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pCO$_2$ variability in the surface waters of the eastern Gulf of Cádiz (SW Iberian Peninsula)

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Abstract. Spatio-temporal variations in the partial pressure of CO_2 (pCO_2) were studied during eight oceanographic cruises conducted between March 2014 and February 2016 in surface waters of the eastern shelf of the Gulf of Cádiz (SW Iberian Peninsula) between the Guadalquivir river and Cape Trafalgar. pCO_2 presents 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. The study area acts as a 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 transects, the CO_2 fluxes decrease towards offshore, whereas in the Trafalgar transect fluxes increase due to the presence of an upwelling. The annual uptake capacity of CO_2 in the Gulf of Cádiz is 4.1 Gg C yr^{-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 Haas et al., 2002). Continental shelves account for about 10 %–15 % of the ocean primary production, and they contribute approximately 40 % of the total carbon sequestration through the mechanism of the biological pump (Muller-Karger et al., 2005).

Generally, waters over the continental shelf account for $\sim$ 15 % of the global ocean CO_2 uptake (-2.6 ± 0.5 Pg C yr^{-1}; Le Quéré et al., 2018). 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 that 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 (Laruelle et al., 2010).

In several works, it has been observed that the continental shelves present different behaviour according to their latitude: they tend to act as a sink of carbon ($-0.33\,\mathrm{Pg\,C\,yr^{-1}}$) at high and middle latitudes (30–90°) and as a weak source ($0.11\,\mathrm{Pg\,C\,yr^{-1}}$) at low latitudes (0–30°) (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 ($-0.24\,\mathrm{Pg\,C\,yr^{-1}}$) and those of the Southern Hemisphere are a weak source of CO_2 ($0.03\,\mathrm{Pg\,C\,yr^{-1}}$).

At the continental shelf, a high spatio-temporal variability in the air–sea CO_2 fluxes occurs due to various effects, such as the thermodynamic effects, the biological processes, the gas exchange, the upwelling zones and the continental inputs (e.g. Chen and Borges, 2009; Ito et al., 2016). Thermodynamic effects are controlled by the inverse relationship between temperature and solubility ($0.0423\,^{\circ}\mathrm{C}^{-1}$; Takahashi et al., 1993). 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 that 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 (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 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). 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 Ocean and Indian Ocean 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) than the outer shelf. The influence of both factors (riverine inputs and human impact) decreases 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 of less than 40 m) also shows greater seasonal variability in temperature than the outer platform, and consequently the effect of temperature on pCO$_2$ will be greater in the inner zone (Chen et al., 2013).

The Gulf of Cádiz is strategically located, connecting the Atlantic Ocean with the Mediterranean Sea through the Strait of Gibraltar, and in addition it receives continental inputs from several major rivers, i.e. the Guadalquivir, Rio Tinto, Odiel and Guadiana. Various studies have been conducted in this area to evaluate the variability in 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 sink of CO_2 with seasonal variations induced mainly by the combination of the fluctuations of biomass concentration and temperature.

In this paper we evaluate the spatial and seasonal variation in the sea-surface pCO$_2$ on the eastern shelf of the Gulf of Cádiz. In addition, we aim to assess the relative contribution of the thermal and non-thermal effects to pCO$_2$ distribution 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 by pCO$_2$ in this area (Ribas-Ribas et al., 2011). In this work we have analysed a surface measurement database of $>26\,000$ values of pCO$_2$ obtained during cruises made between 2014 and 2016 and covering an area of $0.8^{\circ} \times 1.3^{\circ}$ 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 a bilayer flow takes place with an upper Atlantic layer flowing towards the Mediterranean basin and a deeper outflow of higher-density Mediterranean waters flowing 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 Central

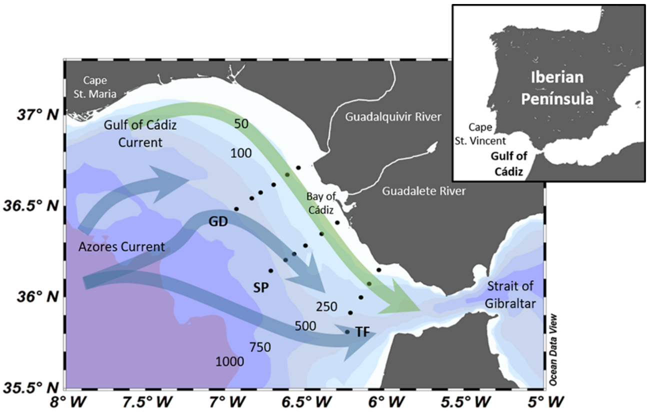

Figure 1. Map of the eastern shelf of the Gulf of Cádiz showing the location of the fixed stations located on three transects at right angles to the coastline: Guadalquivir (GD), Sancti Petri (SP) and Trafalgar (TF). The location of the principal surface currents, rivers and capes of the study area are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

Water (ENACW) at an intermediate depth, characterized 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 systems of the world: the North Atlantic upwelling (e.g. Alvarez et al., 2009) that extends from south of Cap-Vert (Senegal) to Cape Finisterre (northwest of Spain). For this reason, the Gulf of Cádiz presents characteristics typical of this system: 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 system phenomena, and the bilayer flow through the Strait of Gibraltar are two factors that complicate the simple eastern boundary upwelling system conceptual model (Arístegui et al., 2009; Peliz et al., 2009).

In addition, the surface circulation in the Gulf of Cádiz is characterized by several different processes. These are 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); an upwelling process that occurs in the Trafalgar area, produced by tidal interaction with the topography of the zone; and the mixing of surface layers induced by the wind (Vargas-Yáñez et al., 2002; Peliz et al., 2009; Sala et al., 2018). 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 consisted of taking sea surface measurements while underway. The second strategy was to obtain measurements at several discrete surface stations along three transects at right angles to the coastline: the Guadalquivir transect (GD), the Sancti Petri transect (SP) and the Trafalgar transect (TF) (Fig. 1). Data were collected during eight 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 (Table 1). All the cruises were made on the R/V *Ángeles Alvariño*, except the summer 2015 cruise (ST6) that was undertaken on the R/V *Ramón Margalef*. The study area is located between 35.4 and 36.7° N and 6.0 and 7.2° W (52.8×10^2 km^2).

2.2.1 Underway measurements

Sea surface temperature (SST), sea surface salinity (SSS) and pCO_2 were recorded continuously and were averaged with a frequency interval of 1 min from the surface seawater supply of the ship (pump inlet at a depth of 5 m). SST and SSS were measured using a Sea-Bird thermosalinograph (SBE 21) with an accuracy of ± 0.01 °C and ± 0.003 units, 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 (LI-COR®, 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 substandard gas of known concentration (413.2 ppm). CO_2 concentration of the substandard gas was determined from the comparison with standard gases of NOAA with an uncertainty of 0.22 ppm and measured with a LI-COR 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. The xCO_2 was converted into pCO_2 according to the protocol described in DOE (2007). Corrections between the equilibrator and SST were made following Takahashi et al. (1993). The temperature difference between the ship's sea inlet and the equilibrator was less than 1.5 °C.

