



Factors controlling pCO₂ variability in the eastern Gulf of Cádiz (SW Iberian Península)

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Abstract

Spatiotemporal variations of the partial pressure of CO₂ (pCO₂) 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 Península) between the Guadalquivir River and Cape Trafalgar. pCO₂ presented a range of variation between 320.6 and 513.6 µatm, with highest values during summer and autumn and lowest during spring and winter, showing a linear dependence between pCO₂ and temperature. The distributions of pCO₂ 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 study area acted as source of CO₂ to the atmosphere during summer and autumn and as a sink in spring and winter, with a mean value for the study period of $-0.18 \pm 1.32 \text{ mmol m}^{-2} \text{ d}^{-1}$. In the Guadalquivir and Sancti Petri sections, the CO₂ fluxes decreased towards offshore, whereas in the Trafalgar section increased due to the presence of an upwelling. These results highlighted the Gulf of Cádiz as a CO₂ sink, with a capture capacity of 14.9 Gg year⁻¹.

1. Introduction

25 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 particulate organic carbon (Muller-Karger et al., 2005).

35 Generally, waters over the continental shelf account for ~15 % of the global ocean CO₂ uptake ($-2.6 \pm 0.5 \text{ Pg C yr}^{-1}$, Le Quééré et al., 2017). Using direct surface ocean CO₂ measurements from the global Surface Ocean CO₂ Atlas (SOCAT) database, Laruelle et al. (2014) estimated a sea-air exchange of CO₂ in these zones of $-0.19 \pm 0.05 \text{ Pg C yr}^{-1}$, lower than 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 (Laruelle et al., 2010). In several studies, it has been observed that the continental



shelves present different behaviours according to their latitude: they tend to act as a sink of carbon ($-0.33 \text{ Pg C yr}^{-1}$) at high and middle latitudes ($30 - 90^\circ$) and as a weak source ($0.11 \text{ Pg C yr}^{-1}$) at low latitudes ($0 - 30^\circ$) (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 ($-0.24 \text{ Pg C yr}^{-1}$) and those of the Southern Hemisphere are a weak source of CO_2 ($0.03 \text{ Pg C yr}^{-1}$).

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 ($0.0423 \text{ }^\circ\text{C}^{-1}$, 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 (Fennel and Wilkin, 2009). Both, 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 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).

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; Aristegui 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 (Aristegui 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 freshwater inputs from several major rivers, i.e. Guadalquivir, Tinto, Odiel and Guadiana. Various studies have been conducted in this area to evaluate the variability of the sea surface pCO_2 , although they cover smaller areas and shorter duration of time than this work (González-Dávila et al., 2003; Ait-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 by the combination of the fluctuations of biomass concentration and temperature.



In the study reported in this paper, the main objective is to evaluate the spatial and seasonal variation of the sea-surface CO₂ on the eastern shelf of the Gulf of Cádiz. In addition, we aim to assess the relative contribution of the temperature and non-temperature effects to the total CO₂ concentration, and to determine if the area as a whole acts as a sink or a source of CO₂ to the atmosphere over time. To do this, we have analysed a surface measurement database of >26000 values of pCO₂ during cruises made between 2014 and 2016 and covering a 0.8° x 1.3° 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, 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 EBUS 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 EBUS: 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 EBUS phenomena, and the bilayer flow through the Strait of Gibraltar, are two factors that complicate the simple EBUS conceptual model (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, 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, the centre of the Gulf is 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).

2.2. Field sampling and analysis

The database for this study has been obtained following two different sampling strategies. The first one consisted on taking sea surface measurements underway. Meanwhile, the second one acquired the measurement at several discrete surface stations along three transects perpendicular to the coastline: the Guadalquivir transect (GD), the Sancti Petri transect (SP) and the Trafalgar transect (TF) (Fig. 1). Data was recollected 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 carried out on board the R/V Ángeles Alvariño, except the one of summer 2015



115 (ST6) that was carried out on board the R/V Ramón Margalef. The study area is located between 35.4 and 36.7° N and 6.0 and 7.2° W ($52.8 \cdot 10^3$ Km²).

2.2.1. Underway measurements

Sea surface temperature (T), sea surface salinity (S) and the CO₂ partial pressure (pCO₂) 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). T and S were measured using a SeaBird thermosalinograph (SeaBird 21) with an accuracy of ± 0.01 °C and ± 0.003 respectively. 120 The equilibrator design for determining the pCO₂ 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 CO₂ molar fraction (xCO₂) and H₂O 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 CO₂ free-air for the blank and a CO₂ sub-standard gas of known concentration (413.2 ppm). CO₂ 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 °C). A pressure transducer (Setra Systems, accurate to 0.05 %) was used to measure the pressure inside the equilibrator. 125

The xCO₂ was converted into pCO₂ according to the protocol described in DOE (2007): corrections 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 °C. 130

2.2.2. Fixed stations

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

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). For chlorophyll-a determination, 1 L of seawater was filtered (Whatman, GF/F 0.7 μ m) and frozen (-20 °C) until analysis in the lab. 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 μ m) 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). 140

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 μ mol L⁻¹). 145

The accuracies of the determinations obtained are the following: ± 0.003 for pH, ± 0.1 μ g L⁻¹ for chlorophyll-a, ± 0.10 μ mol L⁻¹ for nitrate, ± 0.02 μ mol L⁻¹ for phosphate and ± 0.1 μ mol L⁻¹ for dissolved oxygen.

The corresponding data of T, S and pCO₂ were obtained by the underway measurements averaging data corresponding to 0.5 150 mile around the location of the fixed stations.



2.3. Temperature and biological effects on pCO₂ calculations

To determine the relative importance of the temperature and biological effects on the changes of pCO₂ in sea water, we follow the method proposed by Takahashi et al. (2002). To remove the temperature effect from the observed pCO₂, the data were
155 normalized to a constant temperature, the mean in situ T depending on the focus considered, according to Eq. (1).

$$p\text{CO}_2 \text{ at } T_{\text{mean}} = (p\text{CO}_2)_{\text{obs}} \cdot \exp[0.0423 \cdot (T_{\text{mean}} - T_{\text{obs}})] \quad (1)$$

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

The effect of temperature changes on pCO₂ has been computed by perturbing the mean pCO₂ with the difference between the mean and observed temperature. The pCO₂ value at a given observed temperature (T_{obs}) was calculated based on Eq. (2).

$$160 \quad p\text{CO}_2 \text{ at } T_{\text{obs}} = \text{Mean } p\text{CO}_2 \cdot \exp[0.0423 \cdot (T_{\text{obs}} - T_{\text{mean}})] \quad (2)$$

When the temperature effect is removed, the remaining variations in pCO₂ are due to the effect of biology, such as net biological utilization of CO₂, the vertical and lateral transport and sea-air exchange of CO₂.

