for the area (T_mean) was computed
following Takahashi et al. (1993)
\[(NfCO_2) = fCO_2 \cdot \exp[0.0423(T_{\text{mean}} - SST)] \]  

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 \(fCO_2\) and \(A_T\) and with average annual surface ocean total phosphate and total silicate concentrations of 0.5 and 4.8 \(\mu\text{mol kg}^{-1}\), 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

\[FCO_2 = 0.24 \cdot k \cdot s \cdot (fCO_2^{sw} - fCO_2^{atm})\]  

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 \((fCO_2^{sw} - fCO_2^{atm})\), \(fCO_2^{atm}\) 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 (Nightingale et al., 2000):

\[k = (0.222 \cdot W^2 + 0.333 \cdot w) \cdot (Sc/660)^{-1/2}\]  

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:

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

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where $a_i$ are the fitting coefficients, $t$ is the sampling time expressed as year fraction and $X^*$ represents any of the four fitted variables. This procedure allowed us to re-construct the series of experimental data for periods without monthly data. The variables were decomposed into an interannual term $X(lat)_a^* = a_0 + a_1(t - 2005)$ 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, $X(lat)^* = X(lat)_a^* + X(lat)_p^*$. 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 $fCO_2^{sw*}$, $fCO_2^{atm*}$, SST*, and SSS* were constructed with a daily resolution based on the curve fits given for each variable as in Eq. (4), providing the coefficient $a_0$. The accuracy of this fitting procedure was checked by both computing the correlation between experimental and reconstructed values and by determining the mean residuals. The Pearson coefficients were always over 0.87 for SST (average 0.94 ± 0.03), over 0.69 for both $fCO_2^{sw*}$, $fCO_2^{atm*}$ (average of 0.79 ± 0.07 and 0.82 ± 0.04, respectively) and over 0.67 for SSS (average 0.79 ± 0.07). The mean residual on the determination of those four variables were ± 3.7 µatm, ± 1.5 µatm, ± 0.22 °C, and ± 0.05 for $fCO_2^{sw*}$, $fCO_2^{atm*}$, SST* and SSS*, respectively. When the monthly satellite SST values were considered, the new SST* function averaged for each month produced values within ± 0.47°C, confirming that this procedure was able to fit non-sampled periods. It was assumed that the same procedure was valid for non-sampled $fCO_2$. Finally, daily $FCO_2^*$
time series between 10ºN 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 FCO₂ - FCO₂*) of 0.4 mmol m⁻² d⁻¹ and Pearson correlation coefficients between experimental and computed FCO₂* 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. We used monthly averages with spatial resolution of 9 km supplied by Ocean Color (oceancolor.gsfc.nasa.gov).

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 for 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 (Supplementary Fig. S1) in order to explain changes in seasonal surface salinity distributions.
2. RESULTS AND DISCUSSION

3.1 Physical properties

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. Negative (positive) UI values correspond to upwelling (downwelling) favorable conditions. The strongest negative values of the index correspond to more intense upwelling. Results clearly distinguish two main subareas in the upwelling system.

Fig. 2. Time series of upwelling index (UI*10^{-3} m^2 s^{-1}) in the Mauritanian-Cape Verde upwelling region along the ship track computed following Nykjaer and Van Camp (1994). Cool colours are related to upwelling events and warm colours to downwelling events.

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 with favorable upwelling conditions during autumn and winter, with the maximum intensity observed during January and February. In this region, a downwelling regime is present between May and November when the summer trade winds are replaced by the monsoonal winds advecting warm water (Fig. 3a) northward along the shore (Nykjaer and Van Camp, 1994).
Fig. 3. *In situ* data of a) SST and b) SSS data in the Mauritanian - Cape Verde coastal region grouped by seasons: winter (W, December, January and February), spring (Sp, March, April and May), summer (Sm, June, July and August) and autumn (Au, September, October and November). The averaged values for all cruises in Table S1, are shown in black for each season including the 95% confidence limits. Colour code for each cruise is that indicated in Table S1.
Our results (Fig. 2) are quite consistent with previous research (Nykjaer and Van Camp, 1994; Marcello et al., 2011; Santos et al., 2005; 2012; Cropper et al., 2014) but include the years 2010 to 2012 where UI at around 20-21ºN presented a shift of the upwelling regime intensity from high (-2000 m² s⁻¹) to strong (-2800 m² s⁻¹). 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. 4, green line) for each degree in latitude, indicates an increase in the UI (mean confidence interval of 9 m² s⁻¹) as showed by Santos et al. (2012).

