~~Factors controlling~~ pCO_2 variability in the surface waters of the eastern Gulf of Cádiz (SW Iberian Peniíínsula)

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Abstract

Spatiotemporal variations of the partial pressure of CO_2 (pCO_2) were studied during 8 oceanographic cruises conducted between March 2014 and February 2016 in surface waters of the eastern shelf of the Gulf of Cádiz (SW Iberian Peniíínsula) between the Guadalquivir River and Cape Trafalgar. pCO_2 presents~~ed~~ a range of variation between 320.6 and 513.6 µatm, with highest values during summer and autumn and lowest during spring and winter. For the whole study, pCO_2 shows a linear dependence with temperature, and spatially there is a general decrease from coastal to offshore stations associated with continental inputs and an increase in the zones deeper than 400 m related to the influence of the eastward branch of the Azores Current. ~~, showing a linear dependence between pCO_2 and temperature. The distributions of pCO_2 were not homogeneous. Spatially, there was a general decrease from coastal to off-shore stations associated with continental inputs and presented an increase in the zones deeper than 400 m due to the influence of the eastward branch of the Azores Current. On the other side, the~~The study area acts~~ed~~ as source of CO_2 to the atmosphere during summer and autumn and as a sink in spring and winter, with a mean value for the study period of -0.18 ± 1.32 mmol m^{-2} d^{-1}. In the Guadalquivir and Sancti Petri ~~section~~transects, the CO_2 fluxes decrease~~d~~ towards offshore, whereas in the Trafalgar ~~section~~ transect fluxes increase~~d~~ due to the presence of an upwelling. These results highlight~~ed~~ the Gulf of Cádiz as a CO_2 sink, with an uptake ~~capture~~ capacity of 14.9 Gg C $year^{-1}$.

1. Introduction

Continental shelves play a key role in the global carbon cycle, as this is where the interactions between terrestrial, marine and atmospheric systems take place (Mackenzie et al., 1991; Walsh, 1991; Smith and Hollibaugh, 1993). These zones are considered to be among the most dynamic in biogeochemical terms (Wollast, 1991; Bauer et al., 2013), as they are affected by several factors, particularly high rates of primary production, remineralization and organic carbon burial (Walsh, 1988; Wollast, 1993; de Hass et al., 2002). Continental shelves account for about 10 – 15 % of the ocean primary production and they contribute approximately 40 % of the ocean's total carbon sequestration, by biological pump~~particulate organic carbon~~ (Muller-Karger et al., 2005).

Generally, waters over the continental shelf account for ~15 % of the global ocean CO_2 uptake (-2.6 ± 0.5 Pg C yr^{-1}, Le Quéré et al., 2017). Using direct surface ocean CO_2 measurements from the global Surface Ocean CO_2 Atlas (SOCAT) database, Laruelle et al. (2014) estimated a sea-air exchange of CO_2 in these zones of -0.19 ± 0.05 Pg C yr^{-1}, lower than the estimated in other studies published in the last decade (e.g. Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009; Laruelle et al., 2010; Chen et al., 2013). The discrepancies with respect to this estimation derive from the different definitions of the continental shelf domain and the skewed distribution of local studies~~studies~~ (Laruelle et al., 2010). In several works~~studies~~, it has been observed that the continental shelves present different behaviour~~s~~ according to their latitude: they tend to act as a sink of carbon (-0.33 Pg C yr^{-1}) at high and middle latitudes (30 - 90º) and as a weak source (0.11 Pg C yr^{-1}) at low latitudes (0 - 30º) (Cai et al., 2006; Hofmann et al., 2011; Bauer et al., 2013; Chen et al., 2013; Laruelle et al., 2014, 2017). Laruelle et al. (2010) found differences between the two hemispheres: the continental shelf seas of the Northern Hemisphere are a net sink of CO_2 (-0.24 Pg C yr^{-1}) and those of the Southern Hemisphere are a weak source of CO_2 (0.03 Pg C yr^{-1}).

The behaviour of the continental shelf presents a high spatiotemporal variability of the air-sea CO_2 fluxes due to various processes, particularly thermodynamic effects, biological processes, gas exchange, upwelling zones and continental inputs (e.g. Chen and Borges, 2009; Ito et al., 2016). Thermodynamic effects are controlled by the inverse relationship between temperature and solubility (0.0423 ºC^{-1}, Takahashi et al., 1993)~~, which produces changes in CO_2 dissociation~~. Biological processes can induce CO_2 uptake or release, deriving respectively from phytoplankton photosynthesis that decreases the concentration of inorganic carbon, and respiration by plankton and all other organisms, which increases the concentration of inorganic carbon ~~-~~(Fennel and Wilkin, 2009). Both factors, thermodynamic effects and biological processes, are associated with the sea-air CO_2 exchange by physical and biological pumps (Volk and Hoffert, 1985). The effects of upwelling systems are not clearly defined ~~generate uncertainty~~ (Michaels et al., 2001). Although this process produces a vertical transport that brings up CO_2 and remineralized inorganic nutrients from deep seawater (Liu et al., 2010), upwellings are also responsible for high rates of primary production and a reduction of pCO_2 under the equilibrium with the atmosphere (e.g. van Geen et al., 2000; Borges and Frankignoulle, 2002; Friederich et al., 2002). Several studies indicate that these systems act as either a source or sink of CO_2 depending on their location (Cai et al., 2006; Chen et al., 2013)~~ and the ocean considered~~. Upwelling systems at low latitudes act mainly as a source of CO_2 but as a sink of CO_2 at mid-latitudes (Frankignoulle and Borges, 2001; Feely et al., 2002; Astor et al., 2005; Borges et al., 2005; Friederich et al., 2008; González-Dávila et al., 2009; Santana-Casiano et al., 2009). Upwelling systems in the Pacific and Indian Oceans act as sources of CO_2 to the atmosphere, whereas in the Atlantic Ocean they are sinks of atmospheric CO_2 (Borges et al., 2006; Laruelle et al., 2010). Additionally, the inner shelf is more affected by riverine inputs of nutrients and terrestrial carbon (e.g. Gypens et al., 2011; Vandemark et al., 2011) and by human impact (Cohen et al., 1997). The influence of both factors, riverine inputs and human impact, decrease towards offshore (Walsh, 1991). Several studies have determined that the inner shelf tends to act as a source of CO_2 and the outer shelf as a sink (e.g. Rabouille et al., 2001; Cai, 2003; Jiang et al., 2008, 2013; Arruda et al., 2015). The inner platform (depth less than 40 m) also presents greater seasonal variability of temperature than the outer platform, and consequently the effect of temperature on pCO_2 will be greater in this zone (Chen et al., 2013).

~~The Gulf of Cádiz, located on the south-west of the Iberian Peninsula, is part of the Iberian/Canaries Current System and the Eastern Boundary Upwelling System (EBUS) (Borges et al., 2006; Relvas et al., 2007; Arístegui et al., 2009; Laruelle et al., 2010). Although it is really a sub-region of this upwelling system; however, it has a seasonal behaviour due to the coastline configuration and the exchange of water masses with the Mediterranean Sea (Arístegui et al., 2009). Finally, the inner shelf because it is more affected by riverine inputs of nutrients and terrestrial carbon (e.g. Gypens et al., 2011; Vandemark et al., 2011) and by human impact (Cohen et al., 1997). The influence of both factors, riverine inputs and human impact, decrease towards offshore (Walsh, 1991). Several studies have determined that the inner shelf tends to act as a source of CO_2 and the outer shelf as a sink (e.g. Rabouille et al., 2001; Cai, 2003; Jiang et al., 2008, 2013; Arruda et al., 2015). The inner platform (depth less than 40 m) also presents greater seasonal variability of temperature than the outer platform, and consequently the effect of temperature on pCO_2 will be greater in the inner platform (Chen et al., 2013).~~

The Gulf of Cádiz is a geographical domain of considerable interest due to its location. In addition to receiving the outflow of Mediterranean waters through the Strait of Gibraltar, it receives continentalfreshwater inputs from several major rivers, i.e. the Guadalquivir, Tinto, Odiel and Guadiana. Various studies have been conducted in this area to evaluate the variability of the sea surface partial pressure of CO_2 (pCO_2), although they cover smaller areas and a shorter duration of time than this work (González-Dávila et al., 2003; Aït-Ameur and Goyet, 2006; Huertas et al., 2006; Ribas-Ribas et al., 2011) or only a specific area like the Strait of Gibraltar (Dafner et al., 2001; Santana-Casiano et al., 2002; de la Paz et al., 2009). All of these studies, however, have determined that this zone behaves as a global sink of CO_2, with seasonal variations mainly induced mainly by the combination of the fluctuations of biomass concentration and temperature.

In the study reported in this paper, the main objective is to we evaluate the spatial and seasonal variation of the sea-surface pCO_2 on the eastern shelf of the Gulf of Cádiz. In addition, wwe aim to assess the relative contribution of the temperature thermal and non-temperature thermal effects to pto the total CO_2 concentrationdistribution, and to determine if the area as a whole acts as a sink or a source of CO_2 to the atmosphere over time. It has also been possible to estimate the influence that various sea surface currents have on pCO_2 variability, since this study considers deeper areas than previous works. Therefore, we can analyse the change that has occurred in relation to the CO_2 uptake capacity in the Gulf of Cádiz in the last 10 years, in comparison with other studies that analyse the seasonal variation underway of pCO_2 in this area (Ribas-Ribas et al., 2011). In this workTo do this, we have we have analysed a surface measurement database of >26000 values of pCO_2 obtained during cruises made between 2014 and 2016 and covering an area of 0.8º x 1.3º area of the Gulf of Cádiz.

2. Material and methods

2.1. Study area

This study was carried out over the eastern shelf of the Gulf of Cádiz (Fig. 1), which forms a large basin between the southwest of the Iberian Peninsula and the northwest of Africa, where the Atlantic Ocean connects with the Mediterranean Sea through the Strait of Gibraltar. In the Strait of Gibraltar takes place a bilayer flow takes place, with an upper Atlantic layer flowing towards the Mediterranean basin and a deeper outflow of higher-density Mediterranean waters to the Atlantic Ocean (e.g. Armi and Farmer, 1988; Baringer and Price, 1999; Sánchez-Leal et al., 2017). A similar circulation pattern of opposing flows is found in the Gulf of Cádiz where three main water masses are distributed at well-defined- depth intervals and areas: the Surface Atlantic Water (SAW), with coastal and atmospheric influence, inflowing at the shallowest depths; the Eastern North Atlantic Water (ENACW), at an intermediate depth, characterised by low salinity; and the Mediterranean Outflow Water (MOW), entering at the deepest level (Criado-Aldeanueva et al., 2006; Bellanco and Sánchez-Leal, 2016).

The Gulf of Cádiz is part of one of the four major Eastern Boundary Upwelling SystemEBUS of the world, the North Atlantic upwelling (e.g. Alvarez et al., 2009), that extends from south of Cape Verde (Senegal) to Cape Finisterre (northwest of Spain). For this reason, the Gulf of Cádiz presents characteristics typical of this systemEBUS: seasonal variability of a winds system favourable to the coastal upwelling (Fiúza et al., 1982), high biological productivity (Navarro and Ruiz, 2006), a system of fronts and zonal currents (García Lafuente and Ruiz, 2007) and a zone of water exchange between the coastal zone and open ocean (Sánchez et al., 2008). However, the fact that the coastline of the study area runs more in a W-E direction than the overall N-S direction common to all the Eastern Boundary Upwelling SystemEBUS phenomena, and the bilayer flow through the Strait of Gibraltar, are two factors that complicate the simple Eastern Boundary Upwelling SystemEBUS conceptual model (Arístegui et al., 2009; Peliz et al., 2009).

In addition, the surface circulation in the Gulf of Cádiz is characterised by several different processes. These are: first the presence of an anticyclonic water flow towards the east over the shelf edge as far south as the Strait of Gibraltar, known as the

Gulf of Cádiz Current (Sánchez and Relvas, 2003; Peliz et al., 2007); ~~second,~~ an upwelling process occurs in the Trafalgar area ~~an upwelling process occurs~~, produced by tidal interaction with the topography of the zone; and ~~third,~~ the mixing of surface layers induced by the wind (Vargas-Yáñez et al., 2002~~; Sánchez and Relvas, 2003~~; Peliz et al., 2009; Sala et al., 2018). ~~In addition, t~~The centre of the Gulf is also under the influence of the eastern-end branch of the Azores Current, producing a front subjected to a mesoscale variability (Johnson and Stevens, 2000; García-Lafuente and Ruiz, 2007; Peliz et al., 2007; Sala et al., 2013) (Fig. 1).~~.~~

2.2. Field sampling and analysis

The database for this study has been obtained following two different sampling strategies. The first ~~one~~ consisted o~~f~~n taking sea surface measurements while underway. T ~~Meanwhile, t~~he second strategy was to obtain ~~one acquired the~~ measurements at several discrete surface stations along three transects at right angles ~~perpendicular~~ to the coastline: the Guadalquivir transect (GD), the Sancti Petri transect (SP) and the Trafalgar transect (TF) (Fig. 1). Data was ~~re~~collected during 8 cruises carried out with a seasonal frequency (spring: ST1 and ST5; summer: ST2 and ST6; autumn: ST3 and ST7; winter: ST4 and ST8) during 2014, 2015 and 2016 (~~precise dates are indicated in~~ Table 1). All the cruises were ~~were carried out~~made~~realised~~ on ~~board~~ the R/V Ángeles Alvariño, except the ~~one of~~ summer 2015 cruise (ST6) that was undertaken~~carried out~~~~completed~~ on ~~board~~ the R/V Ramón Margalef. The study area is located between 35.4 and 36.7º N and 6.0 and 7.2º W ($52.8\cdot10^2$ k~~K~~m^2).

2.2.1. Underway measurements

Sea surface temperature (SST), sea surface salinity (SSS) and the ~~CO_2 partial pressure (~~pCO_2~~)~~ were recorded continuously and were averaged with a frequency of 1 min intervals, from the surface seawater supply of the ship (pump inlet at a depth of 5m). SST and SSS were measured using a SeaBird thermosalinograph (SeaBird 21) with an accuracy of ±0.01 ºC and ±0.003 respectively. The equilibrator design for determining the pCO_2 is a combination of a laminar flow system with a bubble type system, similar to that developed by Körtzinger et al. (1996) and described by Padin et al. (2009, 2010).

The surface water CO_2 molar fraction (xCO_2) and H_2O were determined using a non-dispersive infrared gas analyser (Licor®, LI 6262) that has a minimum accuracy of ±0.3 ppm. It was calibrated daily using two standards: a CO_2 free-air for the blank and a CO_2 sub-standard gas of known concentration (413.2 ppm). CO_2 concentration of the sub-standard gas was determined from the comparison with standard gases of NOAA with an uncertainty of 0.22 ppm and measured with a Licor 6262 (±1 ppm). The temperature inside the equilibrator was measured continuously by means of a platinum resistance thermometer (PT100 probe, ±0.1 ºC). A pressure transducer (Setra Systems, accurate to 0.05 %) was used to measure the pressure inside the equilibrator.

The xCO_2 was converted into pCO_2 according to the protocol described in DOE (2007).~~:~~ ~~corrections~~ Corrections between the equilibrator and SST were ~~realised~~made following Takahashi et al. (1993). ~~by water vapour pressure and water surface temperature have been made since the equipment quantifies in dry air and the temperature registered in the equilibrator is different to the T.~~ The temperature difference between the ship's sea inlet and the equilibrator was less than 1.5 ºC.

2.2.2. Fixed stations

Discrete surface samples were ~~taken~~ collected at 5 m depth, using Niskin bottles (10 L) mounted on a rosette-sampler coupled to a SeaBird CTD 911+, to measure pH and dissolved oxygen, ~~pH,~~ chlorophyll-a ~~concentration~~ and nutrients concentration.~~.~~

The pH was measured by potentiometer in duplicate using 100 mL of seawater with a glass-combined electrode (Metrohm, 905) calibrated on the total pH scale using a TRIS buffer solution (Zeebe and Wolf-Gladrow, 2001). Dissolved oxygen values were obtained with the sensor of the rosette (SeaBird 63) pre-calibrated using Winkler titration (±0.1 µmol L^{-1}) of samples collected from several water depths at selected stations (Parsons et al., 1984). Apparent Oxygen Utilization (AOU) was determined as the difference between the solubility calculated applying the expression proposed by Weiss (1974) and the experimental values of dissolved oxygen. For chlorophyll-a determination, 1 L of seawater was filtered (Whatman, GF/F 0.7 µm) and frozen (-20 °C) until analysis in the laboratory. Total chlorophyll-a was extracted with 90 % pure Acetone, and quantified after 24 hours by fluorometry analysis (Hitachi F-2500) (Yentsch and Menzel, 1963). Nutrient samples for analysis of nitrate and phosphate content were filtered through pre-combusted glass-fibre filters (Whatman, GF/F 0.7 µm) and frozen at -20 °C. Analyses were performed in a segmented flow autoanalyzer (Skalar, San Plus) based on classic spectrophotometric methods (Grasshoff et al., 1983). Dissolved oxygen values were obtained with the sensor of the rosette (SeaBird 63) pre-calibrated using Winkler titration (±0.1 µmol L^{-1}) of samples collected from several water depths at selected stations (Parsons et al., 1984). Apparent Oxygen Utilization (AOU) was determined as difference between the solubility calculated applying the expression proposed by Weiss (1974) and the experimental values of dissolved oxygen.

Moreover, at these stations, Apparent Oxygen Utilization (AOU) was calculated applying the solubility expression proposed by Weiss (1974) employing dissolved oxygen values registered by the sensor of the rosette (SeaBird 63) that have been checked using Winkler titrations (±0.1 µmol L^{-1}).

The accuracies of the determinations obtained are the following: ±0.003 for pH, ±0.1 µmol L^{-1} for dissolved oxygen, ±0.1 µg L^{-1} for chlorophyll-a, ±0.10 µmol L^{-1} for nitrate, and ±0.02 µmol L^{-1} for phosphate and ±0.1 µmol L^{-1} for dissolved oxygen.