The biological effect on the surface water pCO₂ in a given area, (ΔpCO₂)_{bio}, is represented by the seasonal amplitude of pCO₂ values normalized to the mean T, (pCO₂ at T_{mean}), using Eq. (1):

$$165 \quad (\Delta p\text{CO}_2)_{\text{bio}} = (p\text{CO}_2, T_{\text{mean}})_{\text{max}} - (p\text{CO}_2, T_{\text{mean}})_{\text{min}} \quad (3)$$

The temperature effect of changes on the mean annual pCO₂ value, (ΔpCO₂)_{temp}, is represented by the seasonal amplitude of (pCO₂ at T_{obs}), using Eq.(2):

$$(\Delta p\text{CO}_2)_{\text{temp}} = (p\text{CO}_2, T_{\text{obs}})_{\text{max}} - (p\text{CO}_2, T_{\text{obs}})_{\text{min}} \quad (4)$$

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

$$170 \quad T/B = (\Delta p\text{CO}_2)_{\text{temp}} / (\Delta p\text{CO}_2)_{\text{bio}} \quad (5)$$

2.4. Estimation of CO₂ fluxes

Fluxes of CO₂ across the sea-air interface were estimated using the relationship:

$$\text{FCO}_2 = \alpha \cdot k \cdot (\Delta p\text{CO}_2)_{\text{sea-air}} \quad (6)$$

where k (cm h⁻¹) is the gas transfer velocity; α is the solubility coefficient of CO₂ (Weiss, 1974); and ΔpCO₂ is the difference
175 between the sea and air values of pCO₂. The atmospheric pCO₂ (pCO₂^{atm}) values were obtained from the monthly atmospheric data of xCO₂ (xCO₂^{atm}) at the Izaña Atmospheric Station (Spain), (Earth System Research Laboratory; <https://www.esrl.noaa.gov/gmd/dv/data/index.php>, last access: 9 January 2019). The xCO₂^{atm} was converted to pCO₂^{atm} as described in DOE (2007).

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

$$180 \quad k = 0.251 \cdot u^2 (Sc/660)^{-0.5} \quad (7)$$

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 CO₂ in seawater, and 660 is the Sc in seawater at 20 °C.



2.5. Statistical analysis

185 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 $p < 0.05$.

3. Results

190 3.1. Underway variables

Table 1 gives the ranges of variation and the mean and standard deviation of T, S and $p\text{CO}_2$ during the 8 sampling cruises. Figure 2 shows the underway distribution of T and $p\text{CO}_2$ in the Gulf of Cádiz.

T values were significantly different among all cruises ($p < 0.05$), varying between 14.3 and 23.4 °C. In general, the samplings made during 2014 presented temperatures higher than 2015 and 2016 (Table 1). For the whole period, the averaged values for 195 both seasons were highest during summer (21.2 ± 1.3 °C) and autumn (21.0 ± 0.8 °C), with the lowest values during spring (15.5 ± 0.5 °C). During winter, T showed an intermediate value of 17.6 ± 0.9 °C. Spatially T tended to increase from coastal to offshore areas, with a difference of ~ 11.8 °C (Fig. 2A). No substantial differences were found between the three transects studied (GD, SP and TF) in terms of temperature data. The lowest values of T were detected near the Guadalquivir River mouth and Cape Trafalgar (36.19° N, 6.03° W), due to freshwater inputs and the frequent upwelled waters, respectively.

200 S values remained practically constant throughout the whole study period, although average values varied significantly among the cruises ($p < 0.05$), with values ranging between 34.68 and 37.06. The highest values were recorded during September 2015 (36.44 ± 0.09) and lowest during February 2016 (35.64 ± 0.08) (Table 1). No spatial or seasonal variations were observed. However, during December 2014, in the area of the Guadalquivir River was measured the lowest salinity value (34.68), related with a storm period that led to very heavy freshwater discharges. On the other hand, TF was the area that presented the highest 205 mean salinity value for the whole study (36.19 ± 0.25).

During our study period, $p\text{CO}_2$ 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, 411.7 ± 13.3 μatm and 411.3 ± 10.7 μatm , respectively. The lower mean value (390.3 ± 15.2 μatm) was logged during winter and the lowest mean value (383.9 ± 22.1 μatm) during spring. In general, the $p\text{CO}_2$ tended to decrease with the distance to the coast (Fig. 2B). $\Delta p\text{CO}_2$ values 210 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 $p\text{CO}_2$ can be observed at some zones. These coincide with those stations where discrete water samples were taken. This may be due to the daily variation (day/night) presented by $p\text{CO}_2$, 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 $p\text{CO}_2$ values 215 were higher than at night.

3.2. Discrete surface variables

Table 2 shows the average values and standard deviation of temperature, salinity, 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 220 mean values were found during summer and autumn of 2014 and 2015 (Table 2), coinciding with the highest average values



of pCO₂ were recorded (Table 1). The minimum value of pH 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 ($p < 0.05$), and a clear seasonal variability was not observed. Values measured ranged from -31.9 to $12.3 \mu\text{mol L}^{-1}$, with the highest values in December 2014 ($7.7 \pm 2.1 \mu\text{mol L}^{-1}$) and the lowest in March 2015 ($-19.1 \pm 9.4 \mu\text{mol L}^{-1}$) (Table 2). During spring was registered the lowest mean value for both years ($-10.9 \pm 11.7 \mu\text{mol L}^{-1}$); higher mean values were found in summer ($-6.3 \pm 6.1 \mu\text{mol L}^{-1}$) and winter ($4.2 \pm 6.3 \mu\text{mol L}^{-1}$). All 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 storm.

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 $2.37 \mu\text{g L}^{-1}$, with the highest mean value measured in March 2015 ($0.76 \pm 0.55 \mu\text{g L}^{-1}$), which coincides with the lowest (negative) mean value of AOU (Table 2). The lowest mean value was in June 2014 ($0.18 \pm 0.14 \mu\text{g L}^{-1}$). With reference to the seasons of both years, the highest value was in spring ($0.72 \pm 0.46 \mu\text{g L}^{-1}$), followed by winter ($0.47 \pm 0.31 \mu\text{g L}^{-1}$), autumn ($0.28 \pm 0.30 \mu\text{g L}^{-1}$) and the lowest value in summer ($0.22 \pm 0.26 \mu\text{g L}^{-1}$). The SP transect presented the mean lowest value of the whole study ($0.33 \pm 0.31 \mu\text{g L}^{-1}$), and the TF zone the highest ($0.49 \pm 0.37 \mu\text{g L}^{-1}$).

Nitrate concentration did not show significant differences among all the cruises ($p > 0.05$), ranging between 0.00 and $1.93 \mu\text{mol L}^{-1}$. The highest value was found in December 2014 ($1.05 \pm 1.96 \mu\text{mol L}^{-1}$) and the lowest in June 2015 ($0.12 \pm 0.14 \mu\text{mol L}^{-1}$) (Table 2). The highest mean value was recorded in winter ($0.87 \pm 1.70 \mu\text{mol L}^{-1}$) and the lowest in summer ($0.27 \pm 0.45 \mu\text{mol L}^{-1}$) of both years. TF presented the highest mean concentration for the whole study ($0.77 \pm 0.76 \mu\text{mol L}^{-1}$).

Phosphate concentration showed significant differences among all the cruises ($p < 0.05$). By season, the highest mean value was obtained during autumn ($0.31 \pm 0.45 \mu\text{mol L}^{-1}$), although the average data in October 2014 ($0.09 \pm 0.03 \mu\text{mol L}^{-1}$) was lower than 2015 ($0.50 \pm 0.55 \mu\text{mol L}^{-1}$) (Table 2). The minimum mean value was observed during summer ($0.11 \pm 0.05 \mu\text{mol L}^{-1}$). GD presented the highest mean value of the whole study ($0.28 \pm 0.39 \mu\text{mol L}^{-1}$), and the lower values were found in the TF, and SP transects, with a similar value, $0.15 \pm 0.07 \mu\text{mol L}^{-1}$ and $0.14 \pm 0.09 \mu\text{mol L}^{-1}$, respectively.