Fig. 4. Latitudinal distribution of the interannual trends for the Upwelling Index (UI*10⁻³) and for the four experimental variables along the QUIMA-VOS line integrated over every degree between 2005 and 2012. The a) panel presents the trends for Upwelling index (UI*10⁻³ m² s⁻¹, mean confidence interval of 9 m² s⁻¹), SST (°C yr⁻¹, confidence interval 0.13°C) and SSS (yr⁻¹, confidence interval 0.06) and the b) panel the trends for fCO₂(sw) and fCO₂(atm) (confidence intervals 4.23 µatm and 0.44 µatm).
North of 15ºN, the upwelling index 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 with satellite data confirmed the intensification of the upwelling regime along the African coast for the period 1982 to 2000 (Santos et al., 2005) extended by Santos et al. (2012) until 2010, and extended in this study until 2012 (data not shown). This has been described as a decadal scale shift of the upwelling regime intensity (Marcello et al., 2011; Santos et al., 2012).

South of 15ºN, the annual UI values and trends (Fig. 2 and 4) both for the upwelling (values close to -2800 m² s⁻¹ in January) and downwelling (values reaching 1850 m² s⁻¹ in July) periods are becoming stronger. At 11-12N, where downwelling is becoming stronger, this results in negative annual temperature rates that approaches to zero. The UI index serves 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 (Mittelstaedt, 1983) promotes phytoplankton growth between Cap Blanc and Cape Verde. Towards 12ºN, 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).

The study area is also affected by the migration of the Inter-Tropical Convergence Zone (ITCZ), related to maximum precipitation rates (Hastenrath, 1995). 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. S1) 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 (>10ºN) from late spring to late summer.

The latitudinal distributions of measured SST and SSS along the vessel track are shown in Fig. 3, grouped by seasons. 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. In situ temperature at 27ºN 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 20ºN, with summer maximum of around 26°C and minimum in spring of about 17°C. At 10ºN, 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 arrival of the ITZC (Supplementary Fig. S1) 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. Only during winter time and the beginning 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 10°N to 16°N 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.

Anomaly fields for temperature and salinity (data not shown) were calculated as the difference between the observations and the mean values at each season for individual latitudes. For temperature, the largest anomalies in winter and spring were located south of 18°N, with values of ±2°C, 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 ±5°C 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 ±3°C 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).

The data conclude a permanent annual upwelling regime observed north of 20°N and a seasonal regime across 10–19°N, in accordance with the climatology of previous studies. The data confirm also an increase in upwelling conditions north of 20°N and an increase in downwelling conditions south of 20°N.
3.2 Carbon dioxide variability

The latitudinal distribution of the seasonal $f$CO$_2$sw data (Fig. 5a) showed the highest values between 18 and 23ºN for all seasons due to the variability imposed by the upwelling off Mauritania. $f$CO$_2$sw was consistently greater than the $f$CO$_2$atm. During winter, when the Cape Verde upwelling develops (Fig. 2), the 12-15ºN region also presented higher $f$CO$_2$sw values than those in the atmosphere. $f$CO$_2$sw data showed a latitudinal shift between the seasons following the shift 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 $f$CO$_2$sw values were recorded in the range 20º to 23ºN. The difference between $f$CO$_2$sw normalized to the mean SST of 22ºC for the region (N$f$CO$_2$sw) and $f$CO$_2$sw ($\Delta f$CO$_2$, Fig. 5b) reinforced the variability at 20-23ºN all year around and at 12-17ºN during winter and spring, indicating that upwelling is the major factor contributing to the $f$CO$_2$ variability.