2.2.2 Fixed stations

Discrete surface samples were collected at 5 m depth, using Niskin bottles (10 L) mounted on a rosette sampler coupled

Table 1. Date, number of measurements (n), range, average values, and standard deviation of underway sea surface temperature (SST), sea surface salinity (SSS), and pCO$_2$ during the eight 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 (°C)		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	35.03–36.79	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

to a Sea-Bird CTD 911+ (conductivity–temperature–depth system), to measure pH, dissolved oxygen, chlorophyll a and nutrient concentrations.

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 (tris(hydroxymethyl) aminomethane; Zeebe and Wolf-Gladrow, 2001). Dissolved oxygen values were obtained with the sensor of the rosette (SBE 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 h by fluorometry analysis (Hitachi F-2500) (Yentsch and Menzel, 1963). Nutrient samples for analysis of nitrate and phosphate contents 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 auto-analyser (Skalar, San Plus) based on classic spectrophotometric methods (Grasshoff et al., 1983). The accuracies of the determinations obtained are the following: ± 0.003 for pH, ± 0.1µmol 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.

The corresponding data of SST, SSS and pCO$_2$ for the fixed stations were obtained by the underway measurements, averaging data corresponding to approximately 0.9 km 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 greater than 0.04 °C and 0.01 units, respectively.

2.3 Thermal and non-thermal effects on pCO$_2$ calculations

To determine the relative importance of the thermal and non-thermal effects on the changes in pCO$_2$ in seawater (e.g. Landschützer et al., 2015; Reimer et al., 2017), we follow the method described by Takahashi et al. (2002). To remove the thermal 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).

$$p\mathrm{CO_2 \ at \ SST_{mean}} = (p\mathrm{CO_2})_{\mathrm{obs}} \cdot \exp\left[0.0423 \cdot (\mathrm{SST_{mean}} - \mathrm{SST_{obs}})\right], \quad (1)$$

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

To analyse the effect of the thermal changes in pCO$_2$ at the given observed temperatures (SST$_{\mathrm{obs}}$) the following expression has been used:

$$p\mathrm{CO_2 \ at \ SST_{obs}} = (p\mathrm{CO_2})_{\mathrm{mean}} \cdot \exp\left[0.0423 \cdot (\mathrm{SST_{obs}} - \mathrm{SST_{mean}})\right]. \quad (2)$$

When the thermal effect is removed, the remaining variations in pCO$_2$ are due to the non-thermal influences, such as the biological utilization of CO$_2$, the vertical and lateral transport, the 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-thermal effects on the surface water pCO$_2$, $(\Delta p\mathrm{CO_2})_{\mathrm{n\text{-}T}}$, can be calculated from the seasonal amplitude of pCO$_2$ values normalized to the mean SST, (pCO$_2$ at SST$_{\mathrm{mean}}$), using Eq. (1):

$$(\Delta p\mathrm{CO_2})_{\mathrm{n\text{-}T}} = (p\mathrm{CO_2 \ at \ SST_{mean}})_{\mathrm{max}} - (p\mathrm{CO_2 \ at \ SST_{mean}})_{\mathrm{min}}. \quad (3)$$

The seasonal amplitude of pCO$_2$ values normalized to the observed SST (pCO$_2$ at SST$_{\mathrm{obs}}$) represents the thermal effect of changes in the mean annual pCO$_2$ value, $(\Delta p\mathrm{CO_2})_{\mathrm{T}}$, and it is calculated with the following expression:

$$(\Delta p\mathrm{CO_2})_\mathrm{T} = (p\mathrm{CO_2} \text{ at } \mathrm{SST_{obs}})_{\max} - (p\mathrm{CO_2} \text{ at } \mathrm{SST_{obs}})_{\min}. \quad (4)$$

The ratio between the thermal effects (T) and non-thermal effects (B) quantifies the relative importance of each effect (Takahashi et al., 2002):

$$T/B = (\Delta p\mathrm{CO_2})_\mathrm{T}/(\Delta p\mathrm{CO_2})_\mathrm{n\text{-}T}. \quad (5)$$

A T/B ratio greater than 1 implies the dominance of thermal effects over non-thermal effects on the $p\mathrm{CO_2}$ dynamics. However, a T/B lower than 1 reveals a greater influence of non-thermal processes. This method was originally designed for open ocean 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 the seasonal signal of $p\mathrm{CO_2}$ data is decomposed into individual components due to variations in SST, in air–sea $\mathrm{CO_2}$ exchange, in SSS, and in combined mixing and biological processes, according to Eq. (6).

$$d\,p\mathrm{CO_2}^{\mathrm{sw},i} = d_\mathrm{SST}\,p\mathrm{CO_2}^{\mathrm{sw},i} + d_\mathrm{AS}\,p\mathrm{CO_2}^{\mathrm{sw},i} + d_\mathrm{SSS}\,p\mathrm{CO_2}^{\mathrm{sw},i} + d_\mathrm{MB}\,p\mathrm{CO_2}^{\mathrm{sw},i}, \quad (6)$$

where the superscript "sw" makes reference to the surface $p\mathrm{CO_2}$ in the seawater and "i" to the mean value between consecutive cruises for all variables; $d\,p\mathrm{CO_2}^{\mathrm{sw},i}$ is the observed change in $p\mathrm{CO_2}$; $d_\mathrm{SST}\,p\mathrm{CO_2}^{\mathrm{sw},i}$ is the change due to SST changes; $d_\mathrm{AS}\,p\mathrm{CO_2}^{\mathrm{sw},i}$ is the change due to air–sea exchange; $d_\mathrm{SSS}\,p\mathrm{CO_2}^{\mathrm{sw},i}$ is the change due to salinity variations; and $d_\mathrm{MB}\,p\mathrm{CO_2}^{\mathrm{sw},i}$ is the change due to mixing plus biology. At the same time, each process is calculated with the following equations (Olsen et al., 2008):

$$d_\mathrm{SST}\,p\mathrm{CO_2}^{\mathrm{sw},i} = p\mathrm{CO_2}^{\mathrm{sw},i} \cdot e^{0.0423(\Delta\mathrm{SST})} - p\mathrm{CO_2}^{\mathrm{sw},i}, \quad (7)$$

where ΔSST is the SST difference between two cruises.

$$d_\mathrm{AS}\,p\mathrm{CO_2}^{\mathrm{sw},i} = -\left(d \cdot F^i\right)/\mathrm{MLD}^i, \quad (8)$$

where d is the number of days passed between two cruises (90 d approximately); F^i is the mean flux of $\mathrm{CO_2}$; and MLD^i is the mean mixed layer depth.

$$d_\mathrm{SSS}\,p\mathrm{CO_2}^{\mathrm{sw},i} = p\mathrm{CO_2}^{\mathrm{sw},n+1}\left(\mathrm{DIC}^{n+1}, \mathrm{TA}^{n+1}, \mathrm{SSS}^{n+1}, \mathrm{SST}^{i}\right) - p\mathrm{CO_2}^{\mathrm{sw},n}\left(\mathrm{DIC}^{n}, \mathrm{TA}^{n}, \mathrm{SSS}^{n}, \mathrm{SST}^{i}\right), \quad (9)$$

where the superscript "n" refers to the mean value of each cruise and the variables DIC (dissolved inorganic carbon) and TA (total alkalinity) have been estimated from pH and $p\mathrm{CO_2}$ using the K1 and K2 acidity constants proposed by Lueker et al. (2000) in the total pH scale through the program CO2SYS (Lewis et al., 1998). $d_\mathrm{MB}\,p\mathrm{CO_2}^{\mathrm{sw},i}$ is calculated as a residual, i.e. as the change in $p\mathrm{CO_2}$ that is not explained by other processes. Additionally, this study includes both coastal areas and deeper areas (the analysis is divided into a function of the system depth) between coastal (water depth < 50 m) and distal (water depth > 50 m) areas. Thus, MLD^i in distal areas (Table 3) was calculated and derived from the thermocline position that separates the SAW and the ENACW (71.3–96.8 m), while the coastal areas correspond to the depth of these areas (15–50 m).

