1	Changes in the partial pressure of carbon dioxide in the Mauritanian-Cape Verde
2	upwelling region between 2005 and 2012.
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4	By
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### 17 ABSTRACT

18 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 19 20 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 21 22 areas are already being affected by global warming, which will modify the intensity of 23 the upwelling and, consequently, the carbon dioxide cycle. Here, we present monthly high resolution surface experimental data for temperature and partial pressure of carbon 24 25 dioxide in one of the four most important upwelling regions of the planet, the 26 Mauritanian-Cape Verde upwelling region, from 2005 to 2012. This data set provides 27 direct evidence of seasonal and interannual changes in the physical and biochemical 28 processes. Specifically, we show an upwelling intensification and an increase of 0.6 Tg a 29 year in CO<sub>2</sub> outgassing due to increased wind speed, despite increased primary productivity. This increase in CO<sub>2</sub> outgassing together with the observed decrease in sea 30 31 surface temperature at the location of the Mauritanian Cape Blanc, 21°N, produced a pH decrease of  $-0.003 \pm 0.001$  per year. 32

### 34 **1. INTRODUCTION**

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The excess of CO<sub>2</sub> in the atmosphere, largely responsible for global climate change, has 36 37 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 38 39 achieve this goal, hight spatial and temporal observations representative of the 40 distribution of CO<sub>2</sub> fluxes between the ocean and atmosphere are necessary. Automated 41 instruments on volunteer observing ships (VOS) serve to provide as many observations 42 throughtout the global ocean as possible, in addition to the data collected on scientific 43 cruises and at long-term moorings (i.e., Astor et al., 2005: Lüger et al., 2004, 2006; 44 González-Dávila et al., 2005; 2009; Schuster et al., 2009; Ullman et al., 2009; Watson et 45 al., 2009; Padín et al., 2010; Gruber et al., 2002; Dore et al., 2003; Santana-Casiano et al., 46 2007; Bates et al., 2014).

47 With the amount of data already gathered (<u>http://www.socat.info/</u>), climatologies that 48 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). 49 50 However, the low spatial resolution of these databases limits the applicability especially 51 in coastal areas. Upwelling regions are particularly under-represented in such large databases. Upwelling presents a dynamic process that raises nutrient and CO<sub>2</sub> rich water 52 53 from relatively deep areas to the surface. The nutrients reaching the photic zone promote primary production, which consumes CO<sub>2</sub>. This process generates a CO<sub>2</sub> flux into the 54 55 ocean. On the other hand, the upwelling also brings up  $CO_2$  from deep seawater, which 56 generates uncertainty about the actual role of upwelling areas as a source or sink of CO<sub>2</sub> (Michaels et al., 2001). Indeed, upwelling areas may act as a source or sink of CO<sub>2</sub> 57 depending on their location (Cai et al., 2006; Chen et al., 2013), where upwelling regions 58

59 at low latitudes mainly act as a source of CO<sub>2</sub> (Feely et al., 2002; Astor et al., 2005; 60 Friederich et al., 2008; Santana-Casiano et al., 2009; González-Dávila et al., 2009) and 61 those at mid-latitudes mainly act as a sink of CO<sub>2</sub> (Frankignoulle and Borges, 2001; Hales 62 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 63 Upwelling Systems (EBUS), including upper ocean warming, ocean acidification and 64 65 ocean deoxygenation (Gruber, 2011; Feely et al., 2008; Keeling et al., 2010). Moreover, evidence of increasee wind speed that would favor upwelling (Bakun, 1990; Demarcq, 66 2009; Oerder et al., 2015) supports the possibility of a change in the dynamics of these 67 68 highly productive areas. Recently, eddy-resolving regional ocean models have shown 69 how upwelling intensification can cause a major impact on the system's biological 70 productivity and CO<sub>2</sub> outgassing (Lachkar and Gruber, 2013; Oerder et al., 2015). Wind 71 observations and reanalysis products are controversial regarding the Bakun intensification hypothesis (Bakun 1990). Using different wind databases for the Canary 72 73 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 74 75 intensification of the upwelling system in the same area during a 20-year period while the 76 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 77 speeds north of 20°N and an increase in downwelling-favorable winds south of 20°N. 78 79 Santos et al. (2005; 2012) showed Sea Surface Temperature (SST) was not homogeneous 80 either along latitude or longitude and depending on the upwelling index (UI intensity). 81 Varela et al. (2015) demonstrated opposite results world wide depending on the length of data, season evaluated, and selected area within the same wind dataset or between 82 datasets. For the Mauritanian region, when wind stress data were used (Varela et al., 83

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 86 87 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 88 89  $CO_2$  expressed as fugacity  $fCO_2$ . This database shows the variations in the  $CO_2$  system under changes in the upwelling conditions in the Canary Ecosystem from 27°N to 10°N 90 91 for the period 2005 to 2012. There exist more data in the region from other surveys 92 (<u>http://www.socat.info/</u>) but they were not considered in this study as they do not follow 93 the same track as the QUIMA-VOS line. Those data are strongly influenced by the 94 distance to the upwelling cells with the corresponding physical effects in the partial pressure 95 of CO<sub>2</sub>.