3.3. Air-sea CO₂ exchange

Table 3 summarizes the mean values and standard deviation for atmospheric pCO₂, wind speed, gas transfer velocity and the air-sea CO₂ fluxes measured in this study.

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

There was a clear seasonal variability in the dataset of CO₂ fluxes ($p < 0.05$). The study area acted as source of CO₂ to the atmosphere during summer and autumn ($0.7 \pm 0.3 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $1.2 \pm 0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ respectively) and as a sink in spring and winter ($-1.3 \pm 1.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ and $-1.3 \pm 0.01 \text{ mmol m}^{-2} \text{ d}^{-1}$ respectively).

4. Discussion

4.1. General trends

Numerous research studies have determined that temperature is one of the most important factors that control the variability of pCO₂ 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 CO₂ with the temperature (Weiss, 1974; Woolf et al., 2016). When pCO₂ is affected only



by the temperature, Takahashi et al. (1993) determined a relative variation of $p\text{CO}_2$ of $0.0423\text{ }^\circ\text{C}^{-1}$, equivalent to $17.4\text{ }\mu\text{atm }^\circ\text{C}^{-1}$ for experimental $p\text{CO}_2$ of $400\text{ }\mu\text{atm}$.

260 Figure 3A shows the dependence of the values of $p\text{CO}_2$ with T for the entire database, where a linear increase of $p\text{CO}_2$ 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 $p\text{CO}_2$ of each cruise ($r^2 = 0.71$, $p < 0.01$, Fig. 3B). The slope, $4.80\text{ }\mu\text{atm }^\circ\text{C}^{-1}$, is lower than the thermal effect on $p\text{CO}_2$ described by Takahashi et al. (1993), and indicates the influence of other processes on the distribution of $p\text{CO}_2$ in this zone of the Gulf of Cádiz.

265 Table 4 gives the values for the dependence of $p\text{CO}_2$ 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 $p\text{CO}_2$ 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).

270 There are previous studies in which the seasonal variations of $p\text{CO}_2$ in more coastal zones of the Gulf of Cádiz (depth $< 100\text{ m}$) are described. In 2003, Huertas et al. (2006) found variations of $p\text{CO}_2$ ranging between $196\text{ }\mu\text{atm}$ in March and $400 - 650\text{ }\mu\text{atm}$ 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 $p\text{CO}_2$ with temperature similar to that found in this study ($5.03\text{ }\mu\text{atm }^\circ\text{C}^{-1}$), and mean annual values of $369.3 \pm 31.3\text{ }\mu\text{atm}$. Also in 2006, de la Paz et al. (2009) established a variation of $p\text{CO}_2$ between $329\text{ }\mu\text{atm}$ in March and $387\text{ }\mu\text{atm}$ in September in the Strait of Gibraltar, a deeper zone situated at the southeastern limit of the Gulf of Cádiz.

280 There are other studies not concerned with seasonal differences that have quantified $p\text{CO}_2$ in different zones of the Gulf of Cádiz. Santana-Casiano et al. (2002) found $p\text{CO}_2$ values of $332.2 \pm 3.9\text{ }\mu\text{atm}$ in the Strait of Gibraltar during September 1997, and González-Dávila et al. (2003) determined $p\text{CO}_2$ values of $330.6 \pm 5.6\text{ }\mu\text{atm}$ 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 $p\text{CO}_2$ ranging between 300 and $450\text{ }\mu\text{atm}$ for an extensive region of the Gulf of Cádiz in 2002.

285 Comparing the data given in those previous studies with the mean value found in this study ($398.9 \pm 15.5\text{ }\mu\text{atm}$), it is evident that there has been an increase of $p\text{CO}_2$ 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 by Ribas-Ribas et al. (2011), who used the same methodology, there has been an increase of $p\text{CO}_2$ of $37.6\text{ }\mu\text{atm}$ in the last decade. For the period of time between 2006 and 2016, the rate of growth of $p\text{CO}_2$ in the surface waters of the Gulf of Cádiz ($3.8\text{ }\mu\text{atm year}^{-1}$) exceeds the rate of increase of $p\text{CO}_2$ in the atmosphere ($2.3\text{ }\mu\text{atm year}^{-1}$ 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); this suggests there may have been changes in the continental inputs of nutrients and C related to anthropogenic activity (Rabouille et al., 2001).

295 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 $36.48^\circ\text{ N} - 6.96^\circ\text{ W}$; 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 °C, is similar to the mean value obtained at the mooring (19.2 °C, Fig. 4). If the dependence of pCO₂ with temperature is taken to be 4.80 µatm °C⁻¹, one would expect that the mean values of pCO₂ obtained in this study would be approximately 2 µatm higher.

300 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 pCO₂ 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 pCO₂ (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 pCO₂ and temperature (404.3 ± 16.5 µatm and 20.1 ± 2.4 °C respectively).

Several authors have described the influence of the continental inputs on the distribution of pCO₂ in surface waters; the coastal zone is usually oversaturated with CO₂, whereas the continental shelf as a whole acts as a sink of atmospheric CO₂ (e.g. Rabouille et al., 2001; Chen and Borges, 2009).

310 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 pCO₂ 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 CO₂ to the adjoining coastal zone. The importance of the contributions from the Guadalquivir on the distribution of pCO₂ depends on the river's flow rate, as can be appreciated in Fig. 3. In March 2014 (ST1, green) high values of pCO₂ (up to 500 µatm) were observed in the zone close to the mouth, as a consequence of the river's high flow rate (between 192.7 and 299.2 m³ s⁻¹, Confederación Hidrográfica del Guadalquivir; <http://www.chguadalquivir.es/saih/DatosHistoricos.aspx>, last access: 19 Juny 2018) while in the spring of 2015 (ST5, dark green) the lowest values of the study were recorded in this zone (as low as 320 µatm) during a period of drought (flow rate 20 m³ 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).

320 The Bay of Cádiz occupies an area of 38 km², and receives urban effluents from a population of 640,000 inhabitants. This shallow zone is oversaturated with CO₂ (Ribas-Ribas et al., 2011) due largely to the inputs of CO₂, 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).

325 Another source of CO₂ 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 originated 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 °C 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 CO₂ flux of 198 ± 80 µmol C m⁻² d⁻¹, which would produce an increase of pCO₂ of 0.25 ± 0.10 µatm d⁻¹.



335 Additionally, in the coastal zone (depth between 50 and 100 m) of the Trafalgar section, an almost permanent upwelling system is located (Prieto et al., 1999; Vargas-Yáñez et al., 2002); this system could affect the pCO₂ values in this part of the Gulf of Cádiz.

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 CO₂ (e.g. Liu et al., 2010; Xue et al., 2015; González-Dávila et al., 2017) can affect the distributions of pCO₂ found in the Gulf of Cádiz.