The corresponding data of SST, SSS and pCO_2 for the fixed stations were obtained by the underway measurements averaging data corresponding to 0.5 mile around the location of the fixed stations. SST and SSS data were compared with the values collected with the CTD coupled to the rosette-sampler and they do not show differences highgreater than 0.04 ºC and 0.01 units, respectively.

2.3. Temperature Thermal and non-thermalbiological effects on pCO_2 calculations

To determine the relative importance of the thermaltemperature and non-thermalbiological effects on the changes of pCO_2 in sea-water (e.g., Landschützer et al., 2015; Reimer et al., 2017), we follow the method proposed by Takahashi et al. (2002). To remove the thermalemperature effect from the observed pCO_2, the data were normalized to a constant temperature, the mean in situ SST depending on the focus considered, according to Eq. (1).

$$pCO_2 \text{ at } SST_{mean} = (pCO_2)_{obs} \cdot \exp[0.0423 \cdot (SST_{mean} - SST_{obs})] \quad (1)$$

where the subscripts “mean” and “obs” indicate the average and observed SST values, respectively.

The effect of temperature thermal changes on pCO_2 has been computed by perturbing the mean pCO_2 with the difference between the mean and observed temperature. The pCO_2 value at a given observed temperature (SST_{obs}) was calculated based on Eq. (2).

$$pCO_2 \text{ at } SST_{obs} = (\text{Mean } pCO_2)_{mean} \cdot \exp[0.0423 \cdot (SST_{obs} - SST_{mean})] \quad (2)$$

When the thermalemperature effect is removed, the remaining variations in pCO_2 are due to the non-thermal influenceseffect of biology, such as net the biological utilization of CO_2, the vertical and lateral transport, the and sea-air exchange of CO_2 and terrestrial inputs (e.g. Qu et al., 2014; Arruda et al., 2015; Ito et al., 2016; Xue et al., 2016)..

The non-thermalbiological effects on the surface water pCO_2 in a given area, $(\Delta pCO_2)_{n\text{-}T\,bio}$, , is represented by the seasonal amplitude of pCO_2 values normalized to the mean SST, (pCO_2 at SST_{mean}), using Eq. (1):

$$(\Delta pCO_2)_{n\text{-}T\,bio} = (pCO_{2,\,SSTmean})_{max} - (pCO_{2,\,SSTmean})_{min} \quad (3)$$

The thermalemperature effect of changes on the mean annual pCO_2 value, $(\Delta pCO_2)_{T\ temp}$, is represented by the seasonal amplitude of pCO_2 values normalized to the observed SST, (pCO_2 at SST_{obs}), using Eq.(2):

$$(\Delta pCO_2)_{T\,temp} = (pCO_{2,\,SSTobs})_{max} - (pCO_{2,\,SSTobs})_{min} \quad (4)$$

The relative importance of each effect can be expressed in terms of the ratio between the thermal effects (T) and non-thermal effects (B):

The relative importance of the temperature and biology effects can be expressed by the ratio, T/B:

$$T/B = (\Delta pCO_2)_{T\,temp} / (\Delta pCO_2)_{n\text{-}T\,bio} \quad (5)$$

In order to identify the overall controls of temperature and biological effects, the T/B ratio has been calculated (Takahashi et al., 2002). A T/B ratio greater than 1 implies the dominance of temperaturehermal effects over non-thermalbiological processes , on the pCO_2 dynamics. However, a T/B lower than 1 reveals a greater influence of non-thermal processes. Strictly speaking, the term that picks up the biological effect in the model of Takahashi et al. (2002), encompasses all those processes that are not thermal, that influence the variations of pCO_2, including the biological utilization of CO_2, continental inputs and the existence of upwellings (Xue et al., 2012; Qu et al., 2014). This method was originally designed for open oceanic systems, but it has been widely used by other authors in coastal areas (e.g. Schiettecatte et al., 2007; Ribas-Ribas et al., 2011; Qu et al., 2014; Burgos et al., 2018).

In addition, Olsen et al. (2008) propose a method in which decompose the seasonal signal of pCO_2 data is decomposed into individual components due to variations in SST, in air-sea CO_2 exchange, in SSS, and in combined mixing and biologicaly processes.

$$d\,pCO_2^{sw,i} = d_{SST}pCO_2^{sw,i} + d_{AS}pCO_2^{sw,i} + d_{SSS}pCO_2^{sw,i} + d_{MB}pCO_2^{sw,i} \quad (6)$$

where the superscript "i" refers to the mean value between consecutives cruises for all variables.; $d\,pCO_2^{sw,i}$ is the observed change in pCO_2;; $d_{SST}pCO_2^{sw,i}$ is the change due to SST changes,; $d_{AS}pCO_2^{sw,i}$ is the change due to air-sea exchange,; $d_{SSS}pCO_2^{sw,i}$ is the change due to salinity variations; and $d_{MB}pCO_2^{sw,i}$ is the change due to mixing plus biology. At the same time, each process is calculated with the followingnext equations (Olsen et al., 2008):

$$d_{SST}pCO_2^{sw,i} = pCO_2^{sw,i} \cdot e^{0.0423(\Delta SST)} - pCO_2^{sw,i} \quad (7)$$

where ΔSST is the SST difference between two cruises~~.~~

$$d_{AS}pCO_2^{sw,i} = - (d\cdot F^i) / MLD^i \quad (8)$$

where d is the number of days passed between two cruises (90 days approximately);~~,~~ F^i is the mean flux of CO_2; ~~-~~and MLD^i is the mean mixed layer depth.

$d_{SSS}pCO_2^{sw,i}$ ~~not~~ is not determined in this study, since data on ~~we do not provide of~~ the variations of total alkalinity and dissolved inorganic carbon are not available, and the spatial SSS changes are only ~~is~~ significant near the Guadalquivir River mouth. $d_{MB}pCO_2^{sw,i}$ is calculated as a residual, that is, as the change in pCO_2 that is not ~~un~~explained by other processes. Additionally, as this study includes both ~~work arrangements~~ coastal areas and deeper areas, ~~it divided~~ the analysis is divided, in function of the system depth, between coastal (< 50 m) and distal (> 50 m) areas. Thus, MLD^i in distal areas (Table 3) was calculated derived from~~of~~ the thermocline position that separates the SAW and the ENACW (71.3 - 96.8 m), while the coastal areas correspond~~ed~~ to the depth of these areas (15 - 50 m).

2.4. Estimation of CO_2 fluxes

Fluxes of CO_2 across the sea-air interface were estimated using the relationship:

$$FCO_2 = \alpha \cdot k \cdot (\Delta pCO_2)_{sea\text{-}air} \quad (~~6~~9)$$

where k (cm h^{-1}) is the gas transfer velocity; α is the solubility coefficient of CO_2 (Weiss, 1974); and ΔpCO_2 is the difference between the sea and air values of pCO_2. The atmospheric pCO_2 (pCO_2^{atm}) values were obtained from the monthly atmospheric data of xCO_2 (xCO_2^{atm}) at the Izaña Atmospheric Station in ~~(~~Spain~~), (), (~~Earth System Research Laboratory; https://www.esrl.noaa.gov/gmd/dv/data/index.php, last access: 9 January 2019). The xCO_2^{atm} was converted to pCO_2^{atm} as described in DOE (2007).

The gas transfer velocity, *k*, was calculated using the parameterization formulated by Wanninkhof (2014):

$$k = 0.251 \cdot u^2 (Sc/660)^{-0.5} \quad (~~7~~10)$$

where *u* (m s^{-1}) is the mean wind speed at 10 m height on each cruise, obtained from the Shipboard Weather Station; Sc is the Schmidt number of CO_2 in seawater;~~,~~ and 660 is the Sc in seawater at 20 ºC.

2.5. Statistical analysis

Statistical analyses were performed with IBM SPSS Statistics software (Version 20.0. Armonk, NY). The dataset was analysed using one-way analysis of variance test (ANOVA) for analysing significant differences between cruises for discrete and continuous surface data on hydrological and biogeochemical characteristics. The threshold value for statistical significance was taken as $p < 0.05$. Moreover, all reported linear correlations are type I and they are statistically significant with p-values smaller than 0.05 in the entire manuscript unless indicated otherwise.

3. Results

3.1. Underway variables

Table 1 gives the ranges of variation and the mean and standard deviation of SST, SSS and pCO_2 during the 8 sampling cruises and ~~the .~~ ~~F~~figure 2 shows the underway distribution of SST and pCO_2 in the Gulf of Cádiz. Among all the cruises the

SST- values ~~were significantly different among all cruises ($p < 0.05$),~~ varying between 14.3 and 23.4 ºC ~~among all cruises~~. T~~In general, t~~he samplings made during 2014 presented ~~temperatures~~ SST values higher than those in 2015 and 2016 (Table 1). For the whole period, the averaged values for both seasons were highest during summer (21.02 ± 0.81.3 ºC) and autumn (21.10 ± 1.20.8 ºC), with the lowest values during spring (15.5 ± 0.5 ºC) and ~~. During winter, T showed~~ an intermediate value ~~of 17.6 ± 0.9 ºC~~during winter (17.5 ± 0.6 ºC). In general, ~~. S~~spatially SST tended to increase from coastal to offshore areas during spring and winter, while in summer and autumn this SST gradient was inverse (Fig. 2A).~~, with a difference of ~11.8 ºC (Fig. 2A).~~ No substantial differences were found between the three transects studied (GD, SP and TF)~~ in terms of temperature data.~~, although ~~The lowest values of T were detected~~ near the Guadalquivir River mouth and Cape Trafalgar (36.19º N, 6.03º W) ~~were detected~~ , the lowest values of SST due to freshwater inputs and the frequent upwelled waters, respectively,. were detected.

Since the cruises were carried out at the beginning of each meteorological season, it is appropriate to analyse how representative is the range of temperatures that has been obtained. Figure 43 shows the mean value overf the last 10 years offor the maximum and minimum temperatures in the Gulf of Cádiz acquired by a oceanographic buoy~~mooring~~ (bottom-mounted at 36.48° N - 6.96° W; Puertos del Estado; http://www.puertos.es/es-es/oceanografia/Paginas/portus.aspx, last access: 12 July 2018);~~, and~~ the mean values and standard deviations of the 8 cruises are superimposed. It can be observed that the mean values for each cruise are within the ranges of variation of the typical temperature in the Gulf of Cádiz, and the mean temperature found, 18.8 ºC, is very close~~similar~~ to the mean value obtained at the oceanographic buoy~~mooring~~ (19.2 ºC, Fig. 43).~~). If the dependence of pCO_2 with temperature is taken to be 4.80 µatm $ºC^{-1}$, one would expect that the mean values of pCO_2 obtained in this study would be approximately 2 µatm higher.~~

~~SSS values remained practically constant throughout the whole study period, although~~ Aaverage -values of SSS -varied significantly among the cruises~~, ($p < 0.05$), with values~~ ranging between ~~34.68~~35.03 and 37.06. The highest values were recorded during February 2016 ~~September 2015~~ (36.44 ± 0.09) and lowest during September 2015 ~~February 2016~~ (35.64 ± 0.08) (Table 1).~~ No spatial or seasonal variations were observed. However,~~ The lowest salinity value (35.03) and the most notable~~ accused~~ spatial variation (35.03 - 36.36) was observed during December 2014 ,-in the area of the Guadalquivir River ~~was measured the lowest salinity value (34.68),~~, associated ~~related~~ with a period of storms with consequent major~~period that led~~ important~~to very heavy~~ freshwater discharges. T~~On the other hand, TF was t~~he area that presented the highest mean salinity value for the whole study ~~(36.19 ± 0.25)~~was TF (36.19 ± 0.25)..

During our study period, pCO_2 values ranged from 320.6 to 513.6 µatm. Highest values were recorded during summer and autumn of 2014 and 2015 (Table 1), with a similar mean value~~ found for both seasons~~, 411.67 ± 13.32 µatm and 410.61.3 ± 10.57 µatm, respectively, found for both seasons. The ~~low~~lowest ~~st er~~ mean value ~~(382.5390.3 ± 16.95.2 µatm)~~ was logged during spring (382.5 ± 16.9 µatm)~~winter~~, while ~~and~~ winter presented an intermediate value~~the lowest mean value~~ (390.883.9 ± 15.422.1 µatm)~~ during spring~~. In general, the pCO_2 tended to decrease with the distance to the coast (Fig. 2B). Comparing these values with pCO_2 values in the atmosphere, ~~it was observed~~ an undersaturation of CO_2 was observed during spring and winter (15.3 ± 15.7 and 18.0 ± 11.4 µatm, respectively) and an oversaturation in summer and autumn (-20.4 ± 24.6 and -8.0 ± 15.3 µatm, respectively)~~ΔpCO_2 values ranged between -37.5 ± 14.9 µatm during March 2015, and 16.5 ± 9.5 µatm during October 2014. Moreover, an oversaturation relative to the atmosphere was evidenced during spring and winter for both years~~.

In Fig. 2B a sharply variation of SST and pCO$_2$ can be observed inat some zones that. These coincides with theose stations where discrete water samples were taken. This may be due to the different sampling time atin these stations, which varied between 2 and 8 hours in function of the depth of the system.

daily variation (day/night) presented by pCO$_2$, since the sampling procedure did not take the same amount of time at each station – it varied in function of the depth of the system in each zone. It is possible that during the daytime, the pCO$_2$ values were higher than at night.The database of this study includes the transition from coastal zones, with depths of the order of 15 –20 m, to distal shelf waters with depths greater than 800 m.. Figure 54 shows the general trend of the mean values of pCO$_2$ and temperatureSST for different intervals of depth of the water column based on the information obtained in the 8 cruises. There is no statistical difference in pCO$_2$ or SST with bottom depth. I, iIt can be observed that the highest values of pCO$_2$ (408.3 ± 26.7 µatm) correspond to the coastal zone (< 50 m), and that values decrease down to a depth of 100 - 200 m of depth (396.1 ± 23 µatm). In addition, towards open waters (> 600 m) there is a progressive increase of pCO$_2$ and temperatureSST (404.3 ± 16.5 µatm and 20.1 ± 2.4 ºC, respectively)..

3.2. Discrete surface variables

Table 2 shows the averageaverage values and standard deviation for the underway averaged measurements of temperatureSST and , salinitySSS, and for the discrete samples of , pH, AOU, chlorophyll-a, nitrate and phosphate measured at fixed stations along the three transects during the 8 cruises.

The pH presented significant differences among the cruises ($p < 0.05$), with a range of variation from 7.84 to 8.34. Lowest mean values were found during summer (8.00 ± 0.04) and autumn (7.96 ± 0.05) of 2014 (8.00 ± 0.04) and 2015 (7.96 ± 0.05) (Table 2), coinciding with the highest average values of pCO$_2$ were recorded (Table 1). The minimum value of pH values for spring and winter were equal practically for both years (8.08 ± 0.08 and 8.07 ± 0.05, respectively).were found in September 2015 (7.49 ± 0.03) and the maximum in March 2015 (8.09 ± 0.12).

AOU was significantly different between all the cruises ($p < 0.05$), butand a clear seasonal variability was not observed. Values measured ranged from -31.9 to 12.3 µmol L^{-1}, with the highest values in December 2014 (7.7 ± 2.1 µmol L^{-1}) and the lowest in March 2015 (-19.1 ± 9.4 µmol L^{-1}) (Table 2). For both years, the lowest mean value was recorded in spring (-11.3 ± 8.9 µmol L^{-1}), and the highest in winter (1.3 ± 2.6 µmol L^{-1}).During spring was registered the lowest mean value for both years (-11.30.9 ± 11.78.9 µmol L^{-1}); higher mean values were found in summer (- 6.3 ± 6.1 µmol L^{-1}) and the higher during winter (4.21.3 ± 2.66.3 µmol L^{-1}). All mean values were negative except for those of December 2014; that exception may have been due to the exceptional mixing of the water column caused by the storms. No gGeneral trend in the spatial variations of pH and AOU wasere found.

Chlorophyll-a values presented significant differences among the cruises and between the same seasons of each year ($p < 0.05$). This parameter varied from 0.02 to 2.37 µg L^{-1}, with the highest mean value measured in March 2015 (0.76 ± 0.55 µg L^{-1}), which coincides with the lowest (negative) mean value of AOU (Table 2). The lowest mean value was in June 2014 (0.18 ± 0.14 µg L^{-1}). With reference to the seasons of both years, the highest value was in spring (0.712 ± 0.46 µg L^{-1}), followed by winter (0.4758 ± 0.331 µg L^{-1}), autumn (0.268 ± 0.3030 µg L^{-1}) and the lowest value in summer (0.232 ± 0.256 µg L^{-1}). The SP transect presented the mean lowest mean value of the whole study (0.33 ± 0.31 µg L^{-1}), and the TF zone the highest (0.49 ± 0.37 µg L^{-1}).

Nitrate concentration did not show significant differences among~~ all~~ the cruises~~ (p > 0.05)~~, ranging between 0.00 and 1.93 µmol L^{-1}. ~~The highest value was found in December 2014 (1.05 ± 1.96 µmol L^{-1}) and the lowest in June 2015 (0.12 ± 0.14 µmol L^{-1}) (Table 2).~~ The highest mean value was recorded in spring~~winter~~ (0.82~~7~~ ± 1.09~~70~~ µmol L^{-1}) and the lowest in summer (0.25~~7~~ ± 0.3~~4~~5 µmol L^{-1}) of both years. The –TF transect presented the highest mean concentration for the whole study (0.77 ± 0.76 µmol L^{-1}).