2.4 Estimation of $\mathrm{CO_2}$ fluxes

Fluxes of $\mathrm{CO_2}$ across the sea–air interface were estimated using the following relationship:

$$F\mathrm{CO_2} = \alpha \cdot k \cdot (\Delta p\mathrm{CO_2})_{\mathrm{sea-air}}, \quad (10)$$

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

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

$$k = 0.251 \cdot u^2 (Sc/660)^{-0.5}, \quad (11)$$

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 $\mathrm{CO_2}$ in seawater and 660 is the Sc in seawater at 20 °C.

2.5 Statistical analysis

Statistical analyses were performed with IBM SPSS Statistics software (version 20.0; Armonk, New York, USA). The dataset was analysed using a 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 article 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 $p\mathrm{CO_2}$ during the eight cruises and Fig. 2 shows the underway distribution of SST and $p\mathrm{CO_2}$ in the Gulf of Cádiz. Among all the cruises, the SST values vary between 14.3 and 23.4 °C. During 2014, SST values were found to be higher than those in 2015 and 2016 (Table 1). For the whole period, the averaged values were highest during summer (21.0 ± 0.8 °C) and autumn (21.1 ± 1.2 °C), lowest during spring (15.5 ± 0.5 °C), and intermediate during winter (17.5 ± 0.6 °C). In general, 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). No substantial differences were found between the three transects studied (GD, SP and TF), although near the Guadalquivir river mouth and Cape Trafalgar (36.19° N, 6.03° W) 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 3 shows the mean value over the last 10 years of the maximum and minimum temperatures in the Gulf of Cádiz acquired by an oceanographic buoy (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); the mean values and standard deviations of the eight cruises are superimposed. It can be observed that the mean values for each cruise are within the range of variation of the typical temperature in the Gulf of Cádiz, and the mean temperature found (18.8 °C) is very close to the mean value obtained at the oceanographic buoy (19.2 °C, Fig. 3). Sampling during our cruises did not detect the highest temperatures occurring in the Gulf of Cádiz during August, which may indicate that the real range of pCO_2 variation is greater than that determined in this study.

Average values of SSS varied significantly among the cruises, ranging between 35.03 and 37.06. The highest mean values were recorded during February 2016 (36.44 ± 0.09) and lowest during September 2015 (35.64 ± 0.08) (Table 1). The lowest salinity value (35.03) and the most notable spatial variation (35.03–36.36) was observed during December 2014 in the area of the Guadalquivir river, associated with a period of storms with consequent major freshwater discharges. The area that presented the highest mean salinity value for the whole study was TF (36.19 ± 0.25).

During our study period, pCO_2 values ranged from 320.6 to 513.6 µatm. The highest values were recorded during summer and autumn of 2014 and 2015 (Table 1) with similar mean values, 411.6 ± 13.2 µatm and 410.6 ± 10.5 µatm, respectively, found for both seasons; the lowest mean value was logged during spring (382.5 ± 16.9 µatm), while winter presented an intermediate value (390.8 ± 15.4 µatm). These mean values are not significantly different and the standard deviations are high, indicating high spatial and inter-annual variability. In general, the pCO_2 tended to decrease with the distance to the coast (Fig. 2b). When comparing these values with pCO_2 values in the atmosphere, 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). In Fig. 2 a sharp variation of SST and pCO_2 can be observed in some zones that coincides with the stations where discrete water samples were taken. This may be due to the different sampling times at these stations, which varied between 2 and 8 h as a function of the depth of the system.

The database of this study includes the transition from coastal zones with depths of the order of 20 m to distal shelf waters with depths greater than 800 m. Figure 4 shows the general trend of the mean values of pCO_2 and SST for different intervals of depth of the water column based on the information obtained in the eight cruises. Although there is no statistical difference in pCO_2 or SST with bottom depth, 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 a depth of 100–200 m (396.1 ± 23 µatm). In addition, towards open waters (> 600 m) there is a progressive increase in pCO_2 and SST (404.3 ± 16.5 µatm and 20.1 ± 2.4 °C, respectively).

3.2 Discrete surface variables

Table 2 shows the average values and standard deviation for the underway averaged measurements of SST and SSS and for the discrete samples of pH, AOU, chlorophyll *a*, nitrate and phosphate at fixed stations along the three transects during the eight cruises. The pH presented significant differences among the cruises 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 and 2015, respectively (Table 2), coinciding with the highest average values of pCO_2 recorded (Table 1). The pH values for spring and winter were practically equal for 2014 and 2015 (8.08 ± 0.08 and 8.07 ± 0.05, respectively). AOU was significantly different between all the cruises but 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}). 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 general trend in the spatial variations in pH and AOU was found.

Chlorophyll *a* values presented significant differences among the cruises and between the same seasons of each year. This variable 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 (0.71 ± 0.46 µg L^{-1}), followed by winter (0.58 ± 0.33 µg L^{-1}) and