According to Takahashi et al. (1993), $f$CO$_2$sw increases with temperature at a rate of 4.3% μatm ºC$^{-1}$ (between 15 and 26 μatm ºC$^{-1}$ in this area) in a thermodynamically controlled system. At 27ºN, as SST increases, the rate was only of 7.45 μatm ºC$^{-1}$ due mainly to biological uptake and also 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. The injection is not being compensated by the solubility nor the biological carbon pumps. At 10ºN, the rate was still negative, but only -4.3 μatm ºC$^{-1}$ as a result of the seasonal upwelling. NfCO$_2$sw was related with SST (data not shown) in order to account for effects not removed during normalization. At 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
Fig 5. Fugacity of CO₂ data in the Mauritanian-Cape Verde coastal region grouped by seasons: winter (W, December, January and February), spring (Sp, March, April and May), summer (Sm, June, July and August) and autumn (Au, September, October and November). a) $f_{\text{CO}_2}$ latitudinal distribution. b) Difference between measured and Normalized $f_{\text{CO}_2}$ 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. Colour code for each cruise is that indicated in Table S1.
inverse relationship was reduced to 12-18 μatm °C⁻¹. While the upwelling indexes at those latitudes were quite constant throughout the year, different rates observed should be related to biological consumption of the CO₂ excess. However, during winter and spring the injection of CO₂ in the upwelling is not decreased by the biological activity in the area. But during the Chl-α maximum (late spring and summer) most of the CO₂ was consumed and/or exported and, therefore, the rate was strongly reduced.

Figure 4 depicts the observed interannual trends (a₁ coefficient in Eq. 4) for the four experimentally recorded detrended parameters, together with the UI trend. Confidence intervals of the computed mean annual values for SST, SSS, fCO₂ atm, fCO₂ sw were 0.13°C, 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 (21°N) and Cape Verde upwellings (15°N) with rates higher than -0.2°C yr⁻¹. Data from the first three years (2005 to 2008) at 21°N showed lower temperatures with higher cooling rates that reached -0.7°C yr⁻¹, although three years of data are not representative. The area crossed by the VOS line along 17°45’W from 22°N to 10°N is located inside the 1000 m isobath that is well inside the mean frontal activity in the Canary region, about 200 km wide (Wang et al., 2015). The different changes 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 SST rates in the upwelling affected area, and only
when the ship approached the Canary Islands, the trends became less negative, reaching
a value of +0.02°C yr\(^{-1}\) at 27°N, 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 yr\(^{-1}\)
observed in atmospheric stations, while \(fCO_2^{sw}\) presented a heterogeneous distribution.

South of 18°N the rate of increase was always higher than that in the atmosphere reaching
a maximum value of 4.1 ± 0.4 μatm yr\(^{-1}\) at 10°N. At 27°N, \(fCO_2^{sw}\) increased at a rate of
1.7 ± 0.2 μatm yr\(^{-1}\) similar to that determined at the ESTOC time series site (González-
Dávila et al., 2010) located at 29°10’ N 15°30’W. In the Cap Blanc area, \(fCO_2^{sw}\) increased
at an average rate of 2.5 ± 0.4 μatm yr\(^{-1}\) with the highest values in the period 2005 to 2008
(a rate of 4.6 ± 0.5 μatm yr\(^{-1}\) 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 yr\(^{-1}\). The observed decrease in SST and the trends in \(fCO_2^{sw}\) can only be
explained by a reinforced upwelling. North of 18°N, 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 4). 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.

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 $f$CO$_2$ 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. (4) for the data and the corresponding linear trend.

Because the upwelling intensity is changing, other variables will also be affected. pH$_{\text{is}}$ at 21 ± 0.25°N was computed from $f$CO$_2$ 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 $f$CO$_2$ values are relatively insensitive to errors in A$_T$, and $f$CO$_2$ 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 depicts the computed pH$_{\text{is}}$(A$_T$, $f$CO$_2$) data
and the harmonic fitting Eq. (4) providing seasonal variability and interannual trend. Considering the small systematic biases in interannual dynamics, we determined a decrease in pH at a rate of \(-0.003 \pm 0.001\) per year (Fig. 6). This decrease is one of 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 \(-0.22 \pm 0.06^\circ\text{C yr}^{-1}\) (Fig. 4). Solely, this decrease in temperature would increase the pH by a rate of \(+0.004\) yr\(^{-1}\) and the \(f_{\text{CO}_2}\) would decrease by \(4\) μatm yr\(^{-1}\). 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 \(-0.007\pm0.002\) units yr\(^{-1}\) and an increase in \(f_{\text{CO}_2}\) of \(+6.5 \pm 0.7\) μatm yr\(^{-1}\) (with periods where those rates could reach values of 0.015 yr\(^{-1}\) in pH and 10.5 μatm yr\(^{-1}\) in \(f_{\text{CO}_2}\) as recorded during 2005-2008). Those values are greatly compensated by the important decrease in the SST resulting in the determined rates of \(-0.003 \pm 0.001\) pH units and \(+2.5 \pm 0.4\) μatm of \(f_{\text{CO}_2}\) per year.