The progressive increase of T and pCO₂ with increasing depth of the system measured below 100 - 200 m (Fig. 5), 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 pCO₂ 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 pCO₂ towards the deep zones (down to ≈ 100 m) on the north-eastern shelf of the Gulf of Cádiz. In general, an oversaturation of CO₂ 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 pCO₂

355 In addition to the influence of temperature, the spatiotemporal distribution of pCO₂ in surface seawater is affected by the biological utilization of CO₂, the vertical and lateral transport, the sea-air exchange of CO₂ 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 activity on the variations of pCO₂, Fig. 6 shows the dependence between the mean values of pCO₂ at the fixed stations, and the temperature, pH, AOU and the concentration of chlorophyll-a (n = 126). The thermal effect on pCO₂ is more intense when the discrete database (pCO₂ = 297 + 5.7 T, r² = 0.48; p < 0.0001) is considered in comparison to the effect obtained using the whole database. The variation of pCO₂ with pH (pCO₂ = 1710 - 162.8 pH, r² = 0.34; p < 0.0001), AOU (pCO₂ = 410 + 1.1 AOU, r² = 0.21; p < 0.0001), and chlorophyll-a (pCO₂ = 413 - 20.8 [Chl-a], r² = 0.14; p < 0.0001) show the influence of the processes of photosynthesis and respiration on the variations of pCO₂ found. For the Gulf of Cádiz, Huertas et al. (2005) found a linear relationship between pCO₂ and chlorophyll-a with a slope similar to that obtained in this study (pCO₂ = 274 - 19.6 [Chl-a], r² = 0.32; p < 0.0001; n = 28). Other authors have also described the interrelationships existing between pCO₂ 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 pCO₂ 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).

370 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 pCO₂ 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 $p\text{CO}_2$, 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 T/B ratio is 1.15, which indicates that temperature is an important factor controlling intra-annual variation of $p\text{CO}_2$. This value is similar to that determined by Ribas-Ribas et al. (2011), in the northeast zone of the shelf of the Gulf of Cádiz, with a ratio of 1.3. De la Paz et al. (2009) 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 presents the values of the T/B ratio grouped in different bottom-depth intervals of the water column in the system. The variations of $\Delta p\text{CO}_2$ bio and $\Delta p\text{CO}_2$ temp 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. This variation of the T/B ratio is largely caused by the variations of $\Delta p\text{CO}_2$ bio, with high values close to the coast (120.2 μatm), 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 $\Delta p\text{CO}_2$ temp with temperature ($r^2 = 0.40$, $p < 0.01$) and of $\Delta p\text{CO}_2$ 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 $p\text{CO}_2$. 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 $\Delta p\text{CO}_2$ 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 $\Delta p\text{CO}_2$ 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).

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. 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 $p\text{CO}_2$ than the non-thermal effects. The T/B ratio varies to the east, with values between 1.0 in the zone of the Guadalquivir and 1.4 in Sancti Petri, and an intermediate value of 1.2 in the Trafalgar 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 $\Delta p\text{CO}_2$ bio. 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., 415 2002). The presence of these emerged water masses could be related to the relatively low values of $\Delta p\text{CO}_2$ temp found in this zone. In fact, the mean temperature in this 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 $\Delta p\text{CO}_2$ temp 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).

420 4.3. Ocean-atmosphere CO₂ exchange

In the Gulf of Cádiz, the flux of CO₂ 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 (Table 5). As can be appreciated in Fig. 10, the fluxes of CO₂ presented seasonal and spatial variations during the period studied. The Gulf of Cádiz acts as a source of CO₂ to the atmosphere during the months of summer (ST2, ST6) and autumn (ST3, ST7), and as a sink in spring (ST1, ST5) 425 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; Ait-Ameur and Goyet, 2006; Ribas-Ribas et al., 2011).

As has been observed with pCO₂, temperature is one of the principal factors that control the fluxes of CO₂. In fact, for each cruise, a linear and positive relationship has been found between the mean values of the CO₂ fluxes and T ($r^2 = 0.72$, $p < 0.01$) (Fig. 11). In parallel, there is a linear and negative relationship between the mean values of the CO₂ fluxes and the concentration 430 of chlorophyll-a at the discrete stations sampled ($r^2 = 0.74$, $p < 0.01$) (Fig. 11), as a consequence of the biological utilisation of the CO₂ (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 CO₂ in the Gulf of Cádiz tend to decrease with the distance from the coast (Fig.10). The coastal zone (< 50 m) presents a mean CO₂ 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 435 open waters with bottom-depth higher than 600 m. This dependence of CO₂ fluxes with distance from the coast has also been described 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 CO₂ fluxes as one moves towards the open sea. Ribas-Ribas et al. (2011) also found that in the Gulf of Cádiz the CO₂ 440 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 GD and SP transects a decrease of the CO₂ 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 CO₂ (-0.4 ± 1.2 mmol m⁻² d⁻¹), and the deeper zone is a weak 445 source of CO₂ 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).



450 The Gulf of Cádiz, during the period of this sampling, acted as a sink of CO₂, with a mean rate of $-0.18 \pm 1.32 \text{ mmol m}^{-2} \text{ d}^{-1}$,
that would give rise to an annual flux of $-0.07 \text{ mol C m}^{-2} \text{ yr}^{-1}$. 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 Ait-Ameur and Goyet (2006) in which
it was estimated that the Gulf of Cádiz acts as a source of CO₂ to the atmosphere, although that study only corresponds to the
455 summer season.

5. Conclusions

The mean value of pCO₂ in the eastern part of the Gulf of Cádiz found in this study ($398.9 \pm 15.5 \text{ } \mu\text{atm}$) indicates that it is
undersaturated in CO₂ with respect to the atmosphere ($402.1 \pm 3.9 \text{ } \mu\text{atm}$). The spatiotemporal variation of pCO₂ found responds
to the influence of different factors that usually affect its distribution in the littoral oceans. In global terms, when the mean
460 values of the 8 cruises are considered, temperature ($p\text{CO}_2 = 302.0 + 5.16 T$, $r^2 = 0.71$, $p < 0.01$) and biological activity ($p\text{CO}_2$
 $= 425.0 - 59.15 [\text{Chl-a}]$, $r^2 = 0.76$, $p < 0.01$) are the two principal factors that explain the temporal variability of pCO₂. Over
and above these general tendencies, there are spatial variations associated fundamentally with two other processes. Firstly, the
effect of the continental 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 pCO₂; it is in this area where the lowest and highest values have been observed in the
465 discrete measurements. In this same coastal zone the highest mean values of pCO₂ were found - values that diminish
progressively in line with increasing distance from the coast, out as far as an approximate depth of some 400 m. Secondly,
there is a relative increase of the temperature and pCO₂ in the zone furthest from the coast (depth > 400 m) that is the
consequence of a change in the origin of the surface water, with the arrival of a warm branch of the Azores current.

The T/B ratio allows the adequately identification of the factors that control the variability of pCO₂ in the Gulf of Cádiz. Its
470 mean value (1.15) suggests that the distribution is principally controlled by the temperature. A 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
475 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 section, where values of up to 1.54 are obtained for depths greater than 100 m.