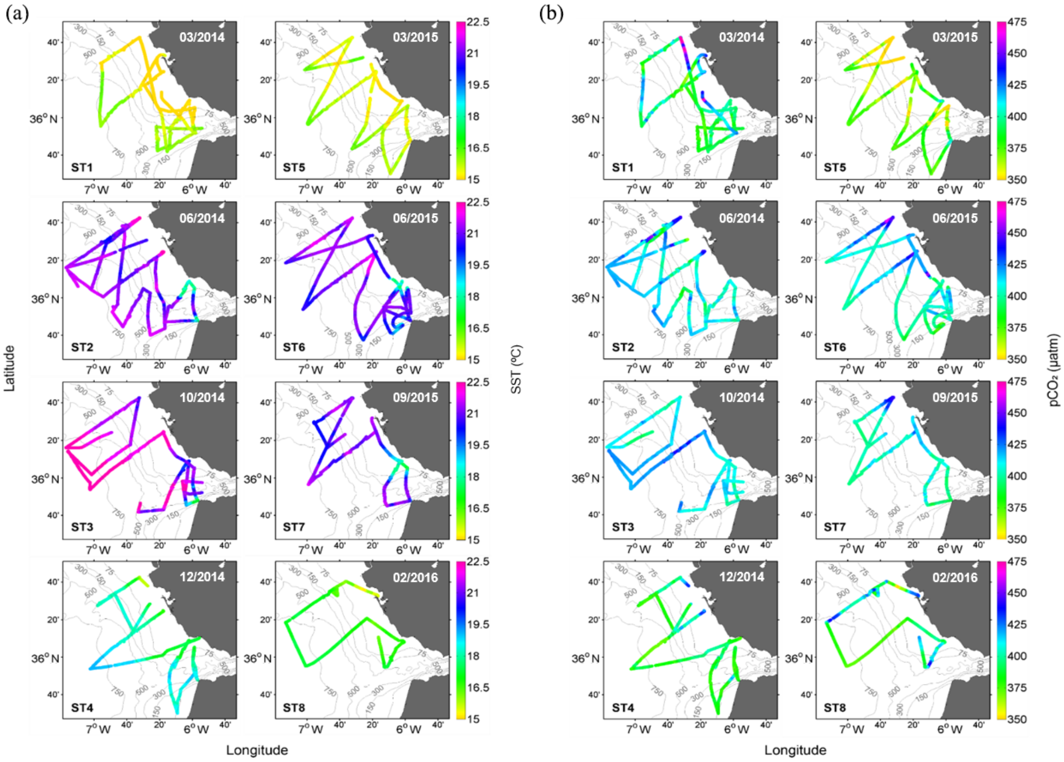

Figure 2. Underway distribution of sea surface temperature (SST (°C), **a**) and pCO_2 (µ atm, **b**) during the eight cruises in the Gulf of Cádiz: March 2014 (ST1), June 2014 (ST2), October 2014 (ST3), December 2014 (ST4), March 2015 (ST5), June 2015 (ST6), September 2015 (ST7) and February 2016 (ST8).

Table 2. Number of samples (n), mean values, and standard deviation for the averaged underway measurements of sea surface temperature (SST), sea surface salinity (SSS), pH, apparent oxygen utilization (AOU), chlorophyll a (data from González-García et al., 2018), and nitrate and phosphate in surface water samples (at depth of 5 m) at fixed stations during the eight 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	SST (°C)	SSS	pH	AOU (μmol L^{-1})	Chlorophyll a (μg L^{-1})*	Nitrate (μmol L^{-1})	Phosphate (μmol L^{-1})
ST1	18	15.2 ± 0.5	36.05 ± 0.13	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	21.6 ± 0.7	36.09 ± 0.28	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	36.03 ± 0.13	8.05 ± 0.05	7.7 ± 2.1	0.46 ± 0.33	1.05 ± 1.96	0.23 ± 0.09
ST5	16	15.4 ± 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 ± 0.03	7.94 ± 0.03	-2.6 ± 5.0	0.29 ± 0.31	0.37 ± 0.50	0.50 ± 0.55
ST8	6	16.8 ± 0.3	36.44 ± 0.04	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).

autumn (0.26 ± 0.30 µg L^{-1}), and the lowest value in summer (0.23 ± 0.25 µg L^{-1}). The SP transect presented the 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 the cruises, ranging between 0.00 and 1.93 µmol L^{-1}. The highest mean value was recorded in spring (0.82 ± 1.09 µmol L^{-1}) and the lowest in summer (0.25 ± 0.35 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. By season, the highest mean value was obtained during autumn (0.31 ± 0.30 µmol L^{-1}), although the average data in October 2014 (0.09 ± 0.03 µmol L^{-1}) were lower than that of 2015 (0.50 ± 0.55 µmol L^{-1}) (Table 2). The lowest mean value was ob-

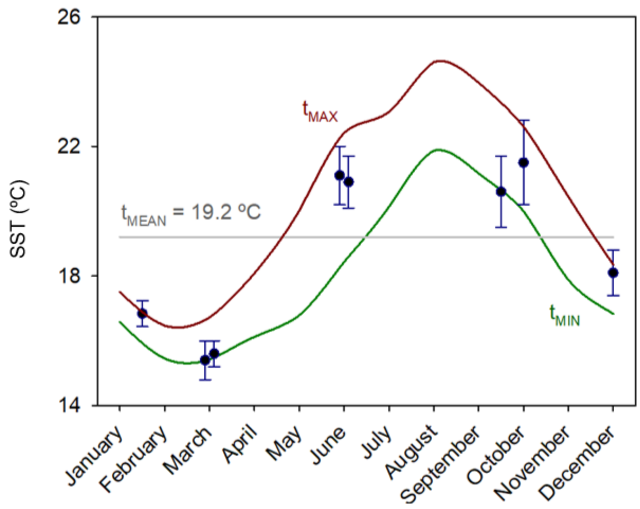

Figure 3. Maximum and minimum sea surface temperature (SST) variation during a 10-year period recorded by an oceanographic buoy located in the Gulf of Cádiz (36.48° N, 6.96° W). The red line shows maximum SST variation. The green line shows minimum SST variation. The grey line shows the average temperature 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.

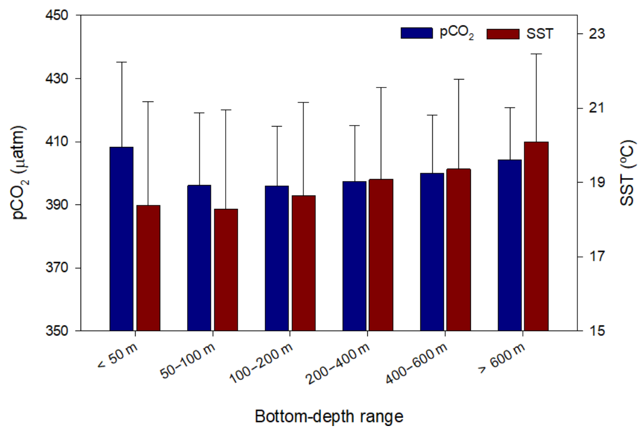

Figure 4. Underway variation in pCO_2 and sea surface temperature (SST) at different bottom-depth ranges of the water column (metres) during the eight cruises. The mean values and standard deviations of pCO_2 (blue) and SST (red) for each range of depth are represented. High standard deviations are associated with the seasonal and interannual variability for the whole sampling period.

served during summer ($0.10 \pm 0.05\,\mu mol\,L^{-1}$). The GD transect presented the highest mean value of the whole study ($0.28 \pm 0.39\,\mu mol\,L^{-1}$), and the lowest values were found in the TF and SP transects with similar values in each, $0.15 \pm 0.07\,\mu mol\,L^{-1}$ and $0.14 \pm 0.09\,\mu mol\,L^{-1}$, respectively. The mean N/P ratio in surface waters for the whole study was 3.5 ± 2.0, similar to that estimated by Anfuso et al. (2010) in the northeast continental shelf of the Gulf of Cádiz, which indicates a relative 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 deviations 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 $5.5 \pm 2.8\,m\,s^{-1}$ (March 2015) and $7.7 \pm 4.2\,m\,s^{-1}$ (December 2014). The gas transfer velocity varied between $6.9 \pm 0.1\,cm\,h^{-1}$ in March 2015 and $14.4 \pm 0.3\,cm\,h^{-1}$ in June 2015 since it is very sensitive to changes in wind speed. There was a slight seasonal variation in the CO_2 fluxes similar to pCO_2, because they are associated to the spatio-temporal variability and they present high standard deviations. The study area acted as a source of CO_2 to the atmosphere during summer and autumn (0.7 ± 1.5 and $1.2 \pm 0.9\,mmol\,m^{-2}\,d^{-1}$, respectively) and as a sink in spring and winter (-1.3 ± 1.6 and $-1.3 \pm 1.6\,mmol\,m^{-2}\,d^{-1}$, respectively).