This new data set of experimental values confirmed a decrease in SST and trends in \(f_{\text{CO}_2}\) than can only be explained by a reinforced upwelling conditions, that favor an increase in the net community production around the Mauritanian upwelling together with a more corrosive environment with pH values that decrease by over \(-0.007\pm0.002\) units at 21°N. However, the decrease in SST in the upwelling cell buffers this rate to values around \(-0.003 \pm 0.001\) pH units yr\(^{-1}\) and \(+2.5 \pm 0.4\) μatm yr\(^{-1}\) in \(f_{\text{CO}_2}\), still among the highest observed in other time series.

### 3.3 Fluxes of CO\(_2\)
Fluxes of CO$_2$ were computed using Nightingale et al. (2000) 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, December, January and February), spring (d, March, April and May), summer (e, June, July and August) and autumn (f, September, October and November).
The annual air-sea CO$_2$ flux for the full domain was positive (Fig. 7a), with the area off
with values close to 3.3 mol CO$_2$ m$^{-2}$ (Fig. 7a). North of 24°N, in the area not affected by
the coastal upwelling, an average flux of $+0.14 \pm 0.03$ mol CO$_2$ m$^{-2}$ was determined. The
ingassing observed during winter and spring of $-0.16 \pm 0.03$ mol CO$_2$ m$^{-2}$ for the full
period (Fig. 7) was surpassed by the outgassing during summer and autumn of $0.28 \pm
0.14$ mol CO$_2$ m$^{-2}$. South of 24°N, 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 thus the area acted as a source of CO$_2$ with values
reaching 1.9 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 20°N and 23°N acted as a source of 1-1.5 mol CO$_2$ m$^{-2}$, while the rest was almost
in equilibrium. Late autumn-winter upwelling in the 14° to 17°N region contributed to an
increased outgassing with a second annual submaximum of about 0.4 mol CO$_2$ m$^{-2}$ in
winter (Fig. 7c). South of 14°N, annual CO$_2$ fluxes decreased from about 0.7 mol m$^{-2}$ at
14°N to being roughly in equilibrium at 10°N.

The integrated CO$_2$ fluxes for the area 10°N to 27°N along the VOS line section for the
years 2005 to 2012 (Fig. 7b) were between 1.6 and 2.1 10$^6$ mol, with an important annual
variability. FCO$_2$ increased during the studied period by $0.05 \pm 0.02 \cdot 10^6$ mol yr$^{-1}$. The
augment in FCO$_2$ is related to the observed increase in wind speed (Fig. 4, indicated as
UI) north of 16°N. North of 19°N, the influence of wind speed far surpassed the effect of
the smaller annual rate of increase in \textit{f}CO$_2^{sw}$ relative to \textit{f}CO$_2^{atm}$, with an exception at
21°N (Fig. 4). South of 16°N, the decrease in wind speed did not exceed the effect of the
incremental change in (\textit{f}CO$_2^{sw}$ - \textit{f}CO$_2^{atm}$) associated with the increased downwelling
indexes (Fig. 4; Santos et al., 2012), resulting in a slightly increasing FCO$_2$. 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) 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 influence of the Azores semi-permanent high-pressure system on the strength of the trade winds. 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$_2$ in the study area. The FCO$_2$ was not significantly correlated with the winter NAO ($r = 0.23$). Also, the EA index, which represents a southward-shifted NAO-like oscillation, presented a lower significant value ($r = 0.48$) (trends not shown), in agreement with the upwelling index (Cropper et al., 2014). Overall, 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.

FCO$_2$ values along the QUIMA-VOS line were used in order to compute a flux budget for the Mauritanean-Cape Verde region. The observed values were assumed to be valid for at least 100 km to both sides of the QUIMA-VOS line. In this case, the total flux of CO$_2$ being ejected to the atmosphere would reach a value of 16 Tg of carbon dioxide a year for the period 2005-2012, with a rate of increase of 0.6 Tg yr$^{-1}$. However, it should be considered that the export of the rich $f$CO$_2$ upwelled water with high nutrient concentration off the coastal areas would promote a decrease in surface $f$CO$_2$ values during productive seasons (as those observed north and south 21ºN) that will result in an
ingassing of CO$_2$. This could balance the observed outgassing increase in a more global scale.