Phosphate concentration showed significant differences among all the cruises~~ (p < 0.05)~~. By season, the highest mean value was obtained during autumn (0.31 ± 0.30~~45~~ µmol L^{-1}), although the average data in October 2014 (0.09 ± 0.03 µmol L^{-1}) was lower than that of 2015 (0.50 ± 0.55 µmol L^{-1}) (Table 2). The lowest~~minimum~~ mean value was observed during summer (0.10~~1~~ ± 0.05 µmol L^{-1}). The GD transect presented the highest mean value of the whole study (0.28 ± 0.39 µmol L^{-1}), and the lowest~~r~~ values were found in the TF~~ ,~~ and SP transects, with a similar value in each, 0.15 ± 0.07 µmol L^{-1} and 0.14 ± 0.09 µmol L^{-1}, respectively. The mean N/P ratio in surface waters for the whole study was~~has been~~ 3.5 ± 2.0, similar to thate estimated by Anfuso et al. (2010) in the northeast continental shelf of the Gulf of Cádiz, which indicates a relative ~~deficit~~ phosphate deficit with respect to the Redfield ratio (Redfield et al., 1963).

3.3. Air-sea CO_2 exchange

Table 3 summarizes the mean values and standard deviation for atmospheric pCO_2, wind speed, gas transfer velocity and the air-sea CO_2 fluxes measured in this study.

The mean wind speeds were relatively similar for the whole study period, ranging between 5.5 ± 2.8 m s^{-1} (March 2015) and 7.7 ± 4.2 m s^{-1} (December 2014). The gas transfer velocity varied between 6.9 ± 0.1 cm h^{-1} in March 2015 and 14.4 ± 0.3 cm h^{-1} in June 2015, since it is very sensitive to changes in wind speed. ~~(4.6 cm h^{-1} / m s^{-1} at 20 ºC).~~

There was a clear seasonal variability in the dataset of CO_2 fluxes~~ (p < 0.05)~~. The study area acted as source of CO_2 to the atmosphere during summer and autumn (0.7 ± 1.5~~0.3~~ mmol m^{-2} d^{-1} and 1.2 ± 0.9~~4~~ mmol m^{-2} d^{-1}, respectively) and as a sink in spring and winter (-1.3 ± 1.6~~4~~ mmol m^{-2} d^{-1} and -1.3 ± 1.6~~0.01~~ mmol m^{-2} d^{-1}, respectively).

4. Discussion

4.1. ~~General trends~~Thermal influence in pCO_2

Numerous research studies have determined that temperature is one of the most important factors that control the variability of pCO_2 in the ocean (e.g. Millero, 1995; Bates et al., 2000; Takahashi et al., 2002; Carvalho et al., 2017), as a consequence of the dependence of the solubility of CO_2 with the temperature (Weiss, 1974; Woolf et al., 2016). When pCO_2 is affected only by the temperature, Takahashi et al. (1993) determined a relative variation of pCO_2 of 0.0423 ºC^{-1}, equivalent to 16.9~~7.4~~ µatm ºC^{-1} for experimental pCO_2 of 400 µatm. In our study ~~was observed~~ a seasonal variation was observed with a linear increase of the values of pCO_2 with SST for the entire database (r^2 = 0.37, Fig. 5A). This relationship becomes more significant when it is obtained from the mean values of pCO_2 and SST of each cruise (r^2 = 0.71, Fig. 5B). The slope, 4.80 µatm ºC^{-1}, is lower than the thermal effect on pCO_2 described by Takahashi et al. (1993), and indicates the influence of other non-thermal processes on the distribution of pCO_2 in this zone of the Gulf of Cádiz.

There are previous studies in which the seasonal variations of pCO_2 in more coastal zones of the Gulf of Cádiz (depth < 100 m) are described (Table 4). Ribas-Ribas et al. (2011) found in the north eastern shelf during June 2006 and May 2007 a dependence of pCO_2 with temperature similar to that found in this study (5.03 µatm ºC^{-1}, r^2 = 0.42), and a pCO_2 that ranged between 338 and 502 µatm. In 2003, Huertas et al. (2006) found variations of pCO_2 ranging between 196 µatm in March and 400 - 650 µatm in August in a zone situated more to the west, between the rivers Guadalquivir and Guadiana. In addition, de la Paz et al. (2009) established a variation of pCO_2 between 387 µatm in September 2005 and 329 µatm in March 2006 in the Strait of Gibraltar, a deeper zone situated at the south eastern limit of the Gulf of Cádiz. This dependence of pCO_2 with temperature has also been determined in other studies of continental shelves, such as, in the east China Sea (Wang et al., 2000), in the northern east China Sea (Shim et al., 2007) and in the northern Yellow Sea (Xue et al., 2012).

Figure 3A shows the dependence of the values of pCO_2 with T for the entire database, where a linear increase of pCO_2 with T ($r^2 = 0.37$, $p < 0.0001$) was observed. This relationship becomes more significant when it is obtained from the mean values of T and pCO_2 of each cruise ($r^2 = 0.71$, $p < 0.01$, Fig. 3B). The slope, 4.80 µatm °C^{-1}, is lower than the thermal effect on pCO_2 described by Takahashi et al. (1993), and indicates the influence of other processes on the distribution of pCO_2 in this zone of the Gulf of Cádiz.

Table 4 gives the values for the dependence of pCO_2 with temperature on various continental shelves determined in other studies. The authors of these studies describe the influence of other processes on the relationship between pCO_2 and temperature, such as the vertical mixing of the water column (Wang et al., 2000; Xue et al., 2012), continental inputs (Shim et al., 2007; Xue et al., 2012), the influence of surface currents at different temperature (Shim et al., 2007; Jiang et al., 2008), upwelling phenomena (Wang et al., 2005; Jiang et al., 2008; Xue et al., 2012) and biological activity (Wang et al., 2005; Shim et al., 2007; Ribas-Ribas et al., 2011).

There are previous studies in which the seasonal variations of pCO_2 in more coastal zones of the Gulf of Cádiz (depth < 100 m) are described. In 2003, Huertas et al. (2006) found variations of pCO_2 ranging between 196 µatm in March and 400 - 650 µatm in August in a zone situated more to the west, between the rivers Guadalquivir and Guadiana. Ribas-Ribas et al. (2011) established during 2006 - 2007, a dependence of pCO_2 with temperature similar to that found in this study (5.03 µatm °C^{-1}), and mean annual values of 369.3 ± 31.3 µatm. Also in 2006, de la Paz et al. (2009) established a variation of pCO_2 between 329 µatm in March and 387 µatm in September in the Strait of Gibraltar, a deeper zone situated at the southeastern limit of the Gulf of Cádiz.

There are other studies not concerned with seasonal differences that have quantified pCO_2 in different zones of the Gulf of Cádiz. Santana-Casiano et al. (2002) found pCO_2 values of 332.2 ± 3.9 µatm in the Strait of Gibraltar during September 1997, and González-Dávila et al. (2003) determined pCO_2 values of 330.6 ± 5.6 µatm on a transect at right-angles to the coastline in the zone of the Guadalquivir, carried out in February 1998. Aït-Ameur and Goyet (2006) reported variations of pCO_2 ranging between 300 and 450 µatm for an extensive region of the Gulf of Cádiz in 2002.

Comparing the data given in those previous studies of the Gulf of Cádiz with the mean value found in this study (398.9 ± 15.5 µatm), it is evident that there has been an increase of pCO_2 in the Gulf of Cádiz during the last decade, even taking into account the uncertainty associated with the different measurement techniques employed. When we compare this mean value with the value found in the shallower and deeper studied zones of the Gulf of Cádiz studied by Ribas-Ribas et al. (2011) (360.6 ± 18.2 µatm), who used the same methodology, there has been an increase of pCO_2 of 38.3 ± 16.9 37.6 µatm in the last decade. For the period of time between 2006 and 2016, the rate of growth of pCO_2 in the surface waters of the Gulf of Cádiz (3.8 ± 1.7 µatm year^{-1}) exceeds the rate of increase of pCO_2 in the atmosphere (2.3 µatm year^{-1}- for the last 10 years in Izaña (Earth System Research Laboratory; https://www.esrl.noaa.gov/gmd/dv/data/index.php, last access: 9 January 2019))). ; Tthis suggests a possible increase of the anthropogenic nutrient and C inputs from land (Mackenzie et al., 2004) since the direction and magnitude of estuarine and continental shelf CO_2 exchange with the atmosphere is highly dependent on the terrestrial organic budget and nutrient supplies to the coastal ocean there may have been changes in the continental inputs of nutrients and C related to anthropogenic activity (Borges and Abril, 2011; Cai, 2011Rabouille et al., 2001).

The thermal effect on pCO_2 is more intense when the discrete database (pCO_2 = 297 + 5.7 T, r^2 = 0.48; $p < 0.0001$) is considered in comparison to the effect obtained using the whole database.Since the cruises were carried out at the beginning of each meteorological season, it is appropriate to analyse how representative is the range of temperatures that has been obtained. Figure 4 shows the mean value of the last 10 years for the maximum and minimum temperatures in the Gulf of Cádiz acquired by a mooring (bottom-mounted at 36.48° N - 6.96° W; Puertos del Estado; http://www.puertos.es/es-es/oceanografia/Paginas/portus.aspx, last access: 12 July 2018), and the mean values and standard deviations of the 8 cruises are superimposed. It can be observed that the mean values for each cruise are within the ranges of variation of the typical temperature in the Gulf of Cádiz, and the mean temperature found, 18.8 ºC, is similar to the mean value obtained at the mooring (19.2 ºC, Fig. 4). If the dependence of pCO_2 with temperature is taken to be 4.80 µatm $ºC^{-1}$, one would expect that the mean values of pCO_2 obtained in this study would be approximately 2 µatm higher.

The database of this study includes the transition from coastal zones, with depths of the order of 15 - 20 m, to distal shelf waters with depths greater than 800 m. Figure 5 shows the mean values of pCO_2 and temperature for different intervals of depth of the water column based on the information obtained in the 8 cruises. It can be observed that the highest values of pCO_2 (408.3 ± 26.7 µatm) correspond to the coastal zone (< 50 m), and that values decrease down to 100 - 200 m of depth (396.1 ± 23 µatm). In addition, towards open waters (> 600 m) there is a progressive increase of pCO_2 and temperature (404.3 ± 16.5 µatm and 20.1 ± 2.4 ºC respectively).

4.2. Non-thermal factors controlling pCO_2

In addition to the influence of temperature, the spatiotemporal distribution of pCO_2 in surface seawater is affected by the biological utilization of CO_2, the vertical and lateral transport, the sea-air exchange of CO_2 and terrestrial inputs (e.g. Arruda et al., 2015; Ito et al., 2016; Xue et al., 2016).

Several authors have described the influence of the continental inputs on the distribution of pCO_2 in surface waters. ;In general, the coastal zone is usually oversaturated with CO_2 (Fig. 4), whereas the continental shelf as a whole acts as a sink of atmospheric CO_2 (e.g. Rabouille et al., 2001; Chen and Borges, 2009). This behaviour has been described in someother systems, such as, inincluding the southern part of the Yellow Sea (Qu et al., 2014), in the southwestern part of the Atlantic Ocean (Arruda et al., 2015), in the North Sea (Clargo et al., 2015), and on the continental shelf of Maranhense (Lefèvre et al., 2017). the coastal zone is usually oversaturated with CO_2, whereas the continental shelf as a whole acts as a sink of atmospheric CO_2 (e.g. Rabouille et al., 2001; Chen and Borges, 2009). Ribas-Ribas et al. (2011) also found a decrease of pCO_2 towards the deep zones (down to ≈ 100 m) on the north-eastern shelf of the Gulf of Cádiz. In general, an oversaturation of CO_2 with respect to the atmosphere in shallower zones and the subsequent undersaturation in distal waters, has also been described in other systems such as, for example, in the southern part of the Yellow Sea (Qu et al., 2014), in the southwestern part of the Atlantic Ocean (Arruda et al., 2015), in the North Sea (Clargo et al., 2015), and on the continental shelf of Maranhense (Lefèvre et al., 2017).

The principal continental inputs in the northeast zone of the Gulf of Cádiz take place from the estuary of the Guadalquivir and from the systems associated with the Bay of Cádiz. De la Paz et al. (2007) found values of pCO_2 higher than 3000 µatm in the internal part of the estuary of the Guadalquivir, and Ribas-Ribas et al. (2013) established that this estuary acts as an exporter system of C, nutrients and water oversaturated with CO_2 to the adjoining coastal zone. The importance of the contributions from the Guadalquivir on the distribution of pCO_2 depends on the river's flow rate, as can be appreciated in Fig. 32B. In March 2014 The (ST1, green) highest values of pCO_2 (up to 500 µatm) were observed during March 2014 in the zone close to the Guadalquivir River mouth, as a consequence of the river's high flow rate- (between 192.7 and 299.2 m^3 s^{-1}, Confederación Hidrográfica del Guadalquivir; http://www.chguadalquivir.es/saih/DatosHistoricos.aspx, last access: 19 JunyJuly 2018). In contrastMoreover, the lowest values of pCO_2 while in were recorded in the spring of 2015 (ST5, dark green) the lowest values of the study were recorded in this zone (as low as 320 µatm) duringin a period of drought (flow rate 20 m^3 s^{-1}) and subject to intense biological activity associated with the highest value found of the concentration of chlorophyll-a (2.4 µg L^{-1}). The Bay of Cádiz occupies an area of 38 km^2, and receives urban effluents from a population of 640,000 inhabitants. This shallow zone is oversaturated with CO_2 (Ribas-Ribas et al., 2011) due largely to the inputs of inorganic carbon, organic matter and nutrients that are received from the Guadalete River and Sancti Petri Channel and the Río San Pedro tidal creeks -(de la Paz et al., 2008a, b; Burgos et al, 2018).

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The Bay of Cádiz occupies an area of 38 km^2, and receives urban effluents from a population of 640,000 inhabitants. This shallow zone is oversaturated with CO_2 (Ribas-Ribas et al., 2011) due largely to the inputs of CO_2, organic matter and nutrients that are received from the river Guadalete and the Sancti Petri and River San Pedro tidal creeks (de la Paz et al., 2008a, b; Burgos et al, 2018).

Another source of CO_2 in the coastal zone results from the net production of inorganic carbon derived from the processes of remineralization of the organic matter in the surface sediments originatinged from the continuous deposition of organic matter through the water column (de Haas et al., 2002; Jahnke et al., 2005). The intensity of this process decreases in line with the increasing depth of the system, and the influence of the primary production and the continental supplies on the deposition of the particulate organic matter is less (Friedl et al., 1998; Burdige, 2007; Al Azhar et al., 2017). Ferrón et al. (2009) quantified the release from the sediment of DIC related to the processes of oxidation of organic matter in the coastal zone (depth < 50 m) of the Gulf of Cádiz, between the Guadalquivir and the Bay of Cádiz. These authors found a mean benthic flux of 27 ± 8 mmol C m^{-2} d^{-1} for stations with a mean depth of 23 m. Considering a well-mixed water column, a pH = 8, in the conditions of mean temperature and salinity in the Gulf of Cádiz (18.8 ºC and 36.19, respectively) and using the K1 and K2 acidity constants proposed by Lueker et al. (2000) in the total pH scale. This flux of DIC is equivalent to a CO_2 flux of 198 ± 80 µmol C m^{-2} d^{-1}, cConsidering a well-mixed water column, a pH = 8, in the conditions of mean temperature and salinity in the Gulf of Cádiz (18.8 ºC and 36.19, respectively) and using the K1 and K2 acidity constants proposed by Lueker et al. (2000) in the total pH scale. Moreover, this estimated CO_2 benthic flux which would produce an increase of pCO_2 of 0.25 ± 0.10 µatm d^{-1} in the water column..

Additionally, another factor presents in the Gulf of Cádiz and that could affect the distribution of pCO_2 is the vertical and lateral transport. For example, Additionallythere are two upwelling systems in our study zone,, one more permanent situated in the coastal zone (depth between 50 and 100 m) of the Trafalgar section section (Prieto et al., 1999; Vargas-Yáñez et al., 2002) and the other located , between the Cape of Santa María and the Guadalquivir River and more sensitive to meteorological forcing (Criado-Aldeanueva et al., 2006). In our databasedatabase, only experimental evidence of the upwelling wasere found only in the TF transecttransect. In our database experimental evidence of the upwelling was found only in the TF transect. A local decrease of the mean values of SST (17.4 ºC) and pCO_2 (399.1 µatm) was observed in this coastal area of TF, with respect to the deeper areas (18.8 ºC and 405.1 µatm, respectively) for the whole period. ~~an almost permanent upwelling system is located (Prieto et al., 1999; Vargas-Yáñez et al., 2002); this system could affect the pCO_2 values in this part of the Gulf of Cádiz.~~ This input of colder waters could cause higher or lower concentrations of CO_2 (e.g. Liu et al., 2010; Xue et al., 2015; González-Dávila et al., 2017).

~~There are other upwelling systems located more to the west of the zone studied. One of these is situated between the cape of Santa María and the river Guadalquivir and is more sensitive to meteorological forcing, and there is another at Cape San Vicente that is almost permanently active (Criado-Aldeanueva et al., 2006). This input of colder waters, with greater loading of nutrients and higher concentrations of CO_2 (e.g. Liu et al., 2010; Xue et al., 2015; González-Dávila et al., 2017) can affect the distributions of pCO_2 found in the Gulf of Cádiz.~~

There is a progressive increase of SST and pCO_2 with increasing depth of the system measured below 100 - 200 m (Fig. 4~~5~~); this~~, it~~ is associated with the presence of a branch of the Azores Current that introduces warmer waters in the central part of the Gulf of Cádiz (Gould, 1985; Käse et al., 1985; Johnson and Stevens, 2000). The influence of warmer surface currents~~ and their influence~~ on the variability of pCO_2 has been observed in other studies, such as~~ that on the influence of~~ the Gulf Stream in the south-eastern continental shelf of the United States (Wang et al., 2005; Jiang et al., 2008), and ~~that on~~ the Kuroshio Current in the northern East China Sea (Shim et al., 2007).