The Gulf of Cádiz acts as a sink of CO₂, with a mean capacity of capture for the period sampled of $14.9 \text{ Gg year}^{-1}$. The CO₂
fluxes present seasonal variation: these waters act as a source of CO₂ to the atmosphere in summer and autumn and as a sink
in winter and spring. The spatiotemporal variability of CO₂ is very similar to that found for the distribution of pCO₂, with
480 larger fluxes close to coast. Based on the information available in the zone, there seems to have been a decrease in the capacity
for CO₂ capture in the zone in recent decades.

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.

485 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 sea surface temperature (T), sea surface salinity (S) and pCO₂ 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	T (°C)			S			pCO ₂ (µatm)		
			Range	Mean ± SD	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	35.02 - 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 average values and standard deviation of temperature, salinity, pH, apparent oxygen utilization (AOU), chlorophyll, 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	Temperature (°C)	Salinity	pH	AOU ($\mu\text{mol L}^{-1}$)	Chlorophyll ($\mu\text{g L}^{-1}$)*	Nitrate ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)
ST1	18	15.3 ± 0.5	36.08 ± 0.14	8.06 ± 0.03	-3.6 ± 8.4	0.65 ± 0.37	0.96 ± 1.01	0.14 ± 0.06
ST2	16	21.0 ± 1.3	36.11 ± 0.11	7.97 ± 0.03	-10.3 ± 5.7	0.18 ± 0.14	0.42 ± 0.60	0.12 ± 0.04
ST3	17	21.7 ± 0.7	36.11 ± 0.14	7.97 ± 0.06	-4.6 ± 3.2	0.24 ± 0.29	0.34 ± 0.27	0.09 ± 0.03
ST4	17	17.7 ± 0.7	36.26 ± 0.27	8.05 ± 0.05	7.7 ± 2.1	0.46 ± 0.33	1.05 ± 1.96	0.23 ± 0.09
ST5	16	15.5 ± 0.3	36.03 ± 0.13	8.09 ± 0.12	-19.1 ± 9.4	0.76 ± 0.55	0.68 ± 1.17	0.17 ± 0.09
ST6	16	21.1 ± 1.0	36.37 ± 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 ± 1.2	35.63 ± 0.02	7.94 ± 0.03	-2.6 ± 5.0	0.29 ± 0.31	0.37 ± 0.50	0.50 ± 0.55
ST8	6	16.8 ± 0.2	36.45 ± 0.05	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).



880 **Table 3: Mean values and standard deviation of atmospheric pCO₂ (pCO₂ μatm), wind speed, gas transfer velocity (k) and CO₂ fluxes 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	pCO ₂ atm (μatm)	Wind speed (m s ⁻¹)	k (cm h ⁻¹)	CO ₂ fluxes (mmol m ⁻² d ⁻¹)
ST1	398.7 ± 1.8	7.7 ± 3.4	13.4 ± 0.2	-0.3 ± 2.3
ST2	404.5 ± 0.5	7.4 ± 3.4	14.0 ± 0.3	0.9 ± 1.4
ST3	397.7 ± 0.6	6.7 ± 4.0	11.8 ± 0.4	1.4 ± 0.8
ST4	399.4 ± 2.2	7.7 ± 4.2	14.3 ± 0.2	-1.3 ± 1.7
ST5	405.5 ± 0.6	5.5 ± 2.8	6.9 ± 0.1	-2.3 ± 0.9
ST6	406.1 ± 0.8	7.5 ± 4.1	14.4 ± 0.3	0.5 ± 1.5
ST7	398.4 ± 0.7	7.0 ± 3.2	12.3 ± 0.3	0.9 ± 1.1
ST8	406.4 ± 0.3	6.8 ± 3.1	10.6 ± 0.1	-1.3 ± 1.6



Table 4: Correlations estimated between pCO₂ and temperature (T, °C) and regression coefficients (r²) 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



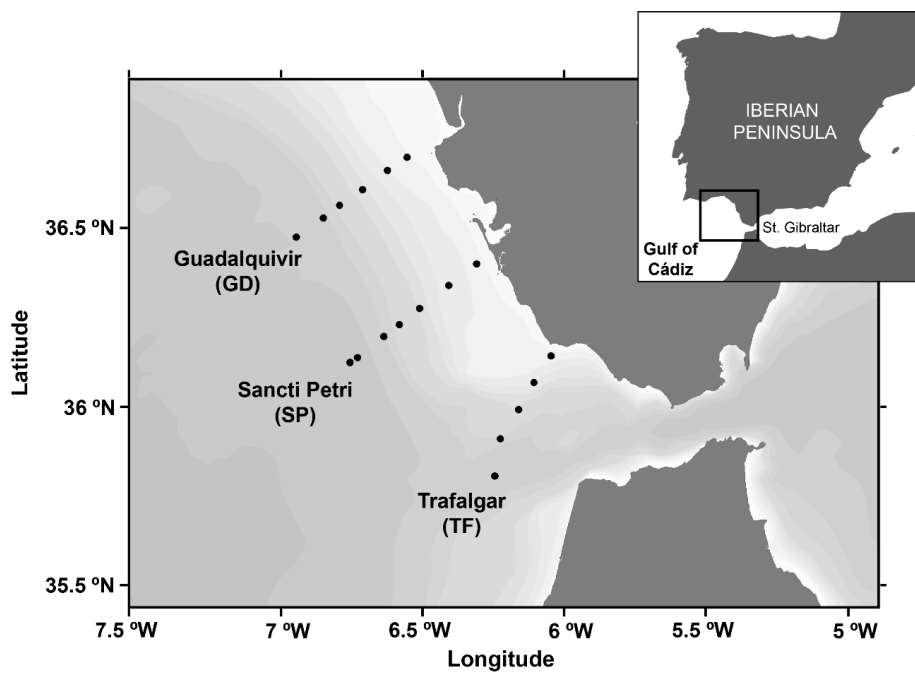
Table 5. Mean average and range of pCO₂ and CO₂ fluxes (FCO₂) in different shelf areas of the North Atlantic.

Site	°E	°N	Date	pCO ₂ (µatm)	FCO ₂ (mmol m ⁻² d ⁻¹) ^a	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)
US Middle Atlantic Bight	-76.0 - -69.0	35.0 - 42.0	February, March, May, June, October 1996	220 - 560	-4.4 - -1.9 ^b	DeGrandpre 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)
Ría de Vigo	-8.9 - -8.6	42.1 - 42.3	April, July, September, October, November, December 1997	285 - 615	-1.5 - 1.8 ^a	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)
North Sea	-3.0 - 10.0	50.0 - 61.0	August, September 2001	220 - 490	-3.4 ^b	Bozec et al. (2005)
Gulf of Cádiz	-8.3 - -6.0	33.5 - 37.0	July 2002		18.6 ± 4 ^b	Ait-Anneur 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	Huertaa 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)
US South Atlantic Bight	-81.5 - -76.5	28.5 - 34.5	January, March, July, August, October, December 2005; May 2006	330 - 1300	-3.8 - 3.3 ^b	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)
Scottian 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)
Northern Bay of Biscay	-11.0 - -5.0	47.0 - 51.5	June 2006; May 2007; May 2008	248 - 342	-11.9 - -7.4 ^d	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 ^c	González-Dávila et al. (2017)
US South Atlantic Bight	-81.0 - -76.0	28.0 - 35.0	July 2007; August, December 2008; May, November 2009; February, April, August, October 2010; March, April, October, December 2011; February, May, August 2012; September 2013; May, July, September, November, December 2014; April, June, July 2015	253 - 567	-1.8 - 2.0 ^c	Reimer et al. (2017)
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

^a Gas transfer coefficient (k); ^b Woolf and Thorpe (1991), ^c Wanninkhof et al. (2000), ^d Ho et al. (2006), ^e Wanninkhof et al. (2009) and ^f Wanninkhof et al. (2014).