4 Discussion

4.1 Thermal influence in pCO_2

Numerous research studies have determined that temperature is one of the most important factors that controls the variability in 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 in pCO_2 of $0.0423\,°C^{-1}$, equivalent to $16.9\,\mu atm °C^{-1}$ for experimental pCO_2 of 400 µatm. In our study, all data from all seasons together exhibited a linear relationship between pCO_2 and SST ($r^2 = 0.37$, Fig. 5a). This relationship becomes even 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, $4.80\,\mu atm\,°C^{-1}$, 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 in 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 ($5.03\,\mu atm\,°C^{-1}$, $r^2 = 0.42$) and a pCO_2 that ranged between 338 and 397 µatm. In 2003, Huertas et al. (2006) found variations in 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

Table 3. Mean values and standard deviations of mixed layer depth (MLD) in distal areas (depth > 50 m), atmospheric pCO_2 (pCO_2 µatm), wind speed, gas transfer velocity (k) and air–sea CO_2 fluxes for the underway measurements during the eight 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

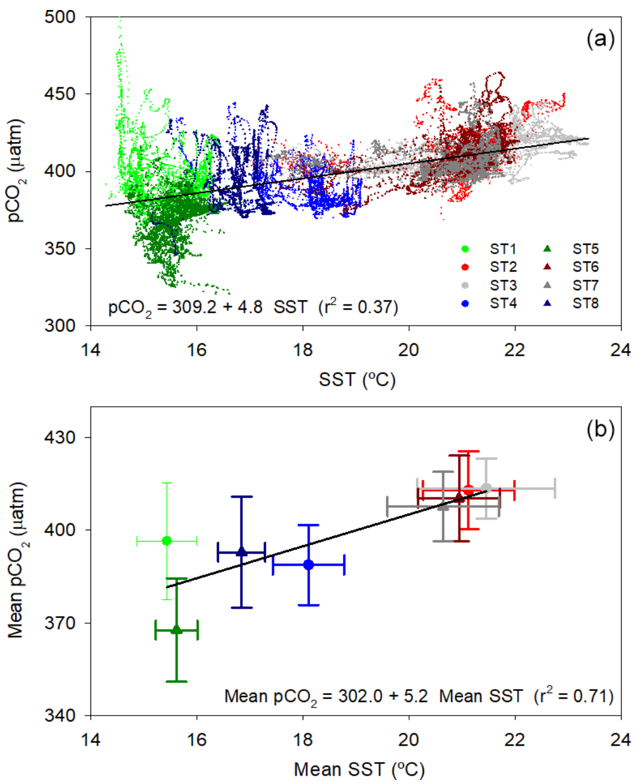

Figure 5. Dependence of pCO_2 with sea surface temperature (SST) for the complete underway database during all the cruises **(a)** and for the mean values of pCO_2 and SST for each cruise showing their standard deviations **(b)**. The solid line shows the linear correlation.

al. (2009) established a variation in 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).

When comparing the data given in 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 in pCO_2 during the last decade, even when 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 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 in pCO_2 of 38.3 ± 16.9 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 ($3.8 \pm 1.7\ µatm\,yr^{-1}$) exceeds the rate of increase in pCO_2 in the atmosphere ($2.3\ µatm\,yr^{-1}$ 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)). The cause of this increase could be a greater input of anthropogenic nutrients and inorganic carbon 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 (Borges and Abril, 2011; Cai, 2011). However, we do not have any additional evidence to confirm this effect in our area of study currently.

4.2 Non-thermal factors controlling pCO_2

In accordance with Olsen et al. (2008), Fig. 6 shows the decomposition of the variations in pCO_2 between cruises due to changes in SST, in air–sea CO_2 exchange, in SSS, in combined mixing and biology, and 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. The average time

Table 4. Range, mean and standard deviation of pCO_2, air–sea CO_2 fluxes (FCO_2) and T/B ratio found in different areas of the Gulf of Cádiz.

Site	° E	° N	Date	pCO_2 (µatm)	FCO_2 (mmol m^{-2} d^{-1})[a]	T/B	Reference
Strait of Gibraltar	−5.5 to −5.2	35.6 to 36.0	September 1997	352.8 ± 2.0 339–381	3 ± 8[b]	–	Santana-Casiano et al. (2002)
Gulf of Cádiz	−7.0 to −6.5	36.3 to 36.7	February 1998	360.2 ± 27.9 334–416	−19.5 ± 3.5[b]	–	González-Dávila et al. (2003)
Gulf of Cádiz	−8.3 to −6.0	33.5 to 37.0	July 2002	– 300–450	18.6 ± 4[b]	–	Aït-Ameur and Goyet (2006)
Northeastern shelf of the Gulf of Cádiz	−7.5 to −6.3	36.6 to 37.3	March 2003 to March 2004	– 130–650	−2.5–1.0[b]	–	Huertas et al. (2006)
Strait of Gibraltar	−6.0 to −5.2	35.8 to 36.1	September, December 2005; March, May 2006	– 320–387	−1.9–1.9[b]	2.4	de la Paz et al. (2009)
Northeastern shelf of the Gulf of Cádiz	−6.8 to −6.3	36.4 to 36.9	June, November 2006; February, May 2007	360.6 ± 18.2 338–397	−2.2–3.6[b]	1.3	Ribas-Ribas et al. (2011)
Gulf of Cádiz	−6.0 to −7.2	35.4 to 36.7	March, June, October, December 2014; March, June, September 2015; March 2016	398.9 ± 15.5 321–514	−2.3–1.5[c]	1.15	This work

[a] Gas transfer coefficient (k): [b] Wanninkhof (1992). [c] Wanninkhof et al. (2014).

between cruises is 86 ± 8 d, with the exception of the last period (between September 2015 and February 2016) that was 140 d. $d\,pCO_2^{sw}$ presents a similar variation between deep and coastal areas but with small differences in the mean values between the distal zones ($d\,pCO_2^{sw} = -3.4 \pm 28.9$ µatm) and the shallower areas ($d\,pCO_2^{sw} = 0.2 \pm 22.7$ µatm). The high standard deviations associated with this variable are due to the spatio-temporal variability in the database. In distal areas (Fig. 6), pCO_2 changes are mainly brought about by SST (−58.4–106.2 µatm) together with mixing and biological processes (−90.8–36.2 µatm). An inverse coupling is observed between $d_{SST}\,pCO_2^{sw}$ and $d_{MB}\,pCO_2^{sw}$ since with the increase in the system SST (increase $d_{SST}\,pCO_2^{sw}$) there is greater biological uptake of CO_2 (decrease $d_{MB}\,pCO_2^{sw}$). As reported in the studies of Olsen et al. (2008) and Omar et al. (2010), the changes produced by the air–sea CO_2 exchange are relatively small. Instead, in coastal areas (Fig. 6), the dominant effects on pCO_2 changes are produced by air–sea CO_2 exchange (−196.2 to 103.4 µatm) and mixing plus biology (−101.1 to 198.5 µatm). In regions with shallower mixed layers, the effect of air–sea exchange on the pCO_2 variation is larger (Olsen et al., 2008). A relative inverse coupling between the two factors was also observed; outgassing is produced (decrease $d_{AS}\,pCO_2^{sw,i}$) when the system receives greater inputs or production of CO_2 (increase $d_{MB}\,pCO_2^{sw}$). There is a different behaviour between the transition from spring to summer of 2014 (ST1 and ST2) and 2015 (ST5 and ST6) for $d_{MB}\,pCO_2^{sw}$, which 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 and 25.3 ± 10.2 m^3 s^{-1}, respectively). Changes in SSS do not have a substantial effect on pCO_2 during the whole period in both areas with a range of variation in $d_{SSS}\,pCO_2^{sw,i}$ between −11.3 and 11.0 µatm. This behaviour was also described by Olsen et al. (2008) in the subpolar North Atlantic, except for an area influenced by continental runoff where pCO_2 decreases.