~~Ribas-Ribas et al. (2011) also found a decrease of pCO_2 towards the deep zones (down to ≈ 100 m) on the north-eastern shelf of the Gulf of Cádiz. In general, an oversaturation of CO_2 with respect to the atmosphere in shallower zones and the subsequent undersaturation in distal waters, has also been described in other systems such as, for example, in the southern part of the Yellow Sea (Qu et al., 2014), in the southwestern part of the Atlantic Ocean (Arruda et al., 2015), in the North Sea (Clargo et al., 2015), and on the continental shelf of Maranhense (Lefèvre et al., 2017).~~

~~4.2. Control factors affecting pCO_2~~

~~In addition to the influence of temperature, the spatiotemporal distribution of pCO_2 in surface seawater is affected by the biological utilization of CO_2, the vertical and lateral transport, the sea-air exchange of CO_2 and terrestrial inputs (e.g. Arruda et al., 2015; Ito et al., 2016; Xue et al., 2016).~~

With the object of investigating the influence of the biological utilization of CO_2~~activity~~ on the variations of pCO_2, Fig. 6 shows the dependence between the mean values of pCO_2~~ at the fixed stations,~~ and~~ the temperature,~~ pH, AOU and the concentration of chlorophyll-a at the fixed stations (n = 126). AOU presents a positive relationship (pCO_2 (µatm) = 410 + 1.1 AOU (µmol L^{-1}), $r^2 = 0.21$), with a slope close to what would be obtained taking into account the processes of formation/oxidation of the organic matter phytoplankton considering a Redfield-–type relationship. Inverse relationships between pCO_2 and dissolved oxygen ~~also~~ were also found in other studies of continental shelf (Zhai et al., 2009; de la Paz et al., 2010; Xue et al., 2012, 2016). However, pCO_2 and pH presents an inverse relationship (pCO_2 (µatm) = 1710 - 162.8 pH, $r^2 = 0.34$), due to the effect of the uptake or production of CO_2 on the~~about~~ pH (Tsunogai et al., 1997; Shaw et al., 2014). ~~The thermal effect on pCO_2 is more intense when the discrete database ($pCO_2 = 297 + 5.7$ T, $r^2 = 0.48$; $p < 0.0001$) is considered in comparison to the effect obtained using the whole database.~~ The variation of pCO_2 with ~~pH ($pCO_2 = 1710 - 162.8$ pH, $r^2 = 0.34$; $p < 0.0001$), AOU ($pCO_2 = 410 + 1.1$ AOU, $r^2 = 0.21$; $p < 0.0001$), and~~ chlorophyll-a (pCO_2 (µatm) = 413 - 20.8 [chlorophyll-a~~Chl-a~~] (µg L^{-1}), $r^2 = 0.14$~~; $p < 0.0001$~~) also show the influence of the~~e~~ processes of photosynthesis and respiration ~~of photosynthesis and respiration on the variations of pCO_2~~(e.g. Cai et al., 2011; Clargo et al., 2015), with a ~~similar~~ slope value similar to thate obtained in the study of ~~found.~~ Huertas et al. (2005), (pCO_2 (µatm) = 274 - 19.6 [chlorophyll-a] (µg L^{-1}), r^2 =

0.32; n = 28). ~~For the Gulf of Cádiz, Huertas et al. (2005) found a linear relationship between pCO_2 and chlorophyll-a with a slope similar to that obtained in this study (pCO_2 = 274 - 19.6 [Chl-a], r^2 = 0.32; $p < 0.0001$; n = 28).~~ Other authors have also described the interrelationships existing between pCO_2 and chlorophyll-a in other coastal areas (Borges and Frankignoulle, 1999; Tseng et al., 2011; Zhang et al., 2012; Qin et al., 2014; Litt et al., 2018). ~~Inverse relationships between pCO_2 and dissolved oxygen as a consequence of the balance between the processes of photosynthesis and respiration have been found in other studies (Zhai et al., 2009; de la Paz et al., 2010; Xue et al., 2012; Xue et al., 2016).~~

In ~~A~~accordance with~~ing to~~ Olsen et al. (2008), Fig. 10 shows the decomposition of the variations of pCO_2 between cruises due to changes in SST, in air-sea CO_2 exchange and in combined mixing and biology, in distal and coastal areas. In general, the variations are greater than those found in other works (Olsen et al., 2008; Omar et al., 2010) because this study considers seasonal changes against the monthly change analysed in previous applications. $d\mathrm{pCO}_2^{sw}$ presents practically the same temporal trend in deep and coastal areas~~ practically~~, but with a global behaviour different since the distal zones act a sink of CO_2 of the system (mean $d\mathrm{pCO}_2^{sw}$ = -3.4 ± 28.9 µatm) and the shallower areas as a source of CO_2 (mean $d\mathrm{pCO}_2^{sw}$ = 0.2 ± 22.7 µatm). In distal areas (Fig. 10), pCO_2 changes are mainly brought about by SST (-58.4 - 106.2 µatm) together with mixing and biology processes (-90.8 - 36.2 µatm). ~~It observed an~~An inverse coupling is observed between $d_{SST}\mathrm{pCO}_2^{sw}$ and $d_{MB}\mathrm{pCO}_2^{sw}$, since with the increase of the system SST (increase $d_{SST}\mathrm{pCO}_2^{sw}$) there is greater biological uptake of CO_2 (decrease $d_{MB}\mathrm{pCO}_2^{sw}$). As reported in the studies ~~it happens in the works~~ of Olsen et al. (2008) and Omar et al. (2010), the change produced by the air-sea CO_2 exchange is lower. Instead, in coastal areas (Fig. 10), the dominant~~te~~ effects on~~about~~ pCO_2 changes are produced by air-sea CO_2 exchange (-196.2 - 103.4 µatm) and mixing plus biology (-101.1 - 198.5 µatm). A relative inverse coupling ~~inverse~~ between the ~~both~~two factors was also observed;~~, a de~~outgassing is produced (decrease $d_{AS}\mathrm{pCO}_2^{sw}$) when the system receives greater inputs/production of CO_2 (increase $d_{MB}\mathrm{pCO}_2^{sw}$). There is a different behaviour between the transition from~~ of~~ spring to ~~and~~ summer of 2014 (ST1 and ST2) and 2015 (ST5 and ST6) for $d_{MB}\mathrm{pCO}_2^{sw}$, which ~~can~~may be due to a greater quantity of continental inputs, as reflected in the Guadalquivir river flow rate in these periods (85.1 ± 75.4 $m^3 s^{-1}$ and 25.3 ± 10.2 $m^3 s^{-1}$, respectively). A larger effect of the air-sea CO_2 exchange on ~~about~~ pCO_2 variation is observed in the shallower mixed layers, as also described by Olsen et al. (2008) in the subpolar North Atlantic.

4.3. T/B ratio~~In order to identify the overall controls of temperature and biological effects, the T/B ratio has been calculated (Takahashi et al., 2002). A T/B ratio greater than 1 implies the dominance of temperature effects over biological processes, on the pCO_2 dynamics. Strictly speaking, the term that picks up the biological effect in the model of Takahashi et al. (2002), encompasses all those processes that are not thermal, that influence the variations of pCO_2, including the biological utilization of CO_2, continental inputs and the existence of upwellings (Xue et al., 2012; Qu et al., 2014). This method was originally designed for open oceanic systems, but it has been widely used by other authors in coastal areas (e.g. Schiettecatte et al., 2007; Ribas-Ribas et al., 2011; Qu et al., 2014; Burgos et al., 2018).~~

In this study, the ~~global~~ total T/B ratio is 1.15, which indicates that ~~temperature~~ the thermal effect is an important factor controlling intra-annual variation of pCO_2. This value is similar to that determined by Ribas-Ribas et al. (2011) (see date and study zone in Table 4)~~)~~, in the northeast zone of the shelf of the Gulf of Cádiz, with a ratio of 1.3.~~.~~ De la Paz et al. (2009) (see date and study zone in Table 4) propose a T/B ratio of 2.4 in the Strait of Gibraltar, indicating very significant thermal control in this relatively deep zone situated to the east of the Gulf of Cádiz. ~~.~~

Figure ~~7~~ 8 presents the values of the T/B ratio grouped in different bottom-depth intervals of the water column in the system. The variations of ΔpCO_2 ~~bio~~ non-thermal and ΔpCO_2 ~~temp~~ thermal found have been superimposed. In the coastal zone (depth < 50 m), the T/B ratio is below 1 (0.9), and increases to values of 1.3 in the central zone of the Gulf of Cádiz, at depths ranging from 100 to 400 m. However, in the deepest zone (depth > 600 m), a progressive decrease to values of 1.1 is found. ~~-~~Qu et al.

(2014) also ~~described~~reported the variation i~~o~~n the values of the T/B ratio with the distance from~~to~~ the coast in the southern Yellow Sea, between 0.4 - 0.6 in the nearshore area (depth < 50 m) to more than 1 (up to 2.4) in the offshore area (depth > 50 m).

This variation of the T/B ratio is largely caused by the variations of ΔpCO_2 ~~bio~~non-thermal. ~~, with~~H ~~h~~igh values close to the coast were observed (120.2 µatm), affected by continental inputs, processes of remineralization in the sediment and biological utilization of CO_2. The increase of the T/B ratio and the decrease of ΔpCO_2 non-thermal (75 µatm) from the coastal zone to the central part of the Gulf of Cádiz are associated with the variations of the chlorophyll-a and nutrient concentrations that diminish exponentially with the depth of the system. Thus, the mean concentrations of chlorophyll-a, nitrate and phosphate in the distal zone are 66.3, 81.9 and 44.8 % less, respectively, than the concentrations found close to the coast. However, the concentrations of chlorophyll-a and nutrients are relatively constant in waters with bottom-depth ~~higher to~~greater than 200 m, and do not explain the decrease of the T/B ratio and the increase of ΔpCO_2 non-thermal (90.7 µatm) in waters with bottom-depth ~~higher~~greater than 400 m. These variations have been associated with the change in the origin of the surface water masses. Thus, in the central zone of the Gulf of Cádiz, the origin of the surface waters is a branch of the larger-scale Portuguese-Canaries eastern boundary current that circulates around a cyclonic eddy off Cape St. Vincent and veers eastward into the Gulf of Cádiz (García-Lafuente et al., 2006). ~~While~~However the deepest zone is under the influence of a branch of the Azores current, which is~~in addition to being~~ a warmer stream that could lead to an increase in primary production; in addition~~,~~ it is the northern border of the subtropical gyre (Klein and Siedler, 1989);~~,~~ these two factors ~~thus~~ favour the accumulation of CO_2 in this area as a convergence zone (Ríos et al., 2005). The observed variations of ΔpCO_2 non-thermal between areas close to the coast and deeper areas agrees with the application of the Olsen et al. (2008) method.

~~, low values in the central zone (75 µatm) and an increase in the deepest zone (90.7 µatm). Qu et al. (2014) have described the variation on the values of the T/B ratio with the distance to the coast, between 0.4 - 0.6 in the nearshore area (depth < 50 m) to more than 1 (up to 2.4) in the offshore sand (depth > 50 m), in the southern Yellow Sea.~~

~~Figure 8 shows the dependence of ΔpCO_2 temp with temperature ($r^2 = 0.40$, $p < 0.01$) and of ΔpCO_2 bio with chlorophyll-a ($r^2 = 0.42$, $p < 0.01$) for the fixed stations; these values confirm the importance of both the thermal and biological processes on the variation of pCO_2. The existence of a certain linear correlation between the mean values of chlorophyll-a and the concentrations of nitrate ($r^2 = 0.66$, $p < 0.01$) and phosphate ($r^2 = 0.63$, $p < 0.01$) has also been observed. The increase of the T/B ratio and the decrease of ΔpCO_2 bio from the coastal zone to the central part of the Gulf of Cádiz are associated with the variations of the chlorophyll-a and nutrient concentrations that diminish exponentially with the depth of the system. Thus, the mean concentrations of chlorophyll-a, nitrate and phosphate in the distal zone are 66.3, 81.9 and 44.8 % less than the concentrations found close to the coast.~~

~~However, the concentrations of chlorophyll-a and nutrients are relatively constant in waters with bottom-depth to 200 m, and do not explain the decrease of the T/B ratio and the increase of ΔpCO_2 bio in waters with bottom-depth higher than 400 m. These variations have been associated with the change in the origin of the surface water masses. Thus, in the central zone of the Gulf of Cádiz, the origin of the surface waters is a branch of the larger-scale Portuguese-Canary eastern boundary current that circulates around a cyclonic eddy off Cape San Vicente and veers eastward into the Gulf of Cádiz (García-Lafuente et al., 2006). While the deepest zone is under the influence of a branch of the Azores current, which in addition to being a warmer stream that could lead to an increase in primary production, it is the northern border of the subtropical gyre (Klein and Siedler, 1989), thus favour the accumulation of CO_2 in this area as convergence zone (Ríos et al., 2005).Qu et al. (2014) have described the variation on the values of the T/B ratio with the distance to the coast, between 0.4 - 0.6 in the nearshore area (depth < 50 m) to more than 1 (up to 2.4) in the offshore sand (depth > 50 m), in the southern Yellow Sea.~~

The T/B ratios have also been calculated for the different transects at right angles to the coast that have been cruised for sampling in the study zone, as shown in Fig. ~~9~~9. It can be appreciated that the T/B ratio increases with the distance from the coast on the three transects, and that the temperature generally has a greater influence on the distribution of pCO_2 than the non-thermal effects. The T/B ratio varies to the east, with values between 1.0 in the zone of the ~~Guadalquivir~~ GD and 1.4 in ~~Sancti Petri~~SP, and an intermediate value of 1.2 in the ~~Trafalgar~~ TF zone. These variations are related to changes in the biological activity and the presence of coastal upwellings. The Guadalquivir zone receives substantial continental supplies that lead to high relative concentrations of chlorophyll-a and nutrients; these give rise to high values of ΔpCO_2 ~~bio~~non-thermal. In particular, coastal waters near the mouth of the Guadalquivir River present the highest primary production of all waters within the Gulf of Cádiz (Navarro and Ruiz, 2006). The coastal zone close to Cape Trafalgar has been characterized as a region with high autotrophic productivity and biomass associated mainly with the nutrients input due to upwelling waters (e.g. Echevarría et al., 2002; García et al., 2002). The presence of these emerg~~ed~~inged water masses could be related to the relatively low values of ΔpCO_2 ~~temp~~ thermal found in this zone; i~~. I~~n fact, the mean temperature in this area~~section~~ is 18.4 ± 2.3 °C, about 0.5 °C lower than in the other two zones. The Sancti Petri zone is the one that receives a smaller supply of nutrients, and presents the lowest concentrations of chlorophyll-a in this study. The high values of ΔpCO_2 ~~temp~~ thermal in this part of the Gulf of Cádiz are associated with a higher mean temperature (19.0 °C) and a wider range of variation (6.8 °C).

4.~~3~~4. Ocean-atmosphere CO_2 exchange

In the Gulf of Cádiz, the flux of CO_2 presents a range of variation from -5.6 to 14.2 mmol m^{-2} d^{-1}. These values are within the ranges observed by other authors in ~~continental shelf zones of the North Atlantic~~different areas of the Gulf of Cádiz (Table 4~~5~~). As can be appreciated in Fig. 10~~10~~, the fluxes of CO_2 presented seasonal and spatial variations during the period studied. The Gulf of Cádiz acts as a source of CO_2 to the atmosphere during the months of summer (ST2, ST6) and autumn (ST3, ST7), and as a sink in spring (ST1, ST5) and winter (ST4, ST8). Previous studies conducted in the Gulf of Cádiz are consistent with the behaviour found in this study (González-Dávila et al., 2003; Aït-Ameur and Goyet, 2006; Ribas-Ribas et al., 2011).

As has been observed with pCO_2, temperature is one of the principal factors that control the fluxes of CO_2. In fact, for each cruise, a linear and positive relationship has been found between the mean values of the CO_2 fluxes and ~~T~~ SST (r^2 = 0.72, Fig. 11~~, p < 0.01~~) ~~(Fig. 11)~~. In parallel, there is a linear and negative relationship between the mean values of the CO_2 fluxes and the concentration of chlorophyll-a at the discrete stations sampled (r^2 = 0.74, Fig. 11~~, p < 0.01~~) ~~(Fig. 11)~~, as a consequence of the biological utiliz~~s~~ation of the CO_2 (Qin et al., 2014). These relationships have also been found in various studies carried out in zones similar to the area studied (Zhang et al., 2010; Arnone et al., 2017; Carvalho et al., 2017).

The fluxes of CO_2 in the Gulf of Cádiz tend to decrease with the distance from the coast (Fig. 10~~10~~). The coastal zone (< 50 m) presents a mean CO_2 flux of 0.8 ± 1.8 mmol m^{-2} d^{-1}, that reduces progressively to reach a value of -0.3 ± 1.6 mmol m^{-2} d^{-1} in open waters with bottom-depth ~~higher~~ greater than 600 m. This dependence of CO_2 fluxes with distance from the coast has also been ~~described~~ reported in other systems, such as in the South Atlantic Bight of the United States (Jiang et al., 2008), in the south-western part of the Atlantic Ocean (Arruda et al., 2015), in the Patagonian Sea (Kahl et al., 2017) and on the continental shelf of Maranhense (Lefèvre et al., 2017). This dependence is the consequence of the decrease of influence of the continental supplies on the CO_2 fluxes as one moves towards the open sea. Ribas-Ribas et al. (2011) also found that in the Gulf of Cádiz the CO_2 fluxes vary with the distance from the coast; the zone close to the estuary of the Guadalquivir and the Bay of Cádiz acts as a source (1.39 mmol m^{-2} d^{-1}) and the zone comprising the rest of the shelf acts as a sink (-0.44 mmol m^{-2} d^{-1}).

In addition, on both the GD and SP transects a decrease of the CO_2 flux is found towards the open ocean, due to the continental inputs associated with the estuary of the Guadalquivir and with the Bay of Cádiz, respectively. On the TF transect, in contrast, it was observed that the zone close to the coast acts as a sink of CO_2 (-0.4 ± 1.2 mmol m^{-2} d^{-1}), and the deeper zone is a weak source of CO_2 to the atmosphere (0.3 ± 1.3 mmol m^{-2} d^{-1}). This finding can be explained by the presence of an upwelling close to the coast that is likely to be causing an increase of the production (e.g. Hales et al., 2005; Borges et al., 2005). With reference to this, on the TF transect there are significant differences between the mean surface concentrations of chlorophyll-a and nitrate in the coastal zone (0.63 ± 0.43 µg L^{-1} and 1.09 ± 0.77 µmol L^{-1}, respectively) and in deeper zones (0.17 ± 0.12 µg L^{-1} and 0.32 ± 0.33 µmol L^{-1}, respectively).