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<sup>-3</sup>)

were included in a MatlabTM routine and annually averaged. The map has been generatedusing Matlab 7.12 R2011a.

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102

### 103 **EXPERIMENTAL**

### 104 2.1 Study Region.

105 The VOS line crosses the East Atlantic Ocean from the north of Europe (English Channel) 106 to South Africa, calling at Gran Canaria, the Canary Islands, with a periodicity of two 107 months, which provides monthly data (southward or northward sections). In this work, 108 the area between Gran Canaria at 27°N and 10 °N has been selected in order to study the 109 Mauritanean-Cape Verde upwelling region. In its route south (Fig. 1), the ship leaves 110 Gran Canaria, and goes straight to 100 km off Cap Blanc, at 21°N 17°45'W. It then 111 follows this longitude, passing at 100 km off Cape Verde until 12°N, where it changes 112 direction to Cape Town, reaching 10°N 17°W at 330 km out of the coast of Guinea. Between 22°N and 20°N, the ship reaches the 500 m isobath. South of 15°N, the ship 113 114 moves between 1000 and 500 m isobath. In its route north, the ship follows the same 115 reverse track.

# 116 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<sub>2</sub> 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 122 123 UK and Cape Town, from July 2005 to January 2013 (Supplementary Table S1). 124 Temperature was measured at three locations along the sampling circuit: in the intake 125 (SeaBird SBE38L), in the equilibrator (SeaBird thermosalinograph SBE21 and internal PT100 thermometer), and in the oxygen sensor (Optode 3835 Aanderaa<sup>TM</sup>). After the 126 127 seawater pump, the intake is divided in two lines, one feeding the  $CO_2$  system and the 128 other the oxygen sensor, the fluorometer and the seabird thermosalinometer. Differences 129 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 130 131 0.06°C when the equipment was placed close to the intake to 0.35°C, when the equipment 132 was one floor above, inside the engine room. The SST was also obtained from the 133 NOAA\_OI\_SST-V2 data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, 134 USA (<u>http://www.esrl.noaa.gov/psd</u>). These data had a spatial resolution of 1° latitude and 1° longitude and monthly averages were used. The correlation between our 135 136 experimental SST data and satellite one was better than  $\pm$  1°C, and improved to  $\pm$  0.4°C after removing the most affected upwelling regions (19-22°N and 14-16°N), related to the 137 high variability imposed by the upwelling. 138

139 The CO<sub>2</sub> molar fraction, xCO<sub>2</sub>, in seawater was obtained every 150 s, while atmospheric 140 xCO<sub>2</sub> data were obtained every 180 min. The seawater intake was located at a 10 m depth. 141 The system was calibrated every three hours, by measuring four different standard gases 142 with mixing ratios in the ranges of 0.0, 250-290 ppm, 380-410 ppm and 490-530 ppm of 143 CO<sub>2</sub> in the air, provided by NOAA and traceable to the World Meteorological 144 Organisation scale. The precision of the system is greater than 0.5 µatm and the accuracy 145 estimated with respect to the standard gases is of 1 µatm inside the standards range. For xCO<sub>2</sub> values higher than the highest standard (532.04 ppm), the accuracy will be reduced, 146

even when linearity was observed in all cases inside the standards range. The fugacity of CO<sub>2</sub>, fCO<sub>2</sub> (µatm), was calculated from xCO<sub>2</sub> after correcting for temperature differences between intake and equilibrator, according to the expressions for the seawater given by DOE (1994). Normalised fCO<sub>2</sub> to the mean SST for the area (T<sub>mean</sub>) was computed following Takahashi et al. (1993)

152 
$$(NfCO_2) = fCO_2 \cdot \exp[0.0423(T_{mean} - SST)]$$
 (1)

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<sub>T</sub> at the in situ temperature was computed from  $fCO_2$  and A<sub>T</sub> and with average annual surface ocean total phosphate and total silicate concentrations of 0.5 and 4.8 µmol kg<sup>-1</sup>, respectively, from the World Ocean Atlas 2009, using the carbonic acid acidity constants by Merbach et al. (1973) refitted by Dickson and Millero (1987).