In relation to the factors that affect the pCO_2 changes brought about by mixing and biological processes, a dependence between the mean values of pCO_2 and pH, AOU and the concentration of chlorophyll a has been observed at the fixed stations ($n = 126$, Fig. 7). AOU and pCO_2 show 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 or oxidation of the organic matter phytoplankton considering a Redfield-type relationship. Inverse relationships between pCO_2 and dissolved oxygen were also found in other studies of a continental shelf (Zhai et al., 2009; de la Paz et al., 2010; Xue et al., 2012, 2016). The pCO_2 and pH dependence 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 pH (Tsunogai et al., 1997; Shaw et al., 2014). The variation in pCO_2 with chlorophyll a (pCO_2 (µatm) $= 413 - 20.8$ [chlorophyll a] (µg L^{-1}), $r^2 = 0.14$) also shows the influence of the processes of photosynthesis and respiration (e.g. Cai et al., 2011; Clargo et al., 2015) with a slope value similar to that obtained in the study of Huertas et al. (2005) (pCO_2 (µatm) $= 274 - 19.6$ [chlorophyll a] (µg L^{-1}), $r^2 = 0.32$; $n = 28$). 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).

Something that could affect the distribution of pCO_2 in the Gulf of Cádiz (and could be considered to be part of mixing

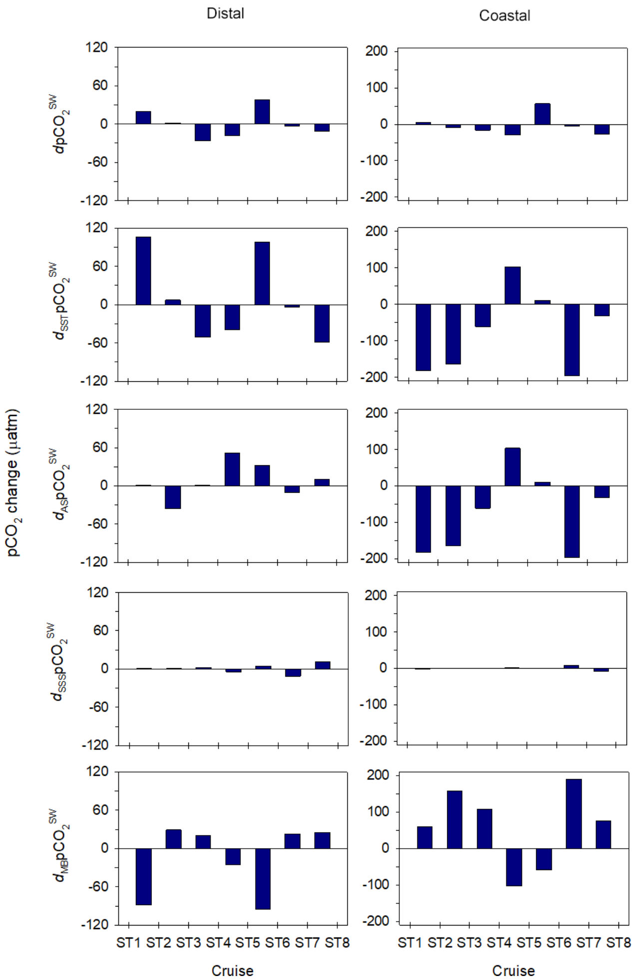

Figure 6. Observed changes in pCO_2 (first row) and pCO_2 changes broken down due to SST changes (second row), air–sea CO_2 exchange (third row), SSS changes (fourth row), and biology plus mixing (last row) in the distal (left column) and coastal areas (right column) between the periods of each cruise: 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).

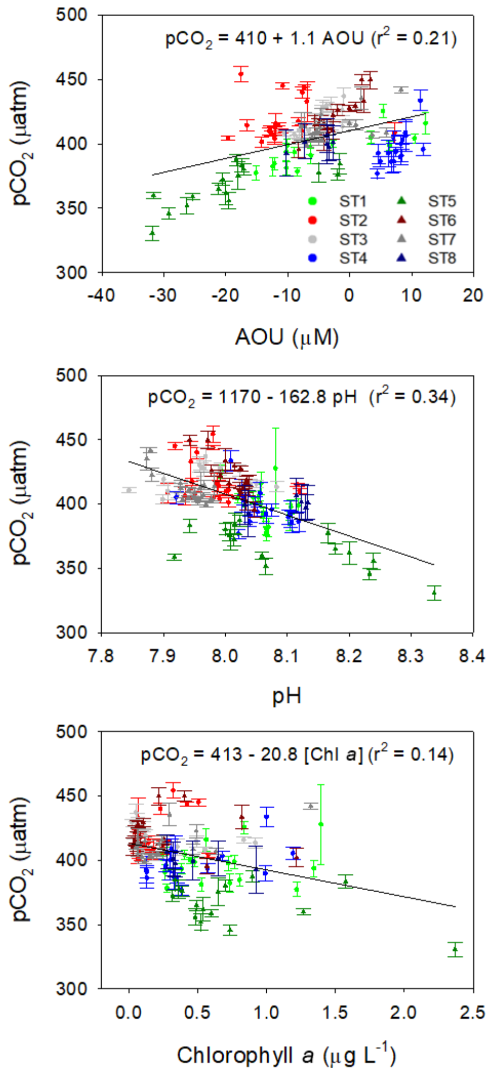

Figure 7. Relationships between the surface values of pCO_2 and apparent oxygen utilization (AOU), pH and chlorophyll *a* (Chl *a*) at the 16 discrete stations during the eight cruises. pCO_2 presents the standard deviation associated with the mean value obtained from the underway measurements.

and biology; sensu Olsen et al., 2008) is the vertical and lateral transport. For example, there 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 (Prieto et al., 1999; Vargas-Yáñez et al., 2002) and the other located between the Cape Santa María and the Guadalquivir river and more sensitive to meteorological forcing (Criado-Aldeanueva et al., 2006). In our database, experimental evidence of the upwelling was found only in the TF transect. A local decrease in the mean values of SST (17.4 °C) and pCO_2 (399.1 µatm) was observed in this coastal area of TF with respect to the deeper areas (18.8 °C and 405.1 µatm, respectively) for the whole period. 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 is a progressive increase in SST and pCO_2 with increasing depth of the system measured below 100–200 m (Fig. 4); this 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 on the variability in pCO_2 has been observed in other studies, such as the Gulf Stream in the southeastern continental shelf of the United States (Wang et al., 2005; Jiang et al., 2008) and the Kuroshio Current in the northern East China Sea (Shim et al., 2007).