The Gulf of Cádiz, during the period of this sampling, acted as a sink of CO_2, with a mean rate of -0.18 ± 1.32 mmol m^{-2} d^{-1}, that would give rise to an annual flux of -0.07 mol C m^{-2} yr^{-1}. With the total surface of the study area (52.8·10^2 km^2) and the mean annual flux during the 8 cruises, the uptake capacity estimated for the Gulf of Cádiz will be 14.9 Gg C $year^{-1}$. The findings of previous studies carried out in the Gulf of Cádiz coincide with the behaviour observed in this study (Santana-Casiano et al., 2002; González-Dávila et al., 2003; Huertas et al., 2006; de la Paz et al., 2009; Ribas-Ribas et al., 2011), with the exception of the study by Aït-Ameur and Goyet (2006) in which it was estimated that the Gulf of Cádiz acts as a source of CO_2 to the atmosphere, although that study only corresponds to the summer season.

5. Conclusions

The mean value of pCO_2 in the eastern part of the Gulf of Cádiz found in this study (398.9 ± 15.5 µatm) indicates that it is undersaturated in CO_2 with respect to the atmosphere (402.1 ± 3.9 µatm). The spatiotemporal variation of pCO_2 found responds to the influence of different factors that usually affect its distribution in the littoral oceans. In global terms, when the mean values of the 8 cruises are considered, temperature SST (pCO_2 (µatm) = 302.0 + 5.16 TSST (ºC), r^2 = 0.71, $p < 0.01$) and biological activity (pCO_2 (µatm) = 425.0 - 59.15 [chlorophyll-aChl-a] (µg L^{-1}), r^2 = 0.76, $p < 0.01$) are the two principal factors that explain the temporal variability of pCO_2. Over and above these general tendencies, there are spatial variations associated fundamentally with two other processes. Firstly, the dominantte effects in the shallower areas are also due to tof the continental inputs, the biological activity and the air-sea CO_2 exchange. supplies is that, in the coastal zone, principally the area close to the mouth of the Guadalquivir, there is a wider dispersion of the values of pCO_2; it is in this area where the lowest and highest values have been observed in the discrete measurements. In this same coastal zone the highest mean values of pCO_2 were found Then pCO_2 values that diminish progressively in line with increasing distance from the coast, out as far as an approximate depth of some 400 m.. Secondly, t There is a relative increase of the temperatureSST and pCO_2 in the zone furthest from the coast (depth > 400 m) that is theas consequence of a change in the origin of the surface water, with the arrival of waters in a warm branch of the Azores current and the change produced by the biological activity..

The total T/B ratio (1.15) suggests that the distribution is principally controlled by the temperature. However, there is llows the adequately identification of the factors that control the variability of pCO_2 in the Gulf of Cádiz. Its mean value (1.15) suggests that the distribution is principally controlled by the temperature. Although a different behaviour in this ratio if it is determined by bottom-depth intervals, decrease of the ratio has been found, related to the existence of non-thermal processes, mainly taking place close to the coast (at depths of 100 m or less). In the proximity of the Guadalquivir estuary the ratio takes a value of 0.93 due to the continental inputs of C and nutrients, and in the zone around the coastal upwelling off Cape Trafalgar the ratio is 1.09. Furthermore, the actual characteristics of the surface water mass that originates under the influence of a branch of the Azores current also produce a decrease of the T/B ratio in the deeper zone studied (1.05 for depths > 600 m). In contrast, the highest T/B ratio values have been found in the Sancti Petri sectiontransect, where values of up to 1.54 are obtained for depths greater than 100 m.

The annual uptake capacity ~~The Gulf of Cádiz acts as a sink~~ of CO_2 by the surface waters in our study area is ~~of , with a mean capacity of capture for the period sampled of~~ 14.9 Gg C year^{-1}. The CO_2 fluxes present seasonal variation: these waters act as a source of CO_2 to the atmosphere in summer and autumn and as a sink in winter and spring. ~~The spatiotemporal variability of CO_2 is very similar to that found for the distribution of pCO_2, with larger fluxes close to coast.~~ Based on the information available in the zone, there seems to have been a decrease in the capacity for CO_2 capture in the zone in recent decades.

~~Au~~Author contributions

D.J.-L. wrote the manuscript with contributions from A.S., T.O. and J.F.. D.J.-L. and J.F. processed the experimental data. D.J.-L., T.O. and J.F. conceived the original idea. All authors contributed to ~~the~~ collecting the data.

Competing interests

The authors declare that they have no conflict of interest.

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Tables

Table 1: Date, number of measurements (n), range, average values and standard deviation of~~-~~ underway sea surface temperature (~~T~~SST), sea surface salinity (SSS) and pCO_2 during the 8 cruises undertaken: March 2014 (ST1), June 2014 (ST2), October 2014 (ST3), December 2014 (ST4), March 2015 (ST5), June 2015 (ST6), September 2015 (ST7) and February 2016 (ST8).

Cruise	Date	n	SST (ºC)		SSS		pCO_2 (µatm)	
			Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
ST1	28/03 - 01/04, 2014	3874	14.3 - 16.4	15.4 ± 0.6	35.57 - 37.06	36.11 ± 0.18	365.4 - 513.6	396.5 ± 19.0
ST2	25/06 - 01/07, 2014	4118	17.0 - 22.9	21.1 ± 0.9	35.90 - 36.45	36.21 ± 0.15	368.7 - 459.5	412.9 ± 12.6
ST3	01/10 - 07/10, 2014	4233	16.1 - 23.4	21.5 ± 1.3	35.80 - 36.79	36.26 ± 0.22	391.6 - 444.5	413.5 ± 9.8
ST4	10/12 - 16/12, 2014	2938	15.6 - 19.1	18.1 ± 0.7	34.68 - 36.72	36.36 ± 0.21	369.6 - 444.5	388.7 ± 12.9
ST5	28/03 - 01/04, 2015	3180	14.6 - 16.9	15.6 ± 0.4	35.54 - 36.52	36.12 ± 0.14	320.6 - 416.5	368.6 ± 14.9
ST6	19/06 - 25/06, 2015	3677	17.4 - 22.1	20.9 ± 0.8	35.63 - 36.92	36.40 ± 0.08	372.1 - 464.1	410.3 ± 13.8
ST7	15/09 - 18/09, 2015	2575	17.0 - 21.9	20.6 ± 1.1	35.03~~2~~ - 36.79	35.64 ± 0.08	387.6 - 457.1	407.6 ± 11.2
ST8	02/02 - 03/02, 2016	1812	15.1 - 17.5	16.8 ± 0.4	35.83 - 36.55	36.44 ± 0.09	346.2 - 442.6	392.9 ± 17.9

Table 2: Number of samples (n) and meanaverage values and standard deviation of for the averaged underway measurements averaged of sea surface temperature (SST) and ,sea surface salinity (SSS), and , pH, apparent oxygen utilization (AOU), chlorophyll-a, nitrate and phosphate in surface water samples (at depth of 5m) at fixed stations during the 8 cruises: March 2014 (ST1), June 2014 (ST2), October 2014 (ST3), December 2014 (ST4), March 2015 (ST5), June 2015 (ST6), September 2015 (ST7) and February 2016 (ST8).

Cruise	n	TemperatureSST (ºC)	SalinitySSS	pH	AOU (µmol L^{-1})	Chlorophyll-a -(µg L^{-1})*	Nitrate (µmol L^{-1})	Phosphate (µmol L^{-1})
ST1	178	15.23 ± 0.5	36.0508 ± 0.134	8.06 ± 0.03	-3.6 ± 8.4	0.65 ± 0.37	0.96 ± 1.01	0.14 ± 0.06
ST2	16	21.021.0 ± 1.3	36.1111 ± 0.111	7.97 ± 0.03	-10.3 ± 5.7	0.18 ± 0.14	0.42 ± 0.60	0.12 ± 0.04
ST3	17	21.67 ± 0.7	36.0911 ± 0.2814	7.97 ± 0.06	-4.6 ± 3.2	0.24 ± 0.29	0.34 ± 0.27	0.09 ± 0.03
ST4	17	17.77 ± 0.7	36.0236 ± 0.1327	8.05 ± 0.05	7.7 ± 2.1	0.46 ± 0.33	1.05 ± 1.96	0.23 ± 0.09
ST5	16	15.45 ± 0.3	36.033 ± 0.133	8.09 ± 0.12	-19.1 ± 9.4	0.76 ± 0.55	0.68 ± 1.17	0.17 ± 0.09
ST6	16	21.11.1 ± 1.01.0	36.3737 ± 0.05	8.01 ± 0.03	-2.4 ± 3.2	0.26 ± 0.34	0.12 ± 0.14	0.10 ± 0.05
ST7	17	20.6 ± 1.22	35.635.63 ± 0.032	7.94 ± 0.03	-2.6 ± 5.0	0.29 ± 0.31	0.37 ± 0.50	0.50 ± 0.55
ST8	6	16.8 ± 0.23	36.445 ± 0.045	8.09 ± 0.05	-5.1 ± 3.1	0.69 ± 0.32	0.41 ± 0.31	0.14 ± 0.11

*González-García et al. (2018).

Table 3: Mean values and standard deviation of mixed layer depth (MLD) in distal areas (depth > 50 m), atmospheric pCO_2 (pCO_2 µatm), wind speed, gas transfer velocity (k) and ~~and~~ CO_2 fluxes for the underway measurements during the 8 cruises: March 2014 (ST1), June 2014 (ST2), October 2014 (ST3), December 2014 (ST4), March 2015 (ST5), June 2015 (ST6), September 2015 (ST7) and February 2016 (ST8).

Cruise	MLD in distal areas (m)	pCO_2 atm (µatm)	Wind speed (m s^{-1})	k (cm h^{-1})	CO_2 fluxes (mmol m^{-2} d^{-1})
ST1	71.3 ± 26.4	398.7 ± 1.8	7.7 ± 3.4	13.4 ± 0.2	-0.3 ± 2.3
ST2	88.6 ± 34.4	404.5 ± 0.5	7.4 ± 3.4	14.0 ± 0.3	0.9 ± 1.4
ST3	90.3 ± 34.0	397.7 ± 0.6	6.7 ± 4.0	11.8 ± 0.4	1.4 ± 0.8
ST4	96.8 ± 34.1	399.4 ± 2.2	7.7 ± 4.2	14.3 ± 0.2	-1.3 ± 1.7
ST5	91.5 ± 31.6	405.5 ± 0.6	5.5 ± 2.8	6.9 ± 0.1	-2.3 ± 0.9
ST6	89.0 ± 33.0	406.1 ± 0.8	7.5 ± 4.1	14.4 ± 0.3	0.5 ± 1.5
ST7	90.2 ± 32.0	398.4 ± 0.7	7.0 ± 3.2	12.3 ± 0.3	0.9 ± 1.1
ST8	87.0 ± 40.3	406.4 ± 0.3	6.8 ± 3.1	10.6 ± 0.1	-1.3 ± 1.6

Table 4: Correlations estimated between pCO_2 and temperature (T, °C) and regression coefficients (r^2) in different shelf areas.

Site	Correlation pCO_2 – T	r^2	Reference
East China Sea	$pCO_2 = 221 + 5.48$ T	0.9	Wang et al., 2000
Southeastern continental shelf of the United States	$\ln(pCO_2) = 5.2505 + 0.0232$ T	0.96	Wang et al., 2005
Northern East China Sea	$pCO_2 = 169.7 + 38.19$ T	0.88	Shim et al., 2007
Southeastern continental shelf of the United States	$\ln(pCO_2) = 4.611 + 0.058$ T	0.73	Jiang et al., 2008
Eastern shelf of the Gulf of Cádiz	$pCO_2 = 269.1 + 5.03$ T	0.42	Ribas-Ribas et al., 2011
Northern Yellow Sea	$pCO_2 = 141.3 + 13.7$ T (Summer)	0.56	Xue et al., 2012
	$pCO_2 = 594.5 - 10.7$ T (Autumn)	0.28	
	$pCO_2 = 232.9 + 22.0$ T (Winter)	0.71	
	$pCO_2 = 813.0 - 46.7$ T (Spring)	0.69	
Continental shelf of Australia	$\ln(pCO_2) = 4.9 + 0.038$ T	0.74	Shaw et al., 2014
Gulf of Cádiz	$pCO_2 = 309.2 + 4.80$ T	0.37	This work

Table 45: Mean average and range of pCO_2 and CO_2 fluxes (FCO_2) found in different shelf areas of the North AtlanticGulf of Cádiz.

Site	ºE	ºN	Date	pCO_2 (µatm)	FCO_2 (mmol m^{-2} d^{-1})*	Reference
North Eastern Atlantic Ocean	-11.0	40.0 - 43.0	May, November, December 1993; July, August 1994	320 - 430	-0.47[a]	Pérez et al. (1999)
Upwelling system off the Galician coast	-9.3 - -10.1	42.1 - 43.2	June, July 1997; January, June, July, August, December 1998; January, August, September 1999	265 - 415	-4.7 - -2.3[b]	Borges and Frankignoulle (2002)
Strait of GibraltarUS Middle Atlantic Bight	-5.5 - -5.2-76.0 - -69.0	35.6 - 36.035.0 - 42.0	September 1997February, March, May, June, October 1996	339 - 381220 - 560	3 ± 8[a]-4.4 - -1.9[b]	Santana-Casiano et al. (2002)DeGranpre et al. (2002)
Strait of Gibraltar	-5.5 - -5.2	35.6 - 36.0	September 1997; February 1998; May 1999	350 - 354	-6.9[b]	Santana-Casiano et al. (2002)
English Channel	-6.0 - -4.0	47.5 - 51.5	March, September 1995; May, June, July 1997; January, June, July, November 1998; August, September 1999	200 - 500	-20.0 - 12.0[c]	Borges and Frankignoulle (2003)
Gulf of CádizRía de Vigo	-7.0 - -6.5-8.9 - -8.6	36.3 - 36.742.1 - 42.3	February 1998April, July, September, October, November, December 1997	334 - 416285 - 615	-19.5 ± 3.5[a]-1.5 - 1.8[a]	González-Dávila et al. (2003)Gago et al. (2003)
Gulf of Cádiz	-7.0 - -6.5	36.3 - 36.7	February 1998	334 - 416	-19.5 ± 3.5[b]	González-Dávila et al. (2003)
Northern and central North Sea	-3.0 - 10.0	50.0 - 62.0	August, September, November 2001; February, March, May 2002		4.6[b]	Thomas et al. (2004)
Gulf of CádizNorth Sea	-8.3 - -6.0-3.0 - 10.0	33.5 - 37.050.0 - 61.0	July 2002August, September 2001	300 - 450220 - 490	18.6 ± 4[a]-3.4[b]	Aït-Ameur and Goyet (2006)Bozec et al. (2005)
Northeastern shelf of the Gulf of CádizGulf of Cádiz	-7.5 - -6.3-8.3 - -6.0	36.6 - 37.333.5 - 37.0	March 2003 to March 2004July 2002	130 - 650	-2.5 - 1.0[a]18.6 ± 4[b]	Huertas et al. (2006)Aït-Ameur and Goyet (2006)
Northeastern shelf of the Gulf of Cádiz	-7.5 - -6.3	36.6 - 37.3	March 2003 to March 2004	196 - 650	-2.5 - 1.0[b]	Huertas et al. (2006)
Southern North Sea	0.5 - 4.5	50.0 - 53.0	February, March, April, June, August, September, October 2001; February, April, June, August, September, October 2002; August, December 2003; February, May 2004	149 - 479	-23.7 - 6.7[b]	Schiettecatte et al. (2007)

Strait of Gibraltar~~US South Atlantic Bight~~	-6.0 - -5.2~~-81.5 - -76.5~~	35.8 - 36.1~~28.5 - 34.5~~	September, December 2005; March, May 2006~~January, March, July, August, October, December 2005; May 2006~~	320 - 400~~330 - 1300~~	-1.9 - 1.9[a]~~-3.8 - 3.3[b]~~	de la Paz et al. (2009)~~Jiang et al. (2008)~~
~~Strait of Gibraltar~~	~~-6.0 - -5.2~~	~~35.8 - 36.1~~	~~September 2005; December 2005; March, May 2006~~	~~320 - 400~~	~~-1.9 - 1.9[b]~~	~~de la Paz et al. (2009)~~
~~Bay of Biscay~~	~~-10.0 - -2.0~~	~~42.0 - 47.5~~	~~September 1994 to December 2004~~	~~310 - 375~~	~~-11.0 - 0.8[b]~~	~~Padin et al. (2009)~~
~~Gulf of Mexico~~	~~-91.0 - -89.7~~	~~28.0 - 29.3~~	~~August 2004; October 2005; April 2006~~	~~200 - 600~~	~~-1.17 - 5.4[b]~~	~~Lohrenz et al. (2010)~~
~~Scotian Shelf~~	~~-66.0 - -57.0~~	~~39.5 - 48.0~~	~~July, August, September, October, December 2007; January, February, March, April, May, June 2008~~	~~203 - 443~~	~~1.8 ± 1.3[b]~~	~~Shadwick et al. (2010)~~
Northeastern shelf of the Gulf of Cádiz~~Northern Bay of Biscay~~	-6.8 - -6.3~~-11.0 - -5.0~~	36.4 - 36.9~~47.0 - 51.5~~	June, November 2006; February, May 2007~~June 2006; May 2007; May 2008~~	338 - 502~~248 - 342~~	-2.2 - 3.6[a]~~-11.9 - -7.4[d]~~	Ribas-Ribas et al. (2011)~~Suykens et al. (2010)~~
~~Northeastern shelf of the Gulf of Cádiz~~	~~-6.8 - -6.3~~	~~36.6 - 37.3~~	~~June 2006; November 2006; February 2007~~	~~338 - 502~~	~~-2.2 - 3.6[b]~~	~~Ribas-Ribas et al. (2011)~~
~~Portuguese Southern outer continental shelf~~	~~-8.0~~	~~36.0~~	~~October 2001~~	~~700 - 1130~~	~~12 ± 8[b]~~	~~Oliveira et al. (2012)~~
~~Northern Gulf of Mexico~~	~~-94.0 - -88.0~~	~~27.5 - 30.5~~	~~August 2004; October 2005; April, June, September 2006; May, August 2007; July 2008; January, April, July, October 2009; March 2010~~	~~171 - 2222~~	~~-14.3 - 13.1[d]~~	~~Huang et al. (2015)~~
~~Cariaco Basin~~	~~-66.3 - 64.0~~	~~10.0 - 11.3~~	~~March 2004, September 2006; September 2008; March 2009~~	~~366 - 525~~	~~0.0 - 10.0[b]~~	~~Astor et al. (2017)~~
~~Mauritanian-Cap Vert upwelling region~~	~~-19.0 - -14.0~~	~~10.0 - 28.0~~	~~From 2005 to 2012~~	~~275 - 750~~	~~-0.2 - 3.3[e]~~	~~González-Dávila et al. (2017)~~
Gulf of Cádiz~~US South Atlantic Bight~~	-6.0 - -7.2~~-81.0 - -76.0~~	35.4 - 36.7~~28.0 - 35.0~~	March, June, October, December 2014; March, June, September 2015; March 2016~~July 2007; August, December 2008; May, November 2009; February, April, August, October 2010; March, April, October, December 2011; February, May, August 2012; September 2013;~~	321 - 514~~253 - 567~~	-2.3 - 1.5[b]~~-1.8 - 2.0[e]~~	This work~~Reimer et al. (2017)~~

			May, July, September, November, December 2014; April, June, July 2015			
Gulf of Cádiz	-6.0 - -7.2	35.4 - 36.7	March, June, October, December 2014; March, June, September 2015; March 2016	321 - 514	-2.3 - 1.5[f]	This work

[*]Gas transfer coefficient (k): [a] [a] Woolf and Thorpe (1991), [b] Wanninkhof (1992) , [c] Nightingale et al. (2000), [d] Ho et al. (2006), [e] Wanninkhof et al. (2009) and [f] [b] Wanninkhof et al. (2014).