Figures



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Figure 1: Map of the eastern shelf of the Gulf of Cádiz showing the location of fixed stations located on 3 transects at right-angles to the coastline: Guadalquivir (GD), Sancti Petri (SP) and Trafalgar (TF).

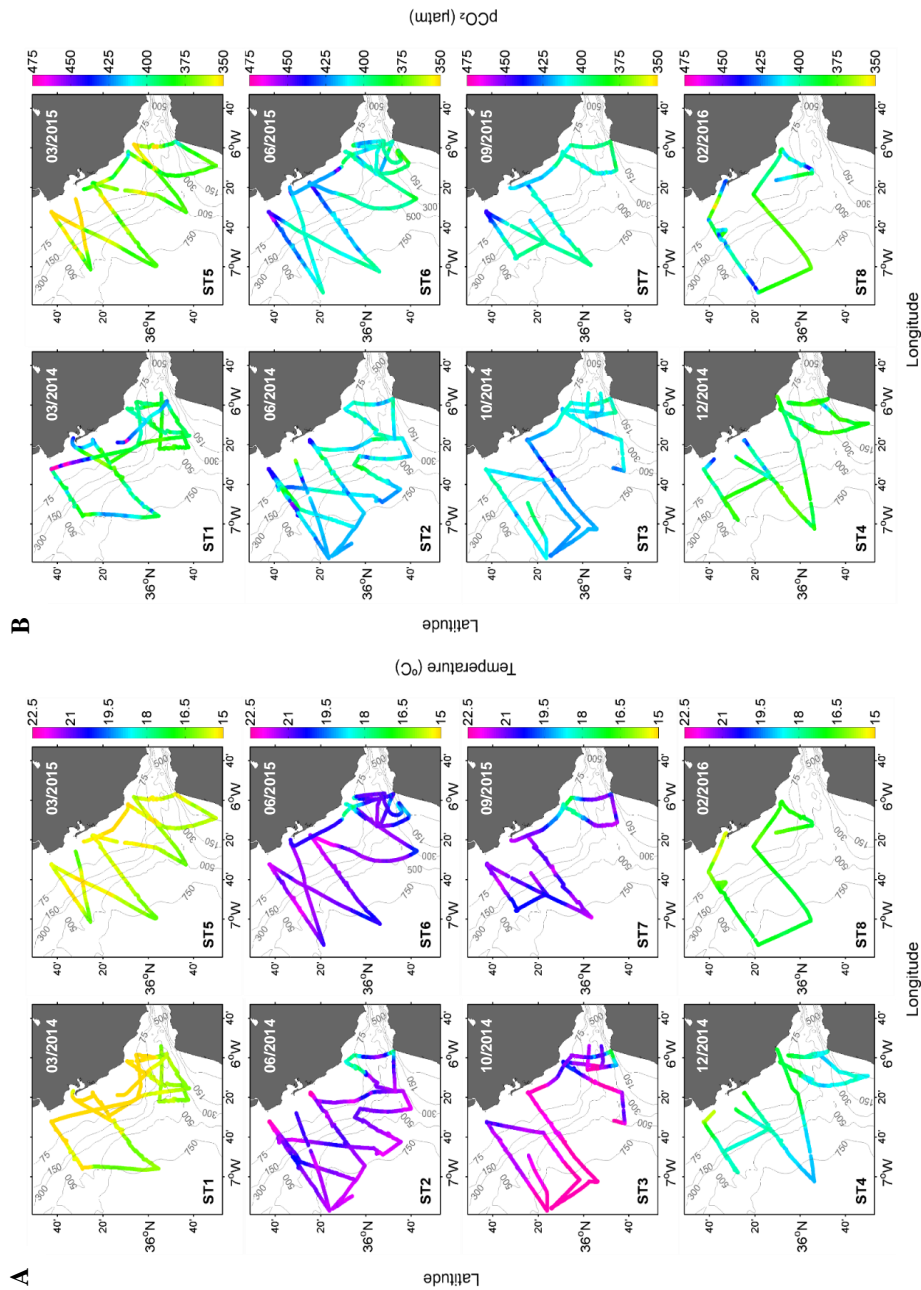
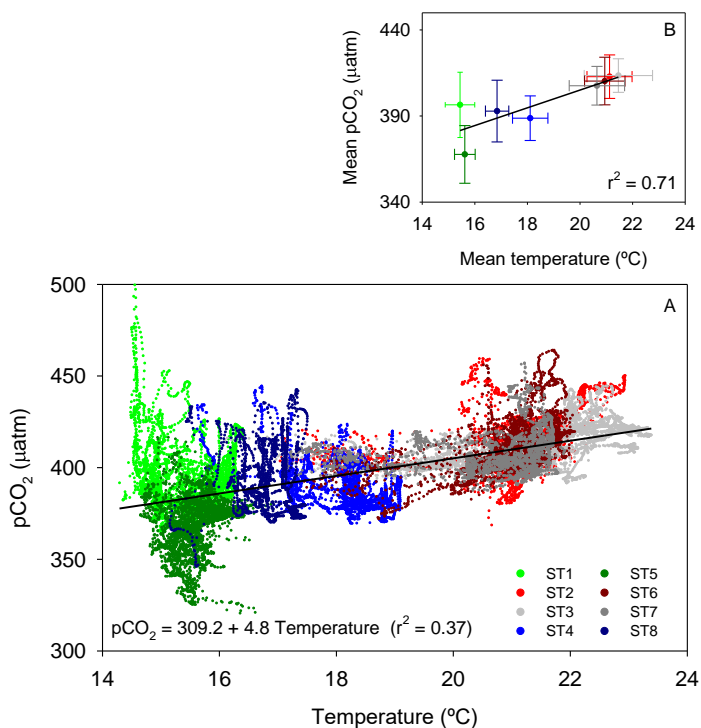


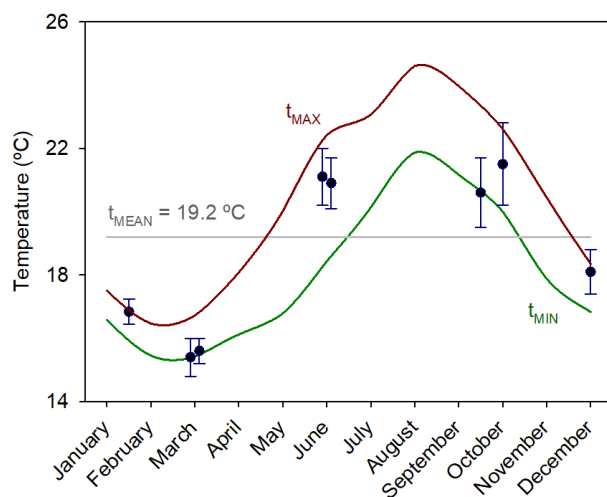
Figure 2: Distribution of sea surface temperature (A) and pCO₂ (B) during the 8 cruises in the Gulf of Cádiz: March 2014 (ST1), June 2014 (ST2), October 2014 (ST3), December 2014 (ST4), March 2015 (ST5), June 2015 (ST6), September 2015 (ST7) and February 2016 (ST8).