Additionally, related to the lateral transport on the distribution of pCO_2 in surface waters, several authors have described the influence of the continental inputs. In general, the continental shelf as a whole acts as a sink of atmospheric CO_2 (e.g. Rabouille et al., 2001; Chen and Borges, 2009), whereas the coastal zone is usually oversaturated with CO_2 (Fig. 4). This behaviour has been described in other systems, including the southern part of the Yellow Sea (Qu et al., 2014), the southwestern part of the Atlantic Ocean (Arruda et al., 2015), 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 derive 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 inorganic carbon, 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. 2b. The highest values of pCO_2 (up to 500 µatm) were observed during March 2014 in the zone close to the Guadalquivir river mouth, 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 July 2018). In contrast, the lowest values of pCO_2 were recorded in spring of 2015 in this zone (as low as 320 µatm) in a period of drought (flow rate 20 $m^3 s^{-1}$) and subject to intense biological activity associated with the highest value found for the concentration of chlorophyll *a* (2.4 $\mu g L^{-1}$). 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, Sancti Petri Channel and the Río San Pedro tidal creeks (de la Paz et al., 2008a, b; Burgos et al., 2018).

Moreover, in the coastal zone another source of CO_2 results from the net production of inorganic carbon derived from the processes of remineralization of the organic matter in the surface sediments originating from the continuous deposition of organic matter through the water column (de Haas et al., 2002; Jahnke et al., 2005). The intensity of this effect decreases towards offshore areas since the influence of primary production and the continental supplies on the deposition of the particulate organic matter are less (Friedl et al., 1998; Burdige, 2007; Al Azhar et al., 2017), which could be related to the greater effect determined by the mixing and biology processes in the coastal areas using the Olsen et al. (2008) method. 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. This flux of DIC is equivalent to a CO_2 flux of 198 ± 80 µmol C $m^{-2} d^{-1}$ through the sediment–water interface when considering a well-mixed water column, a pH of 8, 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 through the program CO2SYS (Lewis et al., 1998). Moreover, this estimated CO_2 benthic flux would produce an increase in pCO_2 of 0.25 ± 0.10 µatm d^{-1} in the water column.

4.3 *T/B* ratio

In this study, the total T/B ratio is 1.15, which indicates that the thermal effect is an important factor controlling intra-annual variation in 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 8 presents the values of the T/B ratio grouped in different bottom-depth intervals of the water column in the system. The variations found in non-thermal ΔpCO_2 and thermal ΔpCO_2 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 a value of 1.1 is found. Qu et al. (2014) also reported the variation in the values of the T/B ratio with the distance from the coast in the southern Yellow Sea: between 0.4 and 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 in the T/B ratio is largely caused by the variations in ΔpCO_2 non-thermal effects, which are observed to decrease from the coast to the deeper zone regardless of which method is used (Takahashi et al., 2002; Olsen et al., 2008). High values of non-thermal ΔpCO_2 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 in the T/B ratio and the decrease in non-thermal ΔpCO_2 (75 µatm) from the coastal zone to the central part of the Gulf of Cádiz are associated with the variations in 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 greater than 200 m and do not explain the

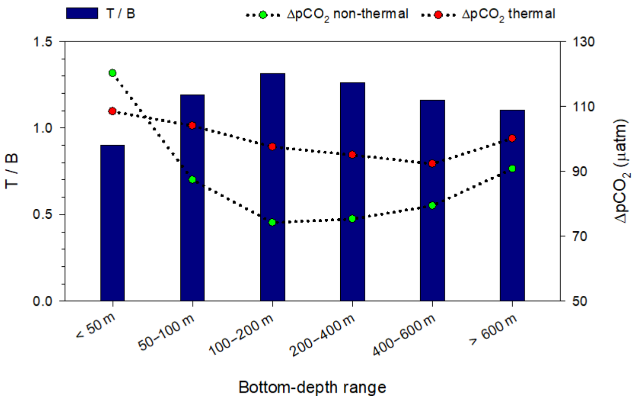

Figure 8. Variation of the T/B ratio (blue bar), non-thermal ΔpCO_2 (green point) and thermal ΔpCO_2 (red point) at different bottom-depth ranges of the water column (metres) for the eight cruises.

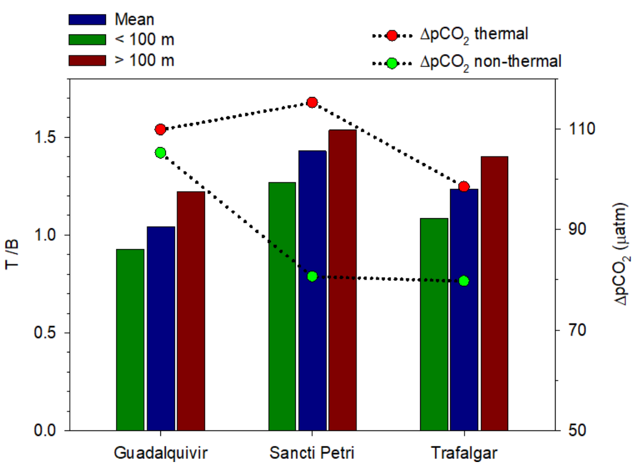

Figure 9. Variation of the T/B ratio (blue bar), the T/B ratio at depths < 100 m (green bar), the T/B ratio at depths > 100 m (red bar), and ΔpCO_2 non-thermal effects (green point) and ΔpCO_2 thermal effects (red point) on the three transects of the study (Guadalquivir, Sancti Petri and Trafalgar) during the eight cruises.

decrease in the T/B ratio and the increase in non-thermal ΔpCO_2 (90.7 µatm) in waters with bottom depth greater than 400 m. These variations have been associated with the change in the origin of the surface water masses. 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). The deepest zone is under the influence of a branch of the Azores Current, which is 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 favour the accumulation of CO_2 in this area as a convergence zone (Ríos et al., 2005).

The T/B ratios have also been calculated for the different transects at right angles to the coast, as shown in Fig. 9. The T/B ratio increases with the distance from the coast for the three transects and 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 GD and 1.4 in SP and an intermediate value of 1.2 in the TF zone. These variations are related to changes in the biological activity and the presence of coastal upwelling. 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 non-thermal ΔpCO_2. In particular, coastal waters near the mouth of the Guadalquivir river show 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 emerging water masses could be related to the relatively low values of thermal ΔpCO_2 found in this zone; in fact, the mean temperature in this area 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 thermal ΔpCO_2 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).