 Figures

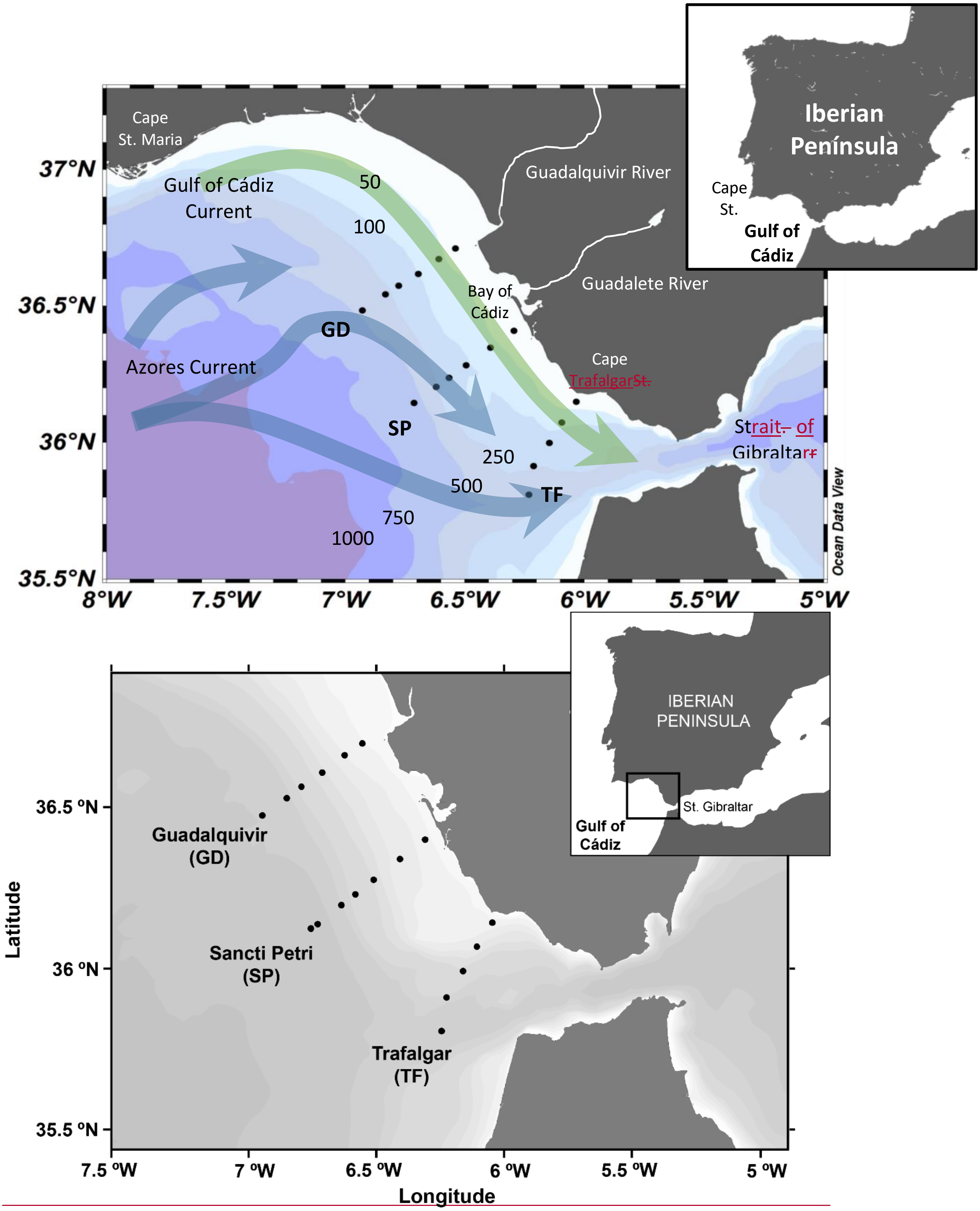

Cape
St. Maria
Gulf of Cádiz
Current
50
100
Guadalquivir River
Guadalete River
Bay of
Cádiz
GD
SP
TF
Azores Current
Cape
TrafalgarSt.
Strait- of
Gibraltarr
250
500
750
1000
Ocean Data View
37°N
36.5°N
36°N
35.5°N
8°W
7.5°W
7°W
6.5°W
6°W
5.5°W
5°W
Iberian
Península
Cape
St.
Gulf of
Cádiz
IBERIAN
PENINSULA
St. Gibraltar
Gulf of
Cádiz
Guadalquivir
(GD)
Sancti Petri
(SP)
Trafalgar
(TF)
36.5 ºN
36 ºN
35.5 ºN
Latitude
7.5 ºW
7 ºW
6.5 ºW
6 ºW
5.5 ºW
5 ºW
Longitude

Figure 1: Map of the eastern shelf of the Gulf of Cádiz showing the location of the fixed stations located on 3 transects at right-angles to the coastline: Guadalquivir (GD), Sancti Petri (SP) and Trafalgar (TF). The location of the principal surface currents, rivers and capes of the study area are also noted.

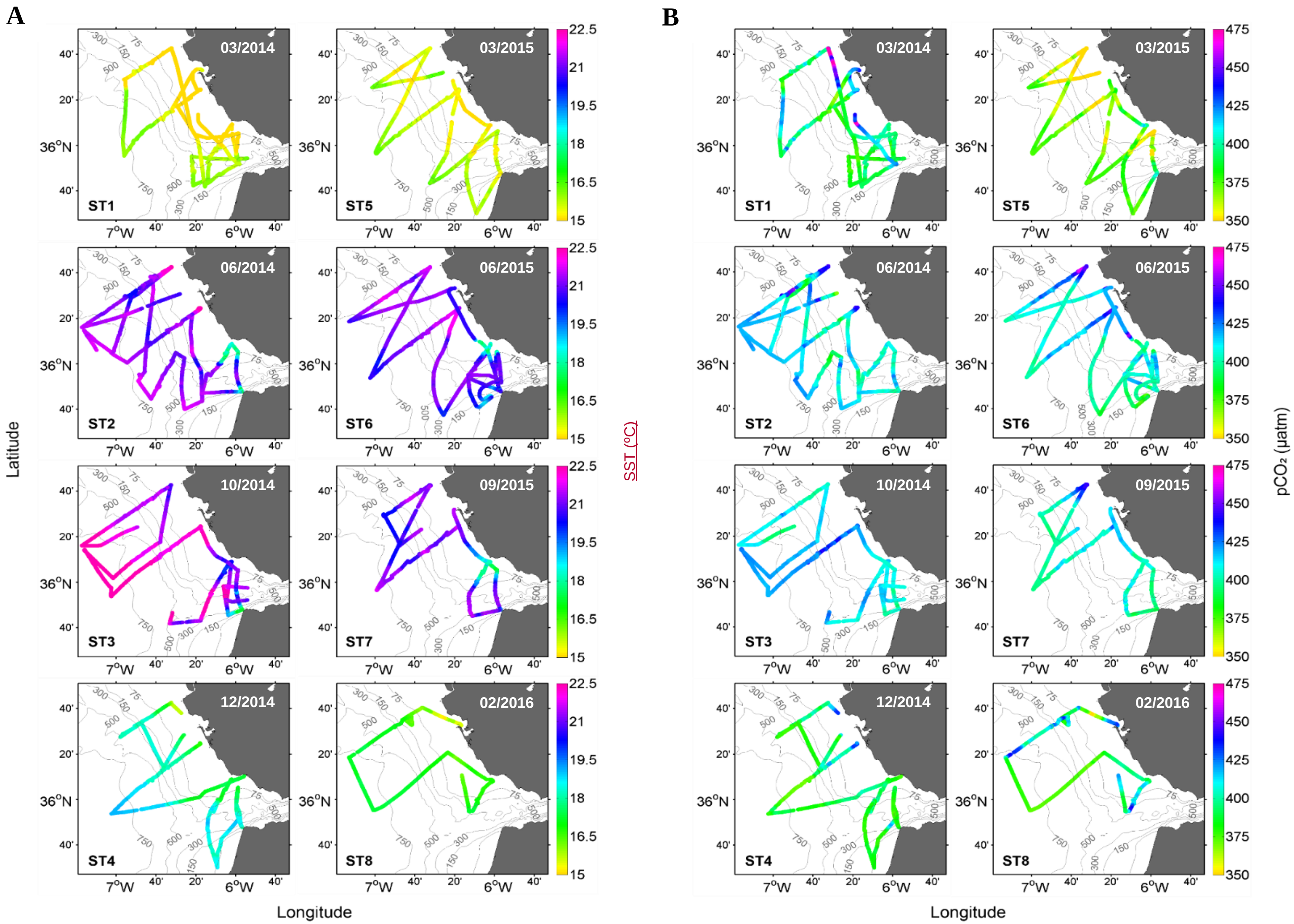


Figure 2: Underway Ddistribution of sea surface temperature (SST, A) and pCO_2 (B) during the 8 cruises in the Gulf of Cádiz: March 2014 (ST1), June 2014 (ST2), October 2014 (ST3), December 2014 (ST4), March 2015 (ST5), June 2015 (ST6), September 2015 (ST7) and February 2016 (ST8).

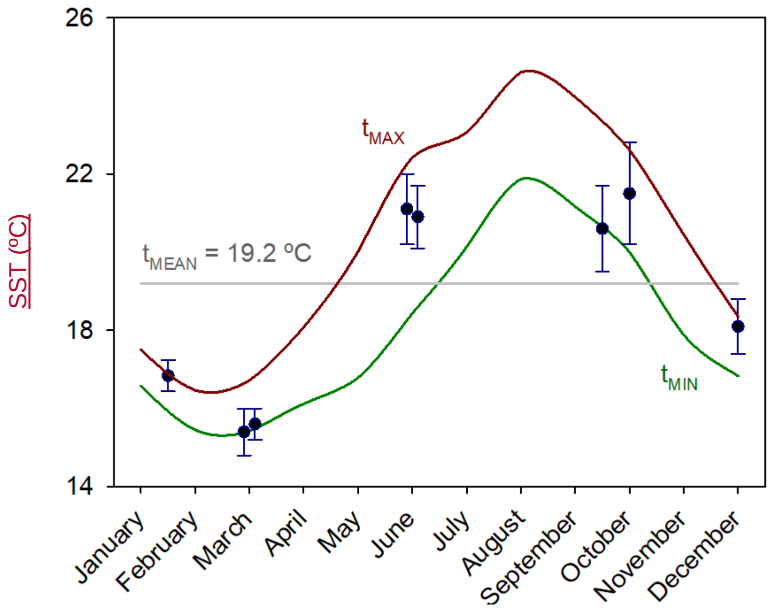


Figure 3: Maximum and minimum sea surface temperature (SST) variation during a 10-year period recorded by an oceanographic buoy located in the Gulf of Cádiz (36.48°N - 6.96°W). The red line shows maximum SST variation. The green line shows minimum SST variation. The grey line shows the average temperature for the 10-year period. Blue circles show mean values and standard deviations of underway SST measured during the eight cruises carried out during this study.

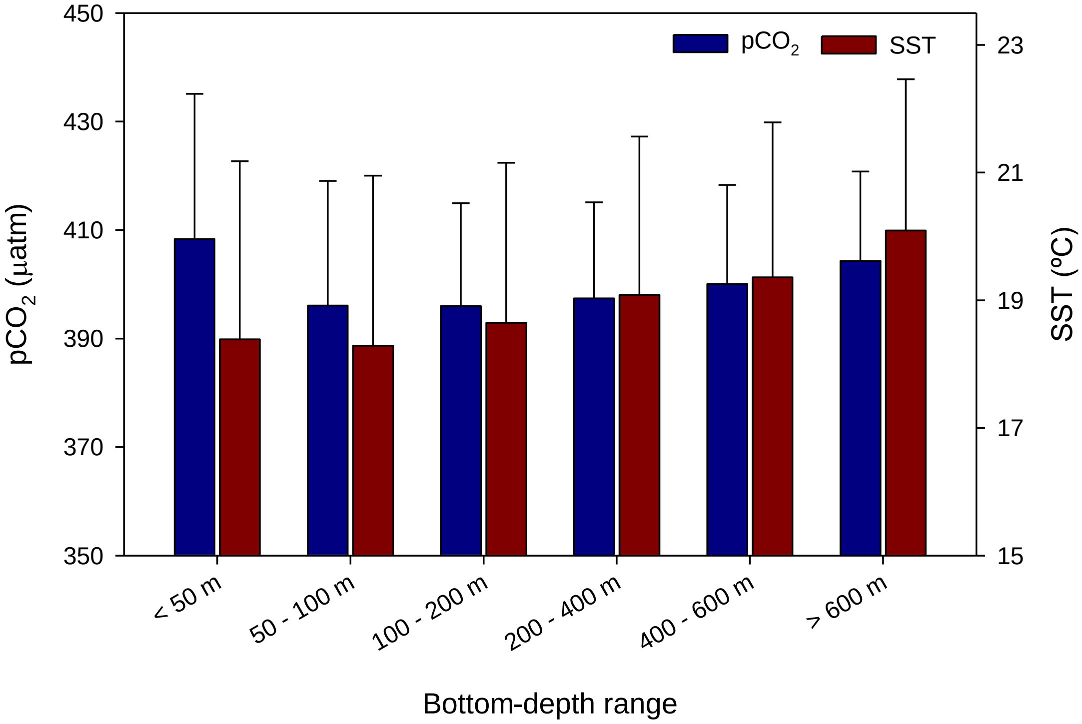


Figure 4: Underway variation of pCO_2 and sea surface temperature (SST) at different bottom-depth ranges of the water column (m) during the 8 cruises. The mean values and standard deviations of pCO_2 (blue) and SST (red) for each range of depth are represented.