159 Air-sea CO<sub>2</sub> fluxes, FCO<sub>2</sub> (mmol 
$$m^{-2} d^{-1}$$
), were evaluated as

160 
$$FCO_2 = 0.24 * k * s * (fCO_2^{sw} - fCO_2^{atm})$$
 (2)

where 0.24 is the scale factor, *k* is the gas transfer velocity, *s* is the CO<sub>2</sub> solubility,  $fCO_2^{sw}$ is the seawater fugacity of CO<sub>2</sub> and  $fCO_2^{atm}$  is the atmospheric fugacity of CO<sub>2</sub>. 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<sub>2</sub> corresponds with a CO<sub>2</sub> outgassing from the ocean. *k* (cm h<sup>-1</sup>) was evaluated with the parametrization (Nightingale et al., 2000):

166 
$$k = (0.222 * W^2 + 0.333 * w) * (Sc/660)^{-1/2}$$
 (3)

167 where *W* is the wind speed at 10 m above the sea surface (m s<sup>-1</sup>) and *Sc* is the Schmidt 168 number. 169

The variables involved in estimating FCO<sub>2</sub> data (i.e.  $fCO_2^{sw}$ ,  $fCO_2^{atm}$ , SST and SSS) were 170 fitted to sinusoidal expressions (Lüger et al., 2004) for a given latitude as:

(4)

171 
$$X(lat)^* = a_0 + a_1(t - 2005) + a_2 sin(2\pi t) + a_3 cos(2\pi t) + a_4 sin(4\pi t) + a_4 sin$$

172 
$$a_5 cos(4\pi t)$$

where *a<sub>i</sub>* are the fitting coefficients, *t* is the sampling time expressed as year fraction and 173  $X^*$  represents any of the four fitted variables. This procedure allowed us to re-construct 174 the series of experimental data for periods without monthly data. The variables were 175 decomposed into an interannual term  $X(lat)_t^* = a_0 + a_1(t - 2005)$  plus a periodical 176  $X(lat)_p^* = a_2 sin(2\pi t) + a_3 cos(2\pi t) + a_4 sin(4\pi t) + a_5 cos(4\pi t)$ , that 177 term is,  $X(lat)^* = X(lat)_t^* + X(lat)_p^*$ . The periodical term accounts for the high frequency 178 179 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 180 181 in a single year (no correction was done for interannual variability). The mean seasonal 182 climatology data associated with the periodic coefficients (i.e. a<sub>2</sub>, a<sub>3</sub>, a<sub>4</sub>, and a<sub>5</sub>) 183 throughout the sampling period were determined. Next, the interannual coefficients a1 184 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<sub>1</sub>-185 as), new distributions for  $fCO_2^{sw^*}$ ,  $fCO_2^{atm^*}$ , SST<sup>\*</sup> and SSS<sup>\*</sup> were constructed with a daily 186 resolution based on the curve fits given for each variable as in Eq. (4), providing the 187 188 coefficient a<sub>0</sub>. The accuracy of this fitting procedure was checked by both computing the 189 correlation between experimental and reconstructed values and by determining the mean 190 residuals. The Pearson coefficients were always over 0.87 for SST (average  $0.94 \pm 0.03$ ), over 0.69 for both  $fCO_2^{sw}$ ,  $fCO_2^{atm}$  (average of 0.79 ± 0.07 and 0.82 ± 0.04, respectively) 191 192 and over 0.67 for SSS (average  $0.79 \pm 0.07$ ). The mean residual on the determination of

those four variables were  $\pm$  3.7 µatm,  $\pm$  1.5 µatm,  $\pm$  0.22 °C, and  $\pm$  0.05 for  $fCO_2^{sw^*}$ , 193  $fCO_2^{atm^*}$ ,  $SST^*$  and  $SSS^*$ , respectively. When the monthly satellite SST values were 194 considered, the new SST\* function averaged for each month produced values within  $\pm$ 195 0.47°C, confirming that this procedure was able to fit non-sampled periods. It was 196 assumed that the same procedure was valid for non-sampled  $fCO_2$ . Finally, daily  $FCO_2^*$ 197 time series between 10°N and 27°N with a latitudinal resolution of 0.5° were calculated 198 with a standard error of estimation of 0.5 mmol  $m^{-2} d^{-1}$  (15% of error) that produced mean 199 residuals (experimental FCO<sub>2</sub> - FCO<sub>2</sub><sup>\*</sup>) of 0.4 mmol m<sup>-2</sup> d<sup>-1</sup> and Pearson correlation 200 coefficients between experimental and computed  $FCO_2^*$  of r > 0.6, p < 0.01. 201

202 Chlorophyll-a was calculated from measurements made by the Moderate Resolution 203 Imaging Spectroradiometer (MODIS) aboard NASA's Aqua satellite. We used monthly 204 averages with spatial resolution of 9 km supplied by Ocean Color (oceancolor.gsfc.nasa.gov). 205

206 Wind data were downloaded from the NCEP CFSR database at 207 http://rda.ucar.edu/pub/cfsr.html developed by NOAA and retrieved from the NOAA 208 National Operational Model Archive and Distribution System and maintained by the NOAA National Climatic Data Center. The spatial resolution is approximately  $0.3 \times 0.3^{\circ}$ 209 and the temporal resolution is 6 hours. The reference height for the wind data is 10 m. 210

Rainfall data were collected by the Precipitation Radar installed on the Tropical Rainfall Measuring Mission (TRMM) satellite (<u>http://precip.gsfc.nasa.gov</u>). Monthly averages with a spatial resolution of  $0.5^{\circ} \times 0.5^{\circ}$  (product 3A12, version 07) were used (Supplementary Fig. S1) in order to explain changes in seasonal surface salinity distributions.