4. CONCLUSIONS

The Mauritanian-Cape Verde upwelling area’s sensitivity to climatic forcing on upwelling processes strongly affects the CO$_2$ surface distribution, ocean acidification rates and air-sea CO$_2$ exchange.

The experimental SST and carbon dioxide system variables results for the period 2005 to 2012 confirm upwelling intensification at the Mauritanian-Cape Verde upwelling system. Furthermore, we have shown that upwelling regions at low-mid latitudes are important sources of CO$_2$ to the atmosphere. As a direct result, the pH is decreasing at a rate of $-0.003 \pm 0.001$ per year. Importantly, the amount of emitted CO$_2$ is increasing annualy at a rate of 0.6 Tg due to stronger wind stress, even when primary production seems to also be enhanced in the upwelling area. The montly record in this EBUS is not yet long enough to determine the extent to which these changes can be attributed to natural decadal variability. These VOS line must be maintained for years to come, and will continue to be on of the most significat contributors to our 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.


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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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LEGEND FOR FIGURES

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. The map has been generated using Matlab 7.12 R2011a.

Fig. 2. Time series of upwelling index (UI*10$^{-3}$ m$^2$ s$^{-1}$) in the Mauritanian-Cape Verde upwelling region along the ship track computed following Nykjaer and Van Camp (1994). Cool colours are related to upwelling events and warm colours to downwelling events.

Fig. 3. In situ data of a) SST and b) SSS data in the Mauritanian - Cape Verde coastal region grouped by seasons: winter (W, December, January and February), spring (Sp, March, April and May), summer (Sm, June, July and August) and autumn (Au, September, October and November). The averaged values for all cruises in Table S1, are shown in black for each season including the 95% confidence limits. Colour code for each cruise is that indicated in Table S1.

Fig. 4. Latitudinal distribution of the interannual trends for the Upwelling Index (UI*10$^{-3}$) and for the four experimental variables along the QUIMA-VOS line integrated over every degree between 2005 and 2012. The a) panel presents the trends for Upwelling index (UI*10$^{-3}$ m$^2$ s$^{-1}$, mean confidence interval of 9 m$^2$ s$^{-1}$), SST (ºC yr$^{-1}$, confidence interval 0.13ºC) and SSS (yr$^{-1}$, confidence interval 0.06) and the b) panel the trends for $f$CO$_2$sw and $f$CO$_2$atm (confidence intervals 4.23 µatm and 0.44 µatm).

Fig 5. Fugacity of CO$_2$ data in the Mauritanian-Cape Verde coastal region grouped by seasons: winter (W, December, January and February), spring (Sp, March, April and May), summer (Sm, June, July and August) and autumn (Au, September, October and November).
November). a) $f\text{CO}_2^{sw}$ latitudinal distribution. b) Difference between measured and normalized $f\text{CO}_2^{sw}$ values to a constant temperature of 22°C. The averaged values for all cruises in Table S1, are shown in black for each season including the 95% confidence limits. Colour code for each cruise is that indicated in Table S1.

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 $f\text{CO}_2$ 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. (4) for the data and the corresponding linear trend.

Fig. 7. Latitudinal distribution of seasonal and annual CO$_2$ fluxes, FCO$_2$ (mol m$^{-2}$). Fluxes of CO$_2$ were computed using Nightingale et al. (2000) 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, December, January and February), spring (d, March, April and May), summer (e, June, July and August) and autumn (f, September, October and November).
Fig. 1

[Image of a map showing the Canary Islands and the surrounding ocean with a color scale indicating values from 0.01 to 60.]

Canary Islands

Latitude

Longitude

Cap Blanc

Cape Verde
Fig. 2
Fig. 3

(a) Temperature (°C) vs. Latitude for W and Sp.

(b) Salinity vs. Latitude for W and Sp.

(c) Temperature (°C) vs. Latitude for Sm.

(d) Salinity vs. Latitude for Sm.

(e) Temperature (°C) vs. Latitude for Au.

(f) Salinity vs. Latitude for Au.
Fig. 4
Fig. 5

(a) $\%CO_2$ (umol) vs. Latitude

(b) $\Delta CO_2$ (umol) vs. Latitude

W

Sp

Sm

Au
Fig. 6