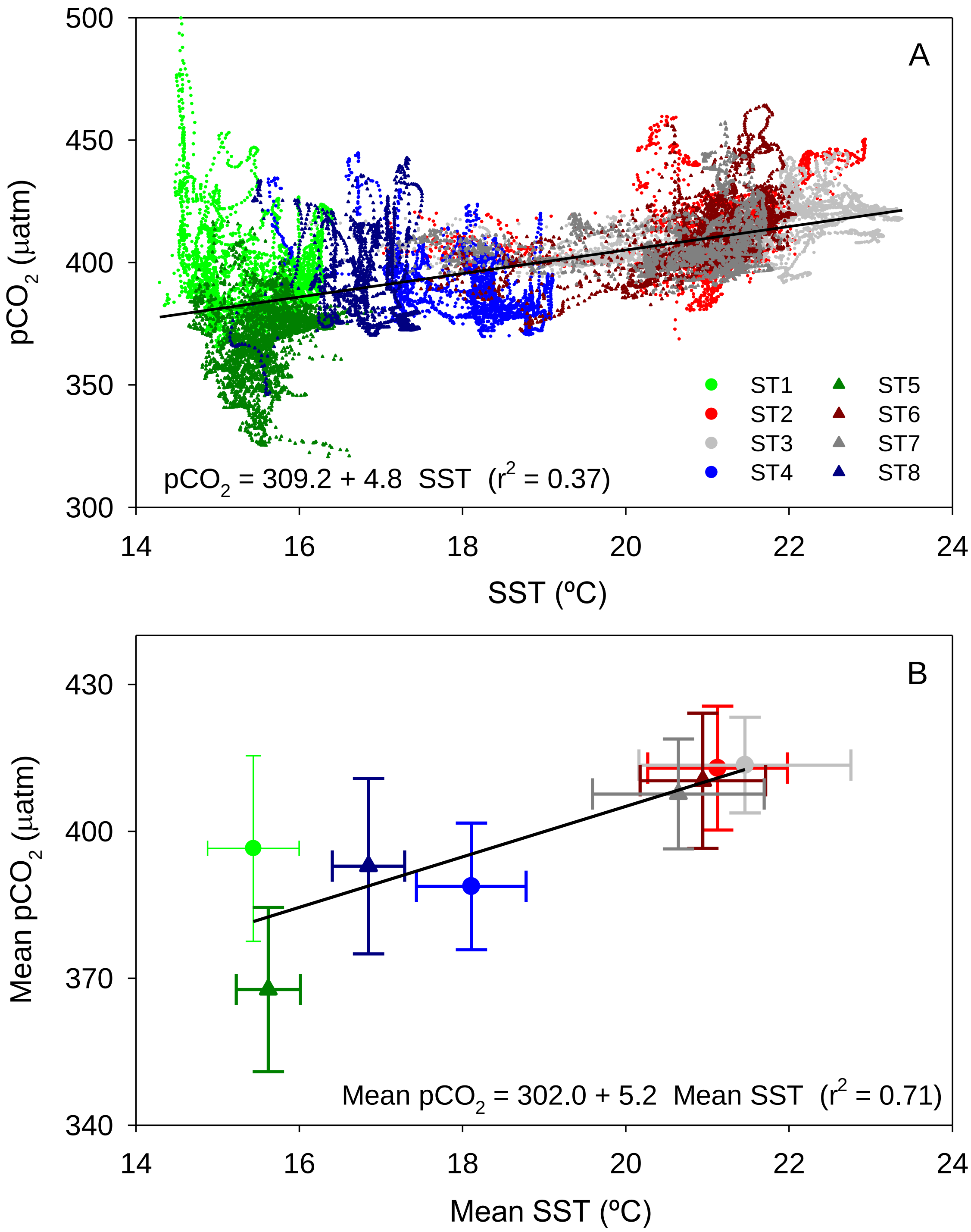
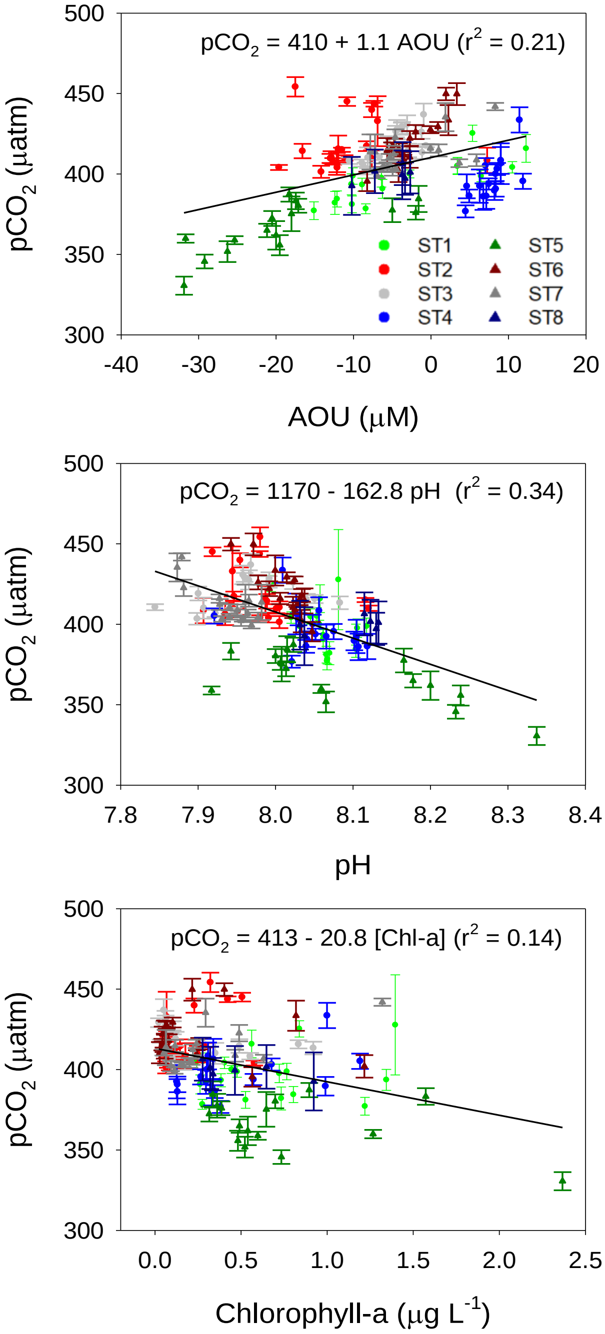
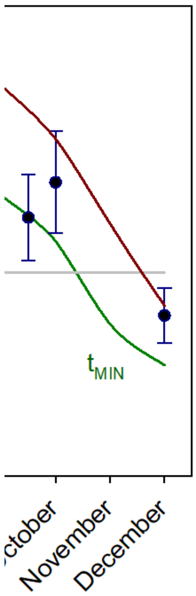
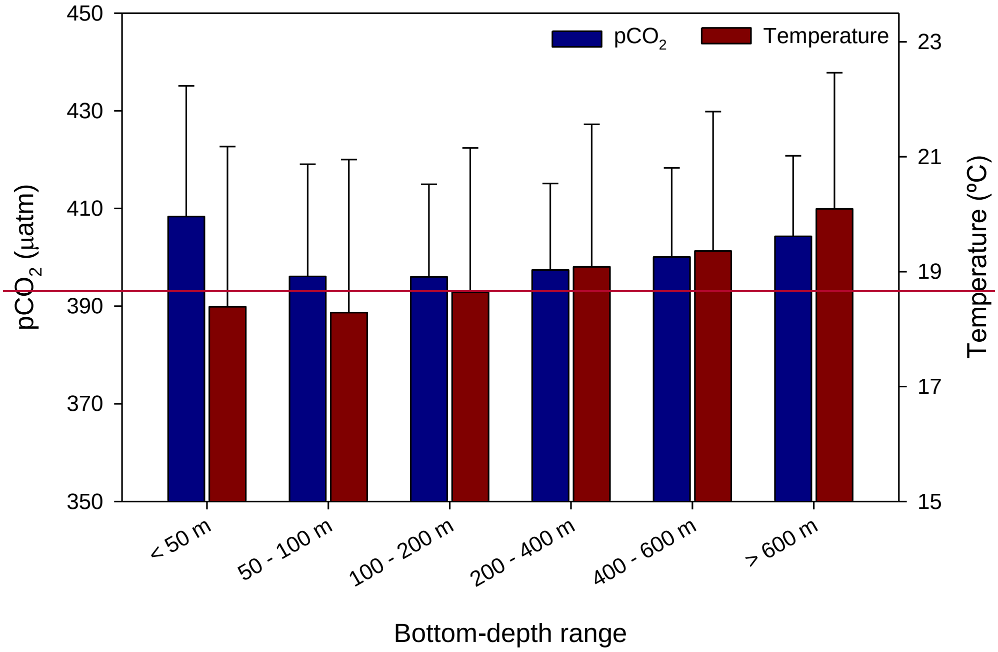


Figure ~~3~~5: Dependence of pCO_2 with sea surface temperature (SST) for the complete underway database during all the cruises (A) and for the mean values of pCO_2 and ~~temperature~~ SST for each cruise showing their standard deviations (B). The solid line shows the linear correlation.





~~**Figure 4: Maximum and minimum sea surface temperature variation during a 10-year period recorded by a mooring located in the Gulf of Cádiz (36.48°N - 6.96°W). The red line shows maximum sea surface temperature variation. The green line shows minimum sea surface temperature variation. The grey line shows the average temperature for the 10-year period. Blue circles show mean values and standard deviations of sea surface temperature measured during the eight cruises carried out during this study.**~~



~~**Figure 5: Variation of pCO_2 (µatm) and temperature (ºC) at different bottom-depth ranges of the water column (m) during the 8 cruises. The mean values and standard deviations of pCO_2 (blue) and temperature (red) for each range of depth are represented.**~~

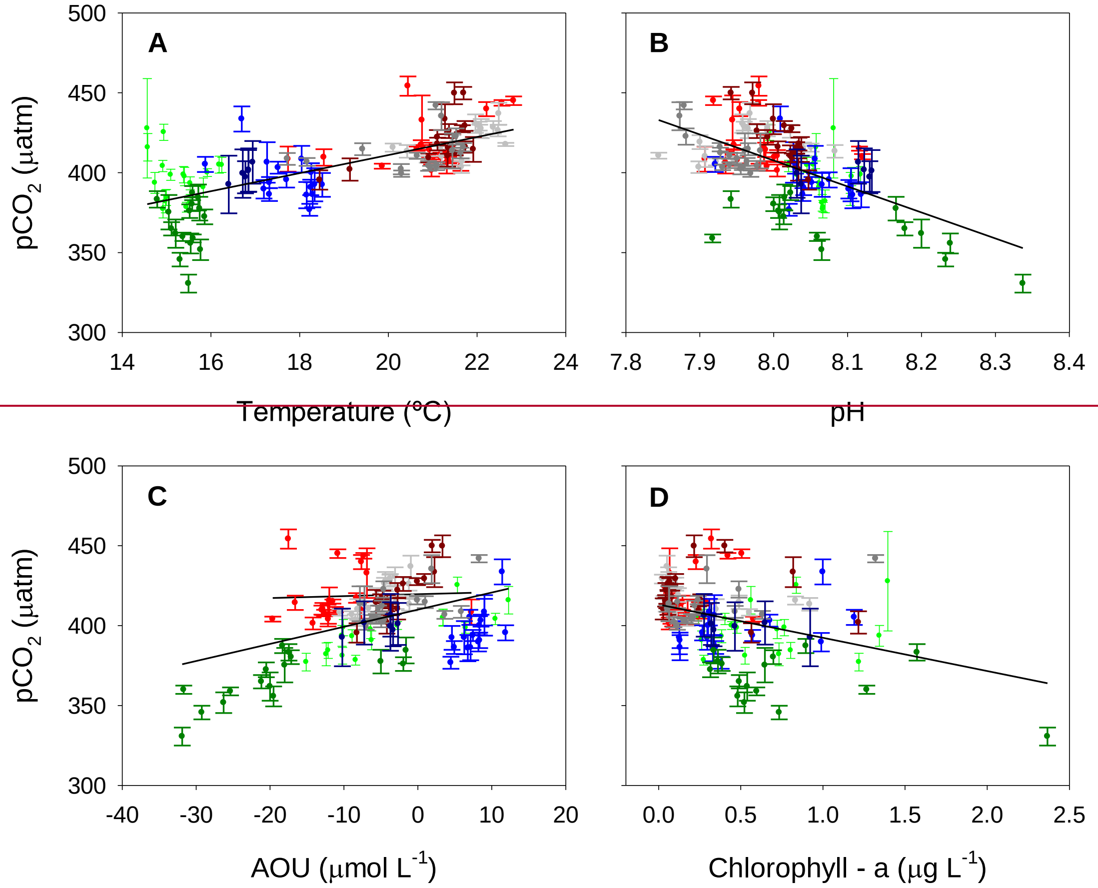

A
B
C
D
pCO2 (µatm)
500
450
400
350
300
14
16
18
20
22
24
Temperature (°C)
7.8
7.9
8.0
8.1
8.2
8.3
8.4
pH
-40
-30
-20
-10
0
10
20
AOU (µmol L-1)
0.0
0.5
1.0
1.5
2.0
2.5
Chlorophyll - a (µg L-1)

Figure 6: Dependence between the surface values of pCO_2 and Apparent Oxygen Utilization (AOU), temperature (A, r^2 = 0.48), pH (B, r^2 = 0.34), AOU (C, r^2 = 0.21) and chlorophyll-a (Chl-a) (D, r^2 = 0.14) at the 16 discrete stations during the 8 cruises. pCO_2 presents the standard deviation associated with the mean value obtained from the underway measurements.

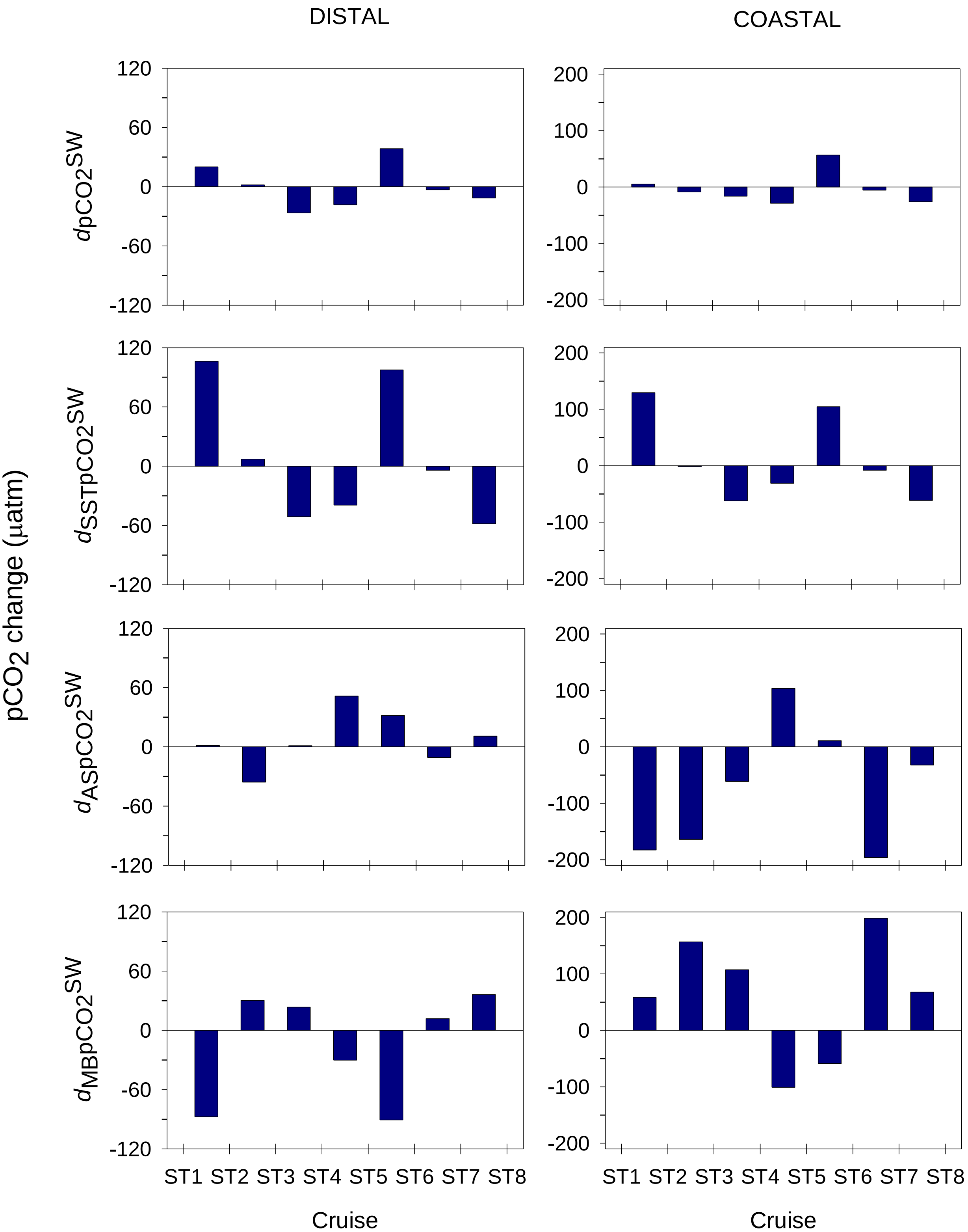
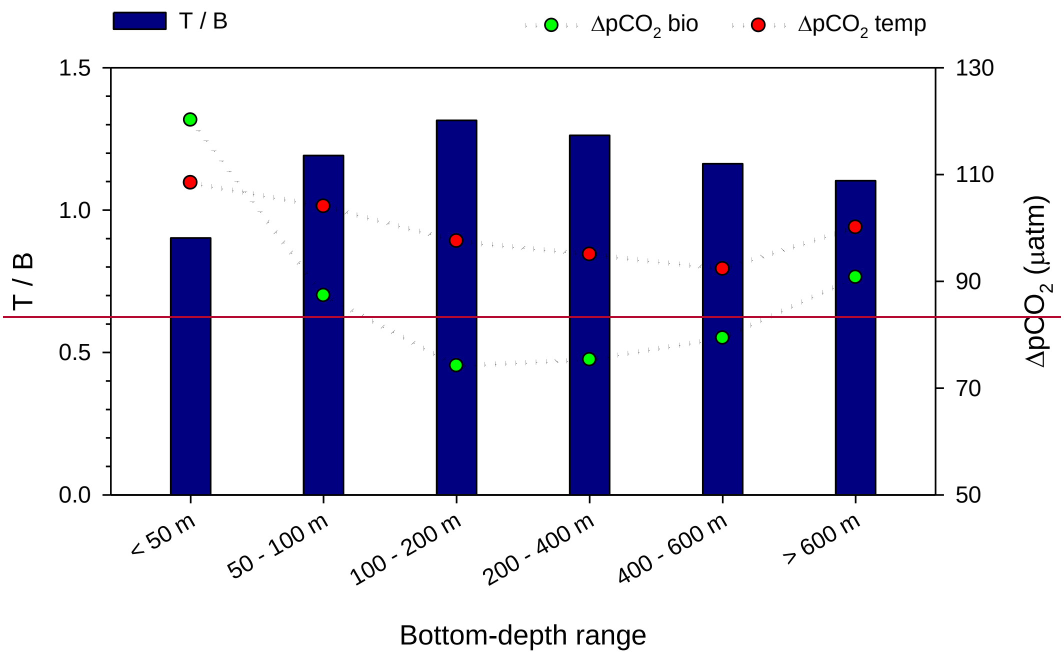


Figure 7: Observed changes in pCO_2 (first row) and expected due to: SST changes (second row), air-sea CO_2 exchange (third row) and biology plus mixing (last row) in the distal (left column) and coastal areas (right column) between the periods of each cruise: ST1 (March 2014), ST2 (June 2014), ST3 (October 2014), ST4 (December 2014), ST5 (March 2015), ST6 (June 2015), ST7 (September 2015) and ST8 (February 2016).