4.4 Ocean–atmosphere CO_2 exchange

In the Gulf of Cádiz, the air–sea flux of CO_2 exhibits a range of variation from −5.6 to 14.2 $\text{mmol m}^{-2}\text{ d}^{-1}$. These values are within the ranges observed by other authors in different areas of the Gulf of Cádiz (Table 4). As can be seen in Fig. 10, seasonal and spatial variations were observed in the air–sea fluxes 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 discussed above for pCO_2, temperature change is one of the principal factors that controls the fluxes of CO_2. In fact, for each cruise, a linear and positive relationship was found between the mean values of the CO_2 fluxes and SST ($r^2 = 0.72$, 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) as a consequence of the biological utilization of the CO_2 and the subsequent tendency for CO_2 undersaturation (Qin et al., 2014). Such relationships have also been found in various studies carried out in zones

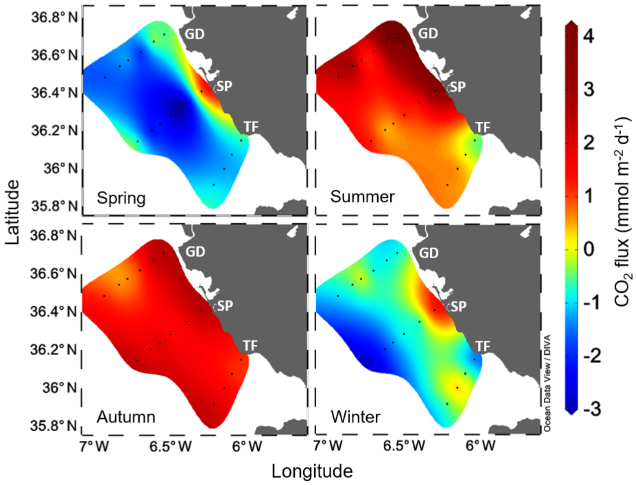

Figure 10. Spatial distribution of mean values of air–sea CO_2 fluxes in the eastern shelf of the Gulf of Cádiz at the 16 discrete stations during spring (ST1, ST5), summer (ST2, ST6), autumn (ST3, ST7) and winter (ST4, ST8).

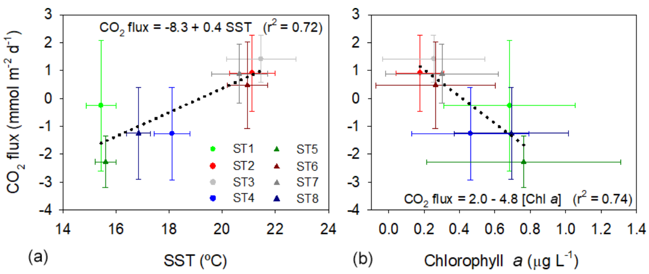

Figure 11. Correlations between the mean values of air–sea CO_2 fluxes and sea surface temperature (SST) for the underway database **(a)** and the CO_2 fluxes and chlorophyll *a* (Chl-*a*) at the 16 discrete surface stations **(b)** for each cruise and showing the standard deviations.

similar to the area studied (Zhang et al., 2010; Arnone et al., 2017; Carvalho et al., 2017).

The air–sea fluxes of CO_2 in the Gulf of Cádiz tend to decrease with the distance from the coast (Fig. 10). The coastal zone (< 50 m) presents a mean air–sea CO_2 flux of $0.8 \pm 1.8\,\text{mmol m}^{-2}\,\text{d}^{-1}$ that reduces progressively to reach a value of $-0.3 \pm 1.6\,\text{mmol m}^{-2}\,\text{d}^{-1}$ in open waters with bottom depth greater than 600 m. However, these differences are not statistically significant because of the high standard deviations associated with the seasonal variations. This dependence of the air–sea CO_2 fluxes with distance from the coast has also been reported in other systems, such as in the South Atlantic Bight of the United States (Jiang et al., 2008), in the southwestern 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 in 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 air–sea 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 ($1.39\,\text{mmol m}^{-2}\,\text{d}^{-1}$) and the zone comprising the rest of the shelf acts as a sink ($-0.44\,\text{mmol m}^{-2}\,\text{d}^{-1}$).

In addition, on both the GD and SP transects a decrease in the air–sea 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 ($-0.4 \pm 1.2\,\text{mmol m}^{-2}\,\text{d}^{-1}$) and the deeper zone is a weak source of CO_2 to the atmosphere ($0.3 \pm 1.3\,\text{mmol m}^{-2}\,\text{d}^{-1}$), although these variations are not statistically significant due to the seasonal variability associated with the values. This finding can be explained by the presence of an upwelling close to the coast that is likely to be causing an increase in 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 ($0.63 \pm 0.43\,\mu\text{g L}^{-1}$ and $1.09 \pm 0.77\,\mu\text{mol L}^{-1}$, respectively) and in deeper zones ($0.17 \pm 0.12\,\mu\text{g L}^{-1}$ and $0.32 \pm 0.33\,\mu\text{mol L}^{-1}$, respectively).

The Gulf of Cádiz carbon flux, during the sampling period, shows a mean rate of $-0.18 \pm 1.32\,\text{mmol m}^{-2}\,\text{d}^{-1}$ even though it is necessary to consider the intrinsic variability in the database that generates a high standard deviation. With the total surface of the study area ($52.8 \times 10^2\,\text{km}^2$) and the mean annual flux during the eight cruises, the uptake capacity estimated for the Gulf of Cádiz will be $4.1\,\text{Gg C yr}^{-1}$. 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 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

A high variability in pCO_2 in the Gulf of Cádiz was observed which is associated with its location as a transition zone between coastal and shelf areas, superimposed on the usual seasonal variation due to thermal and biological effects. The mean value of pCO_2 found in this study ($398.9 \pm 15.5\,\mu\text{atm}$) indicates that the Gulf of Cádiz could be slightly undersaturated in CO_2 with respect to the atmosphere ($402.1 \pm 3.9\,\mu\text{atm}$). The spatio-temporal variation in pCO_2 found responds to the influence of different factors that usually affect its distribution in the littoral oceans. The temporal variability in pCO_2 is principally explained by two factors, considering the mean values of the eight cruises: SST (pCO_2 (µatm) =

$302.0 + 5.16\,\text{SST}$ (°C), $r^2 = 0.71$) and biological activity, represented by chlorophyll a (pCO$_2$ (µatm) $= 425.0 - 59.15$ [chlorophyll a] (µg L^{-1}), $r^2 = 0.76$). Over and above these general tendencies, there are spatial variations associated fundamentally with other processes. Firstly, the dominant effects in the shallower areas are also due to the continental inputs, the biological activity and the air–sea CO_2 exchange. Then pCO$_2$ values diminish progressively in line with increasing distance from the coast, out as far as an approximate depth of some 400 m. There is a relative increase in SST and pCO$_2$ as a 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) of the region suggests that the distribution is principally controlled by temperature changes. However, the situation is more complicated if the ratio is considered a function of bottom depth, which is associated with the existence of non-thermal processes. 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 in 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 SP transect, where values of up to 1.54 are obtained for depths greater than 100 m, probably related to the greater effect of thermal processes.

The annual uptake capacity of CO_2 by the surface waters in our study area is 4.1 Gg C yr^{-1}. The air–sea 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. 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 since the pCO$_2$ has increased from 360.6 ± 18.2 µatm in a study realized between 2006 and 2007 (Ribas-Ribas et al., 2011) to 398.9 ± 15.5 µatm in actuality and this exceeds the rate of increase in pCO$_2$ in the atmosphere (2.3 µatm yr^{-1} for the last 10 years).

Data availability. All data used in this study are compiled in Tables 1, 2 and 3. Research data are not yet deposited in a public data repository.

Author contributions. DJL wrote the article with contributions from AS, TO and JF. DJL and JF processed the experimental data. DJL, TO and JF conceived the original idea. All authors contributed to collecting the data.

Competing interests. The authors declare that they have no conflict of interest.

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