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930 **Figure 3: Dependence of pCO₂ with sea surface temperature for the complete underway database during all the cruises (A) and for the mean values of pCO₂ and temperature for each cruise showing their standard deviations (B). The solid line shows the linear correlation.**



945 **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.

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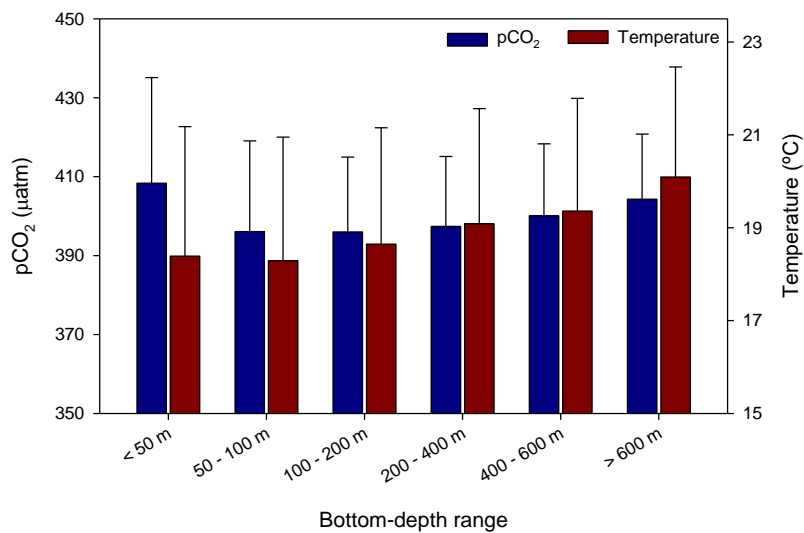


Figure 5: Variation of pCO₂ (µatm) and temperature (°C) at different bottom-depth ranges of the water column (m) during the 8 cruises. The mean values and standard deviations of pCO₂ (blue) and temperature (red) for each range of depth are represented.

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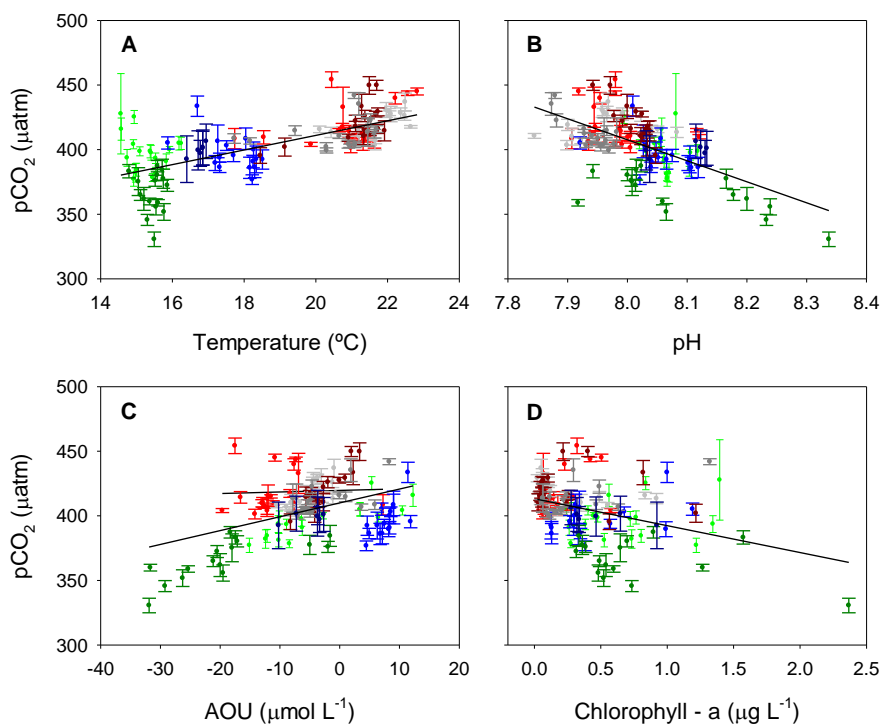
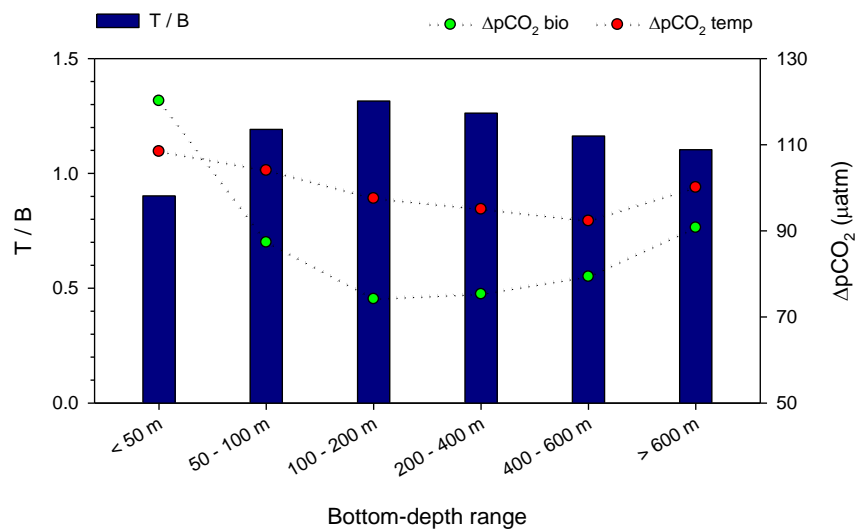
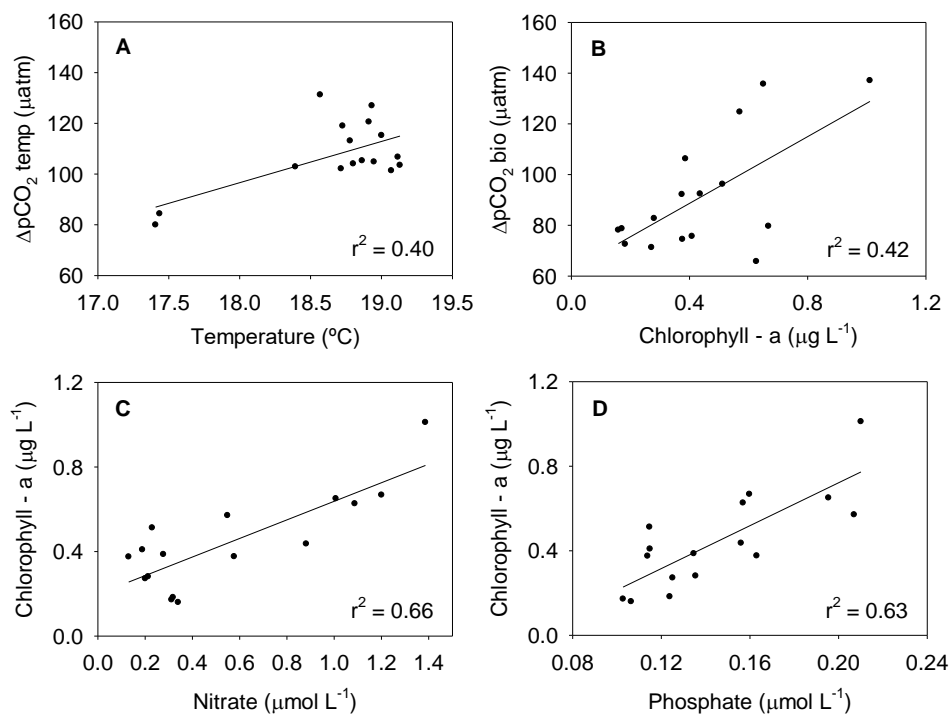


Figure 6: Dependence between the surface values of pCO₂ and temperature (A, $r^2 = 0.48$), pH (B, $r^2 = 0.34$), AOU (C, $r^2 = 0.21$) and chlorophyll-a (D, $r^2 = 0.14$) at the 16 discrete stations during the 8 cruises. pCO₂ presents the standard deviation associated with the mean value obtained from the underway measurements.