### 217 2. RESULTS AND DISCUSSION

## 218 **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. 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<sup>-3</sup> m<sup>2</sup> s<sup>-1</sup>) 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.

229 1) North of 20°N, the upwelling conditions were favorable throughout the year, although 230 the highest upwellings were observed from March to September with a northward shift 231 from 20° to 22°N. 2) South of 20°N, a marked seasonality was observed with favorable 232 upwelling conditions during autumn and winter, with the maximum intensity observed during January and February. In this region, a downwelling regime is present between 233 234 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, 235 236 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, 243 1994; Marcello et al., 2011; Santos et al., 2005; 2012; Cropper et al., 2014) but include 244 the years 2010 to 2012 where UI at around 20-21°N presented a shift of the upwelling 245 regime intensity from high (-2000 m<sup>2</sup> s<sup>-1</sup>) to strong (-2800 m<sup>2</sup> s<sup>-1</sup>). The analysis of 246 upwelling trends along this area has been controversial since it is highly dependent on the 247 selected region (Santos et al., 2012). The inter-annual evolution of UI over the period 248 2005 to 2012 (Fig. 4, green line) for each degree in latitude, iindicates an increase in the 249 UI (mean confidence interval of 9  $m^2 s^{-1}$ ) as showed by Santos et al. (2012). 250



Fig. 4. Latitudinal distribution of the interannual trends for the Upwelling Index (UI\*10<sup>-3</sup>) 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<sup>-3</sup> m<sup>2</sup> s<sup>-1</sup>, mean confidence interval of 9 m<sup>2</sup> s<sup>-1</sup>), SST (°C yr<sup>-1</sup>, confidence interval 0.13°C) and SSS (yr<sup>-1</sup>, confidence interval 0.06) and the b) panel the trends for  $fCO_2^{sw}$  and  $fCO_2^{atm}$  (confidence intervals 4.23 µatm and 0.44 µatm).

North of 15°N, the upwelling index confirmed the stronger upwelling observed since 258 259 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 260 261 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) 262 extended by Santos et al. (2012) until 2010, and extended in this study until 2012 (data 263 264 not shown). This has been described as a decadal scale shift of the upwelling regime 265 intensity (Marcello et al., 2011; Santos et al., 2012).

South of 15°N, the annual UI values and trends (Fig. 2 and 4) both for the upwelling (values close to -2800 m<sup>2</sup> s<sup>-1</sup> in January) and downwelling (values reaching 1850 m<sup>2</sup> s<sup>-1</sup> in July) periods are becoming stronger. At 11-12N, were downwelling is becoming stronger, this results in negative annual temperature rates that appraches 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).

272 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 273 filaments with chlorophyll concentrations above  $1 \text{ mg m}^{-3}$  persist year-round, spreading 274 275 from the coast several hundred kilometers offshore (Fig. 1). North of Cap Blanc the 276 upwelled water originates from the North Atlantic Central Water, and mixes with South 277 Atlantic Central Water, SACW, towards the south (Mittelstaedt, 1983). South of Cap Blanc, the upwelling of nutrient rich SACW (Mittelstaedt, 1983) promotes phytoplankton 278 growth between Cap Blanc and Cape Verde. Towards 12°N, upwelling is also fed by the 279 280 North Equatorial Under Current (Hagen and Schemainda, 1984). Moreover, the entire 281 northwest African coast is also influenced by the African desert dust transport by the midtropospheric Harmattan winds originating from the central Sahara, which supplements 282

the levels of micronutrients (such as iron) to the adjacent marine ecosystem (Mittelstaedt,
1983; Neuer et al., 2004).

285 The study area is also affected by the migration of the Inter-Tropical Convergence Zone 286 (ITCZ), related to maximum precipitation rates (Hastenrath, 1995). To have a significant satellite precipitation record in our region of interest, precipitation data were integrated 287 288 longitudinally between 25.25°W and 9.75°W. Time series for the latitudinal distribution of integrated precipitation (Supplementary Fig. S1) identified the average position of the 289 290 ITCZ related to maximum precipitation rates. The ITCZ was located at its southernmost 291 position (2°N) during winter, reaching its northernmost position (14-16°N) around 292 summer. The ITCZ reached our area of interest (>10°N) from late spring to late summer.