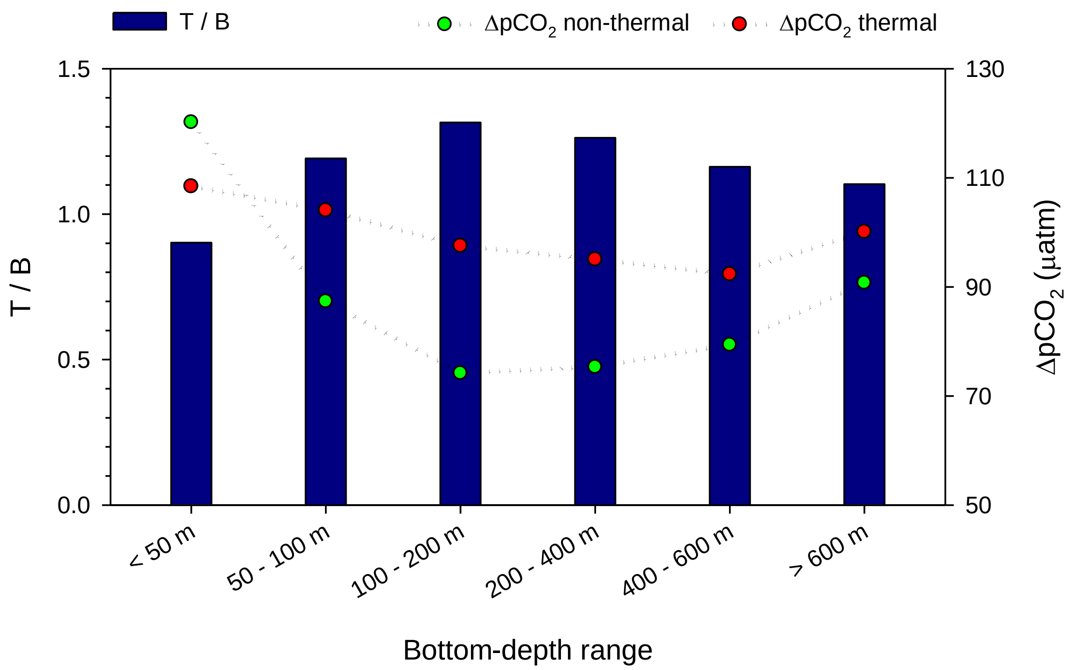


Figure ~~7~~8: Variation of the T/B ratio (blue bar), ΔpCO_2 ~~bio~~ non-thermal (green point) and ΔpCO_2 thermal~~emp~~ (red point) at different bottom-depth ranges of the water column (m) for the 8 cruises.

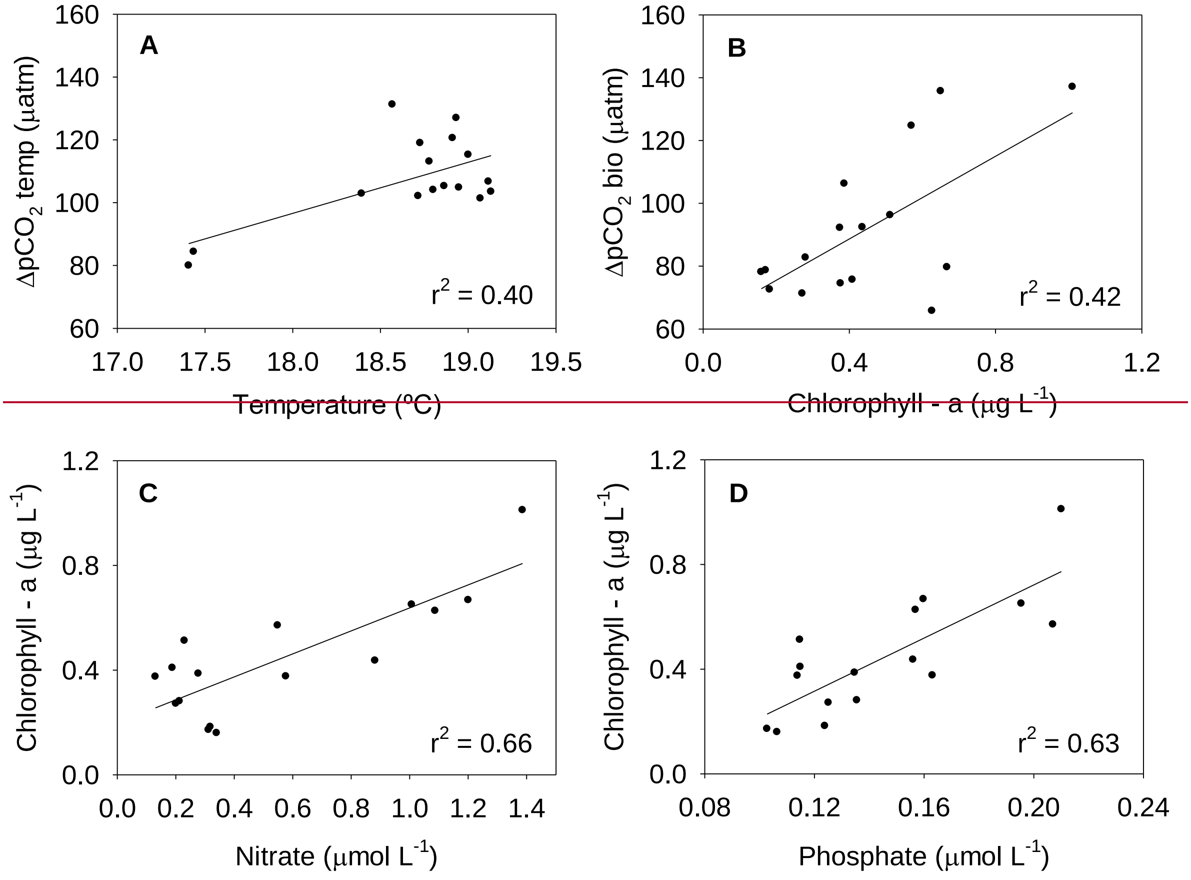


Figure 8: Correlations between A) ΔpCO_2 temp and temperature, B) ΔpCO_2 bio and chlorophyll-a, C) chlorophyll-a and nitrate and D) chlorophyll-a and phosphate for the mean values at the 16 discrete stations during the 8 cruises.

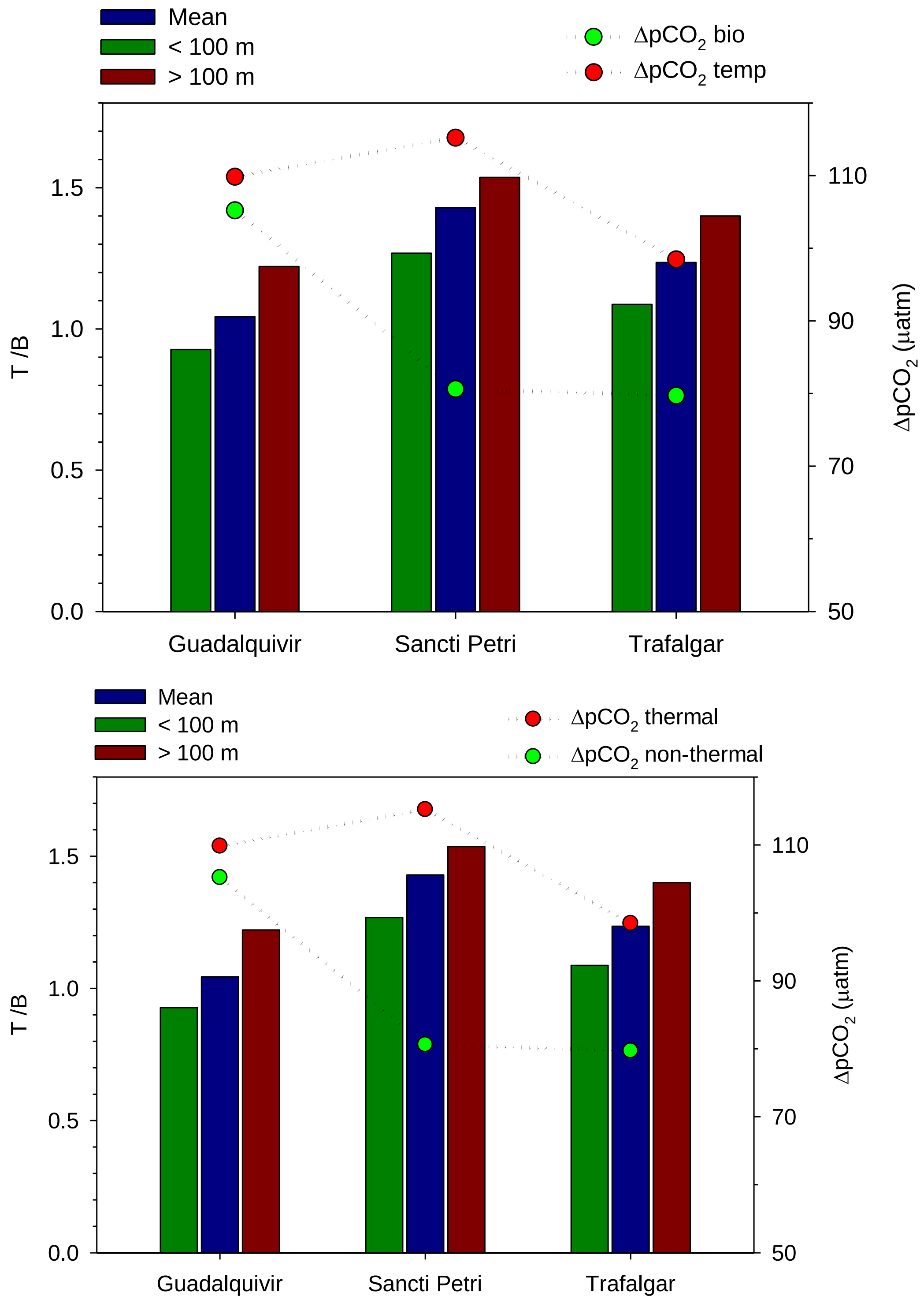


Figure 99: Variation of the ~~mean~~ T/B ratio (blue bar), the ~~mean~~ T/B ratio at depths < 100 m (green bar), the ~~mean~~ T/B ratio at depths > 100 m (red bar), ΔpCO_2 non-thermal~~bio~~ (green point) and ΔpCO_2 thermal~~emp~~ (red point) on the ~~various~~3 transects of the study (Guadalquivir, Sancti Petri and Trafalgar) during the 8 cruises.

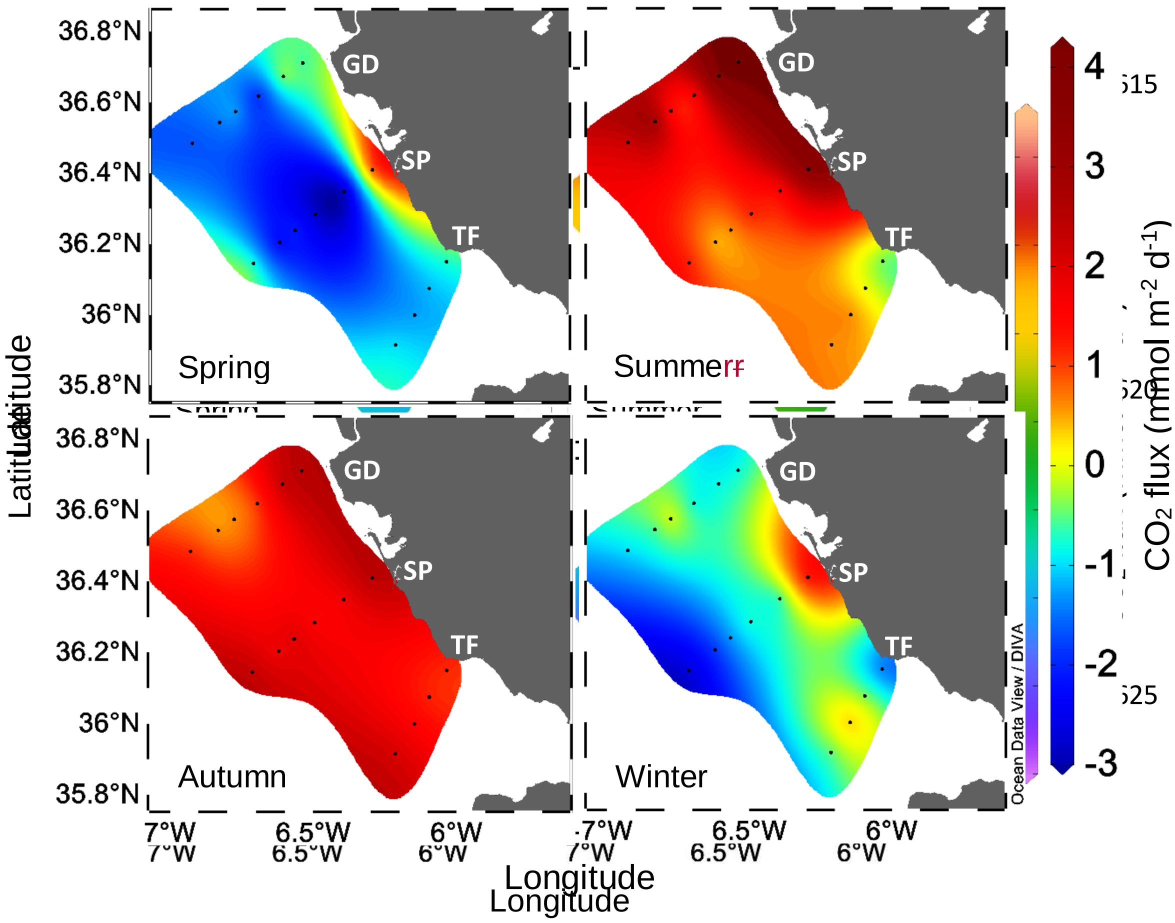


Figure ~~10~~10: Spatial distribution of mean values of CO_2 fluxes in the eastern shelf of the Gulf of ~~Cádiz~~ Cádiz at the 16 discrete stations during spring (ST1, ST5), summer (ST2, ST6), autumn (ST3, ST7) and winter (ST4, ST8).

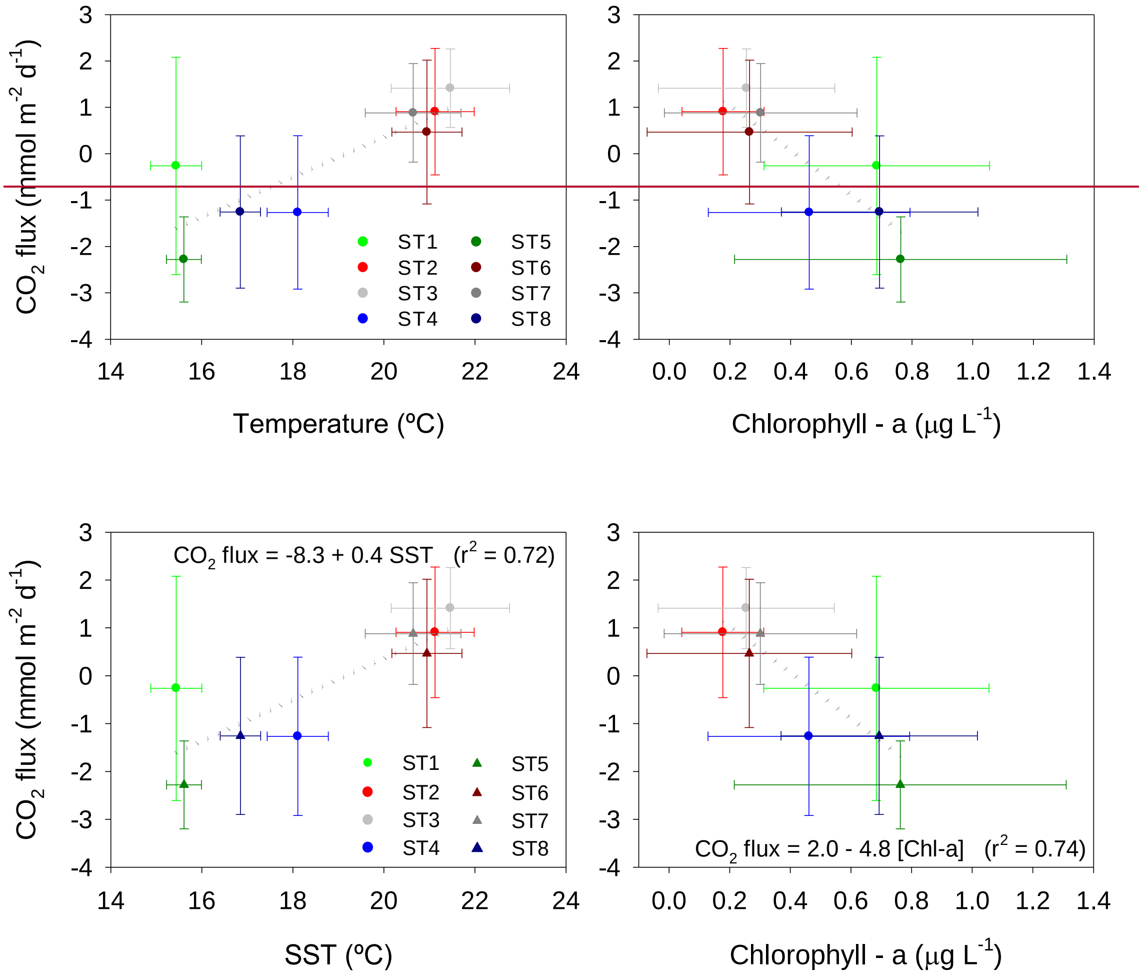


Figure 11~~1~~: Correlations between the mean values of CO_2 fluxes and sea surface temperature (SST) fo~~o~~r the underway database (left~~, r^2 = 0.72~~), and the CO_2 fluxes and chlorophyll-a (Chl-a) at the 16 discrete surface stations (right~~, r^2 = 0.74~~) for each cruise and showing the standard deviations.