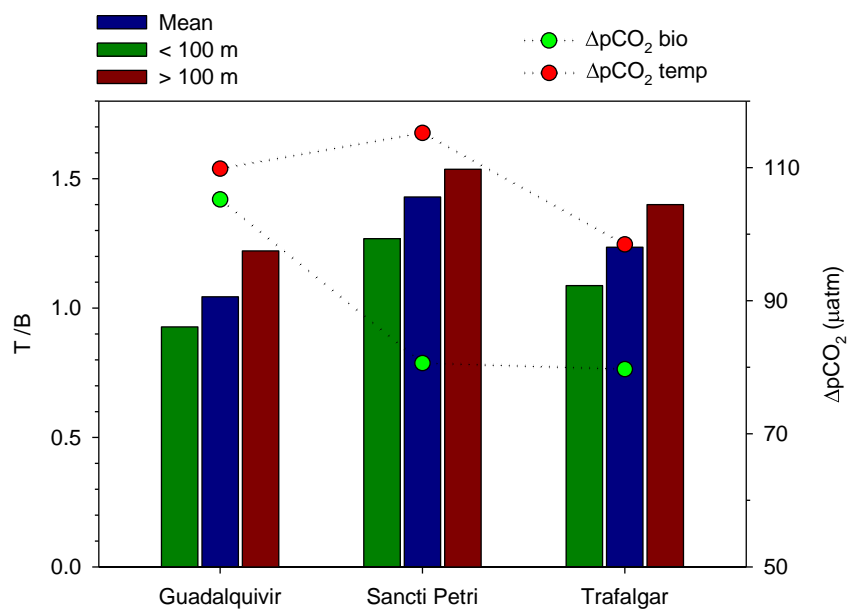
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965 **Figure 7: Variation of the T/B ratio (blue bar), $\Delta p\text{CO}_2$ bio (green point) and $\Delta p\text{CO}_2$ temp (red point) at different bottom-depth ranges of the water column (m) for the 8 cruises.**



970 **Figure 8: Correlations between A) $\Delta p\text{CO}_2$ temp and temperature, B) $\Delta p\text{CO}_2$ 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.**



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Figure 9: 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), $\Delta p\text{CO}_2$ bio (green point) and $\Delta p\text{CO}_2$ temp (red point) on the various transects of the study (Guadalquivir, Sancti Petri and Trafalgar) during the 8 cruises.

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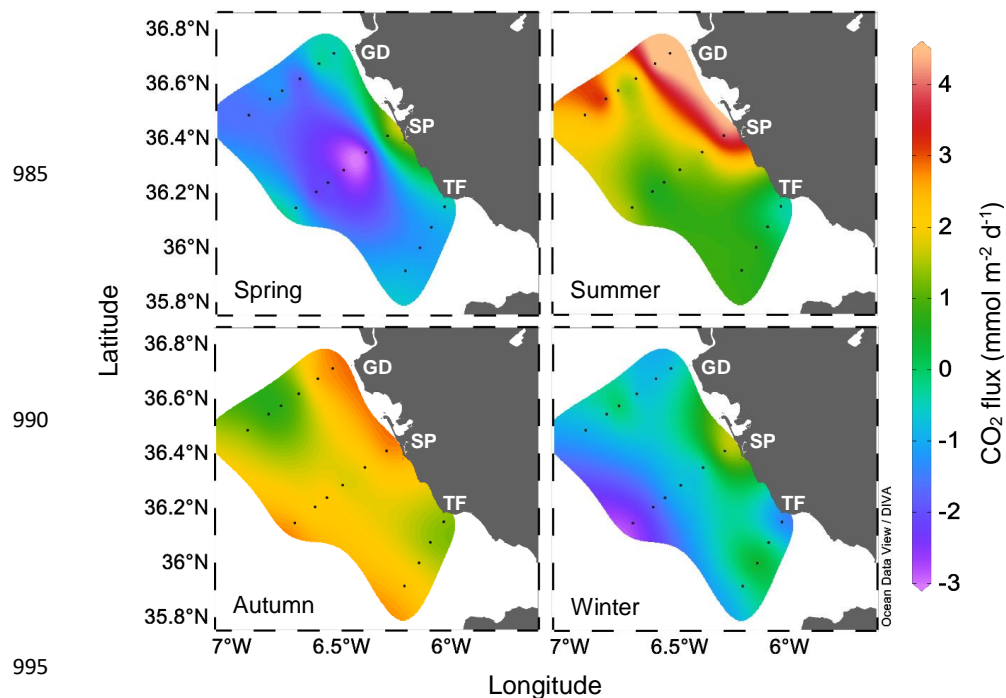
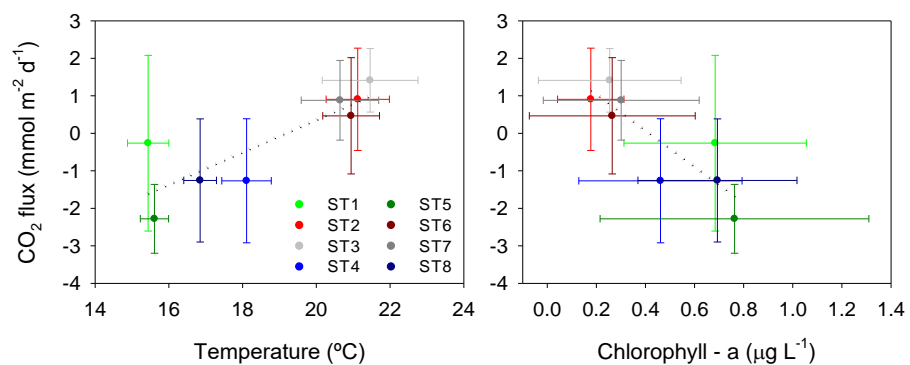


Figure 10: Spatial distribution of mean values of CO₂ fluxes in the eastern shelf of the Gulf of Cádiz during spring (ST1, ST5), summer (ST2, ST6), autumn (ST3, ST7) and winter (ST4, ST8).



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Figure 11: Correlations between the mean values of CO₂ fluxes and sea surface temperature (T) for the underway database (left, $r^2 = 0.72$), and the CO₂ fluxes and chlorophyll-a at the 16 discrete surface stations (right, $r^2 = 0.74$) for each cruise and showing the standard deviations.