293 The latitudinal distributions of measured SST and SSS along the vessel track are shown 294 in Fig. 3, grouped by seasons. The temperature generally decreased from 10°N to about 295 20°N to 21°N, where the ship meets the Mauritanian upwelling. From there to the north, 296 the temperature rises as the ship leaves the upwelling area on its way to the Canary 297 Islands. In situ temperature at 27°N shows temperatures in the range of 18 to 24°C with 298 the minimum in winter and maximum in late summer-early autumn. The annual 299 temperature range was somewhat higher at 20°N, with summer maximum of around 26°C 300 and minimum in spring of about 17°C. At 10°N, temperatures were the highest throughout 301 the year (>25°C), with minimum values in winter and maximum in late spring and late 302 autumn. The low values observed during the end of summer are related to the arrival of 303 the ITZC (Supplementary Fig. S1) at those latitudes. The thermal distribution shows a 304 temperature increase as we move to the Equator and a notable cooling at the upwelled 305 waters off Mauritania. Only during winter time and the begining of the spring, the 306 upwelling of cold water from Cape Verde area was detected. Salinity minimum values were normally located at 10°N, increasing to maximum values at the Canaries' latitude. 307

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 312 313 difference between the observations and the mean values at each season for individual 314 latitudes. For temperature, the largest anomalies in winter and spring were located south 315 of  $18^{\circ}$ N, with values of  $\pm 2^{\circ}$ C, related to the seasonal cycle of the Cape Verde upwelling. 316 During summer the pattern changed and the largest anomalies were detected in the 317 upwelling area at 18-22°N, with values of ±5°C when the upwelling index for the 318 Mauritanian area was highest (Fig. 2). In autumn the temperature anomalies were shifted 319 slightly to the north, 20-24°N, with values of  $\pm$ 3°C related to the observed pulses in upwelling favorable winds that affected the surface seawater properties. On the other 320 321 hand, salinity anomalies showed a very homogeneous pattern in all latitudes for winter, 322 spring and summer, with values generally within  $\pm 0.5$ . However, during autumn 323 important anomalies south of  $18^{\circ}$ N were observed, with values in the range of  $\pm 1.5$ . In 324 this region, the upwelling development, the river discharge and the rainy season 325 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.

330

## 332 **3.2** Carbon dioxide variability

The latitudinal distribution of the seasonal fCO2<sup>sw</sup> data (Fig. 5a) showed the highest values 333 between 18 and 23°N for all seasons due to the variability imposed by the upwelling off 334 Mauritania.  $fCO_2^{sw}$  was consintently greater than the  $fCO_2^{atm}$ . During winter, when the 335 Cape Verde upwelling develops (Fig. 2), the 12-15°N region also presented higher fCO2<sup>sw</sup> 336 values than those in the atmosphere.  $fCO_2^{sw}$  data showed a latitudinal shift between the 337 seasons following the shift observed in the upwelling index: i.e., in winter, the largest 338 values were located between 19° and 24°N; in spring, they were located between 16° and 339 22°N; during summer and autumn, the largest  $fCO_2^{sw}$  values were recorded in the range 340 341 20° to 23°N. The difference between fCO2<sup>sw</sup> normalized to the mean SST of 22°C for the 342 region (NfCO<sub>2</sub><sup>sw</sup>) and fCO<sub>2</sub><sup>sw</sup> ( $\Delta$ fCO<sub>2</sub> =NfCO<sub>2</sub><sup>sw</sup> - fCO<sub>2</sub><sup>sw</sup>, Fig. 5b) reinforced the variability at 20-23°N all year around and at 12-17°N during winter and spring, indicating 343 344 that upwelling is the major factor contributing to the fCO<sub>2</sub> variability.

According to Takahashi et al. (1993), fCO2<sup>sw</sup> increases with temperature at a rate of 345 4.3% µatm °C<sup>-1</sup> (between 15 and 26 µatm °C<sup>-1</sup> in this area) in a thermodynamically 346 controlled system. At 27°N, as SST increases, the rate was only of 7.45 µatm °C<sup>-1</sup> due 347 348 mainly to biological uptake and also to the CO<sub>2</sub> outflux. At 20°N the rate became negative with a value of -10.9 µatm °C<sup>-1</sup>, clearly indicating the important injection of cool and CO<sub>2</sub> 349 350 rich seawater at the upwelling area. The injection is not being compensated by the 351 solubility nor the biological carbon pumps. At 10°N, the rate was still negative, but only -4.3 µatm °C<sup>-1</sup> as a result of the seasonal upwelling. NfCO2<sup>sw</sup> was related with SST (data 352 353 not shown) in order to account for effects not removed during normalization. At latitudes 19° to 21°N, in the upwelling vicinity of Cap Blanc, an inverse relationship of 70-354 100  $\mu$ atm °C<sup>-1</sup> was found during winter and spring, while in summer and autumn the 355



Fig 5. Fugacity of CO<sub>2</sub> 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)  $fCO_2^{sw}$  latitudinal distribution. b) Difference between measured and Normalized (normalized- measured)  $fCO_2^{sw}$  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.

inverse relationship was reduced to 12-18  $\mu$ atm °C<sup>-1</sup>. While the upwelling indexes at those latitudes were quite constant throughout the year, different rates observed should be related to biological consumption of the CO<sub>2</sub> excess. However, during winter and spring the injection of CO<sub>2</sub> in the upwelling is not decreased by the biological activity in the area. But during the Chl-*a* maximum (late spring and summer) most of the CO<sub>2</sub> was consumed and/or exported and, therefore, the rate was strongly reduced.

Figure 4 depicts the observed interannual trends (a<sub>1</sub> coefficient in Eq. 4) for the four 370 371 experimentally recorded detrended parameters, together with the UI trend. Confidence intervals of the computed mean annual values for SST, SSS, fCO2<sup>atm</sup>, fCO2<sup>sw</sup> were 0.13°C, 372 373 0.06, 0.44 µatm and 4.23 µatm, respectively. There was a clear SST trend whereby 374 seawater along the VOS line track was getting cooler with maximum cooling rates at the 375 location of Cap Blanc (21°N) and Cape Verde upwellings (15°N) with rates higher than -376 0.2°C yr<sup>-1</sup>. 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<sup>-1</sup>, although three years of 377 data are not representative. The area crossed by the VOS line along 17°45'W from 22°N 378 379 to 10°N is located inside the 1000 m isobath that is well inside the mean frontal activity 380 in the Canary region, about 200 km wide (Wang et al., 2015). The different changes in 381 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 382 spread off the coastal area. The offshore water SST is less variable owing to longer 383 384 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, 385 386 contributes to the observed spatial variability. There was no attempt to compare 387 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 388

when the ship approached the Canary Islands, the trends became less negative, reaching a value of  $+0.02^{\circ}$ C yr<sup>-1</sup> 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 yrr<sup>-1</sup> 392 observed in atmospheric stations, while  $fCO_2^{sw}$  presented a heterogeneous distribution. 393 South of 18°N the rate of increase was always higher than that in the atmosphere reaching 394 a maximum value of  $4.1 \pm 0.4$  µatm yr<sup>-1</sup> at 10°N. At 27°N, fCO<sub>2</sub><sup>sw</sup> increased at a rate of 395  $1.7 \pm 0.2 \mu$ atm yr<sup>-1</sup> similar to that determined at the ESTOC time series site (González-396 Dávila et al., 2010) located at 29°10' N 15°30'W. In the Cap Blanc area, fCO2<sup>sw</sup> increased 397 at an average rate of  $2.5 \pm 0.4 \,\mu$ atm yr<sup>-1</sup> with the highest values in the period 2005 to 2008 398 (a rate of 4.6  $\pm$  0.5 µatm yr<sup>-1</sup> was computed with only those years). Around Cap Blanc, 399  $fCO_2^{sw}$  always presented lower rates of increase than in the atmosphere with values well 400 401 below 1  $\mu$ atm yr<sup>-1</sup>. The observed decrease in SST and the trends in  $fCO_2^{sw}$  can only be 402 explained by a reinforced upwelling. North of 18°N, the lowest rate of increase in fCO2<sup>sw</sup> 403 compared to  $fCO_2^{atm}$ , together with a decrease in temperature, indicated that upwelling is 404 also favoring an increase in the net community production around the Mauritanian upwelling, consuming and/or exporting the CO<sub>2</sub> rich upwelled waters favored by the 405 406 lateral transport of the Mauritanian current (Lachkar and Gruber, 2013; Varela et al., 407 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 408 409 et al., 2012) of increased upwelling-favorable winds, at least for the period 2005-2012 in 410 the Canary upwelling region (Fig. 2 and 4). The intensification of the upwelling results 411 in a change in the measured upwelled water properties due to either higher upwelling 412 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 413

414 forcing versus natural decadal variability in the upwelling areas occurring over415 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  $fCO_2$  at  $21 \pm 0.25$  °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<sub>T,is</sub> at 21  $\pm$  0.25°N was computed from *f*CO<sub>2</sub> 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<sub>2</sub> values are relatively insensitive to errors in A<sub>T</sub>, and *f*CO<sub>2</sub> controls the magnitude and variability of pH (a 60 µmol kg<sup>-1</sup> change in A<sub>T</sub> will affect a 0.1% in pH, that is, about 0.01 pH units). Figure 6 depicts the computed pH<sub>T,is</sub>(A<sub>T</sub>, *f*CO<sub>2</sub>) data and

429 the harmonic fitting Eq. (4) providing seasonal variability and interannual trend. 430 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 431 highest rate values determined in several time series stations (Bates et al., 2014), where 432 oceanic SST has only slightly increased in the last decades. However, at the Mauritanian 433 upwelling area and at the location where our VOS line approached this region, SST 434 decreased at a rate of  $-0.22 \pm 0.06$ °C yr<sup>-1</sup> (Fig. 4). Solely, this decrease in temperature 435 would increase the pH by a rate of +0.004 yr<sup>-1</sup> and the fCO<sub>2</sub> would decrease by 4 µatm yr<sup>-1</sup> 436 <sup>1</sup>. The net effect of the increase in the amount of rich CO<sub>2</sub>/low pH upwelled waters in the 437 438 Mauritanian upwelling would be, therefore, a decrease in the pH of over -0.007±0.002 units yr<sup>-1</sup> and an increase in  $fCO_2$  of +6.5 ± 0.7 µatm yr<sup>-1</sup> (with periods where those rates 439 could reach values of 0.015 yr<sup>-1</sup> in pH and 10.5  $\mu$ atm y<sup>-1</sup> in fCO<sub>2</sub> as recorded during 2005-440 441 2008). Those values are greatly compensated by the important decrease in the SST 442 resulting in the determined rates of  $-0.003 \pm 0.001$  pH units and  $+2.5 \pm 0.4$  µatm of fCO<sub>2</sub> 443 per year.

This new data set of experimental values confirmed a decrease in SST and trends in  $fCO_2^{sw}$  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±0.002 units at 21°N. However, the decrease in SST in the upwelling cell buffers this rate to values around -0.003 ± 0.001 pH units yr<sup>-1</sup> and +2.5 ± 0.4 µatm yr<sup>-1</sup> in *f*CO<sub>2</sub>, still among the highest observed in other time series.

451

# 452 **3.3 Fluxes of CO<sub>2</sub>**



Fig. 7. Latitudinal distribution of seasonal and annual CO<sub>2</sub> fluxes, FCO<sub>2</sub> (mol m<sup>-2</sup>). Fluxes
of CO<sub>2</sub> 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<sub>2</sub> 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 461 with values close to 3.3 mol CO<sub>2</sub> m<sup>-2</sup> (Fig. 7a). North of 24°N, in the area not affected by 462 the coastal upwelling, an average flux of  $+0.14 \pm 0.03$  mol CO<sub>2</sub> m<sup>-2</sup> was determined. The 463 ingassing observed during winter and spring of  $-0.16 \pm 0.03$  mol CO<sub>2</sub> m<sup>-2</sup> for the full 464 period (Fig. 7) was surpassed by the outgassing during summer and autumn of 0.28  $\pm$ 465 0.14 mol CO<sub>2</sub> m<sup>-2</sup>. South of 24°N, it was observed that during spring (Fig. 7d) the 466 467 photosynthetic activity was not intense enough to uptake the CO<sub>2</sub> injected by the strongest 468 upwelling in the surface waters and thus the area acted as a source of CO<sub>2</sub> with values reaching 1.9 mol CO<sub>2</sub> m<sup>-2</sup> in 2012. During summer (Fig. 7e), primary producers and 469 470 lateral advection of warm waters by the Mauritanian current could consume/export the  $CO_2$  rich waters reaching values of 0.5 mol m<sup>-2</sup>. During autumn (Fig. 7f), only the area 471 between 20°N and 23°N acted as a source of 1-1.5 mol CO<sub>2</sub> m<sup>-2</sup>, while the rest was almost 472 473 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<sup>-2</sup> in 474 winter (Fig. 7c). South of 14°N, annual CO<sub>2</sub> fluxes decreased from about 0.7 mol m<sup>-2</sup> at 475 476 14°N to being roughly in equilibrium at 10°N.

The integrated CO<sub>2</sub> fluxes for the area 10°N to 27°N along the VOS line section for the 477 years 2005 to 2012 (Fig. 7b) were between 1.6 and 2.1 10<sup>6</sup> mol, with an important annual 478 variability. FCO<sub>2</sub> increased during the studied period by  $0.05 \pm 0.02 \cdot 10^6$  mol yr<sup>-1</sup>. The 479 480 augment in FCO<sub>2</sub> is related to the observed increase in wind speed (Fig. 4, indicated as 481 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  $fCO_2^{sw}$  relative to  $fCO_2^{atm}$ , with an exception at 21°N 482 (Fig. 4). South of 16°N, the decrease in wind speed did not exceed the effect of the 483 incremental change in (fCO2<sup>sw</sup> - fCO2<sup>atm</sup>) associated with the increased downwelling 484 indexes (Fig. 4; Santos et al., 2012), resulting in a slightly increasing FCO<sub>2</sub>. The 485

486 variability observed in the annual integrated CO<sub>2</sub> fluxes (Fig. 7b) was related with the 487 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 488 489 et al. (2014) found winter upwelling variability was strongly correlated with the winter NAO (r values ranged from 0.50 at 12-19°N to 0.59 at 21-26°N), due to the influence of 490 491 the Azores semi-permanent high-pressure system on the strength of the trade winds. The 492 annual integrated FCO<sub>2</sub> was related with the annual NAO index (Fig. 7b) with a similar r 493 = 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 494 495 to FCO<sub>2</sub> in the study area. The FCO<sub>2</sub> was not significantly correlated with the winter NAO (r = 0.23). Also, the EA index, which represents a southward-shifted NAO-like 496 497 oscillation, presented a lower significant value (r = 0.48) (trends not shown), in agreement 498 with the upwelling index (Cropper et al., 2014). Overall, the correlation between fluxes 499 and climate indexes describing the main mode of variability across the Atlantic sector 500 may be directly related to the Azores High and its influence on the trade wind strength.

501 FCO<sub>2</sub> values along the QUIMA-VOS line were used in order to compute a flux budget 502 for the Mauritanean-Cape Verde region. The observed values were assumed to be valid 503 for at least 100 km to both sides of the QUIMA-VOS line. In this case, the total flux of CO<sub>2</sub> being ejected to the atmosphere would reach a value of 16 Tg of carbon dioxide a 504 year for the period 2005-2012, with a rate of increase of 0.6 Tg yr<sup>-1</sup>. However, it should 505 506 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 507 508 during productive seasons (as those observed north and south 21°N) that will result in an 509 ingassing of CO<sub>2</sub>. This could balance the observed outgassing increase in a more global 510 scale.

### 511 **4. CONCLUSIONS**

512 The Mauritanian-Cape Verde upwelling area's sensitivity to climatic forcing on 513 upwelling processes strongly affects the CO<sub>2</sub> surface distribution, ocean acidification 514 rates and air-sea CO<sub>2</sub> exchange.

515 The experimental SST and carbon dioxide system variables results for the period 2005 to 516 2012 confirm upwelling intensification at the Mauritanian-Cape Verde upwelling system. 517 Furthermore, we have shown that upwelling regions at low-mid latitudes are important 518 sources of CO<sub>2</sub> to the atmosphere. As a direct result, the pH is decreasing at a rate of -519  $0.003 \pm 0.001$  per year. Importantly, the amount of emitted CO<sub>2</sub> is increasing annualy at 520 a rate of 0.6 Tg due to stronger wind stress, even when primary production seems to also 521 be enhanced in the upwelling area. The montly record in this EBUS is not yet long enough 522 to determine the extent to which these changes can be attributed to natural decadal 523 variability. These VOS line must be maintained for years to come, and will continue to 524 be on of the most significat contributors to our knowledge of how ocean surface waters 525 are being affected by present and future climate change. The results from VOS lines can provide accurate data for changes in SST, FCO2 and, consequently, upwelling 526 527 intensification effects due to global change conditions under decadal natural variability.

## 529 Data availability.

- 530 All data are free available at the SOCAT data base, <u>http://www.socat.info/</u> and at the
- 531 Carboocean and Carbochange web pages <u>www.CarboOcean.org</u>,
- 532 <u>https://carbochange.b.uib.no/</u>, respectively
- 533
- 534

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# 543 Author contributions

- 544 M.G.D. and J.M.S.C worked in the equipment installation, data collection and designed
- 545 the study. F.M. processed the data, generated figures and results. All of them collaborated
- 546 in the discussion of the data and the writing of the paper.
- 547

## 548 **Competing interests**

- 549 There is not any competing interest.
- 550 551
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### 725 **LEGEND FOR FIGURES**

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<sup>-3</sup>)
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<sup>2</sup> s<sup>-1</sup>) 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<sup>-3</sup>) 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<sup>-3</sup> m<sup>2</sup> s<sup>-1</sup>, mean confidence interval of 9 m<sup>2</sup> s<sup>-1</sup>), SST (°C yr<sup>-1</sup>, confidence interval 0.13°C) and SSS (yr<sup>-1</sup>, confidence interval 0.06) and the b) panel the trends for  $fCO_2^{sw}$  and  $fCO_2^{atm}$  (confidence intervals 4.23 µatm and 0.44 µatm).

Fig 5. Fugacity of CO<sub>2</sub> 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)  $fCO_2^{sw}$  latitudinal distribution. b) Difference between measured and Normalized  $fCO_2^{sw}$  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  $fCO_2$  at  $21 \pm 0.25$  °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<sub>2</sub> fluxes, FCO<sub>2</sub> (mol  $m^{-2}$ ). Fluxes

of CO<sub>2</sub> 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)

162 latitudinally integrated for 2005 to 2012 together with annual values for NAO index.

763 Latitudinal distribution of FCO<sub>2</sub> seasonally integrated from 2005 to 2012 are depicted for

vinter (c, December, January and February), spring (d, March, April and May), summer

765 (e, June, July and August) and autumn (f, September, October and November).

766 Fig. 1



768 Fig. 2









777 Fig. 4





779 Fig. 5



782 Fig. 6



785 Fig. 7



