Dear Editor:

The authors are very grateful to the three anonymous reviewers for their constructive comments and suggestions in the previous version. We have addressed the reviewers' annotations and revised carefully the manuscript in order to improve our work. In this revised version, several mistakes pointed out by the reviewers have been corrected. We think that the manuscript has been significantly improved thanks to all the contributions made.

Below you will find the comments they made and our comments as authors (marked AC) on each point. In response to all the comments the manuscript has been modified, resulting in changes to line numbers. Therefore, we have included the new line numbers (whenever applicable) so that you can refer to either the current or (former) version if you wish.

Thank you very much for your consideration.

Sincerely,

Dolores Jiménez-López, on behalf of all co-authors.

*** Reviewer 1:**

Jiménez-López et al. discuss spatio-temporal variability of pCO_2 in the Gulf of Cádiz based on a new dataset collected between March 2014 and February 2016. These results will eventually help to better understand carbon cycle processes on continental shelves and their contribution to the global carbon cycle. And although the authors discuss many different and interesting local features, the submitted manuscript lacks clarity and should be revised and restructured before publication.

- ***General comments***

The separation of the driving mechanisms of pCO_2 into temperature and biological effects follows the line of argumentation of Takahashi et al. (2002), however, the authors actually calculate thermal and non-thermal components of pCO_2 (e.g. Landschützer et al. (2015)). This is also stated by the authors themselves (Line 161 or 372), but not implemented or followed in their discussion, which is a consequence of the fact that the wording in the method section 2.3 is almost identical to the description of the method in Takahashi et al. (2002) (but not cited as such). Especially in the continental shelves, complex interactions of air-sea gas exchange, primary production, lateral and vertical transport, entrainment of high-DIC waters from below, anthropogenic runoff and freshwater addition lead to changes in salinity, DIC and alkalinity and thereby affect the non-thermal trend in pCO_2. Moreover, the authors show seasonality, which they attribute to temperature and biological effects only, while at the same time, they discuss how, e.g., river runoff changes in magnitude over the year and thereby affects pCO_2. Although the authors present many different drivers of pCO_2 variability, they go back in the temperature-biology framework, which is inconsistent and difficult to follow.

The discussion section needs to be restructured accordingly. First, only results of the 8 cruises should be interpreted without repeating the results. Second, the results should be put in context with previous studies that took place in the same study area and its vicinity; here, it is crucial to include the reference years and seasons. And last, the findings for the Gulf of Cádiz may be compared to other continental shelf areas in the North Atlantic and globally. At the moment, the authors list many results, in the result and discussion section, with little interpretation and no clear line of argumentation that leads to the presented conclusion.

AC: Thank you very much for your suggestions. We have changed the terms "temperature and biological effects" to "thermal and non-thermal" components of pCO_2. In addition, we have determined the contribution of SST, air-sea CO_2 exchange and mixing plus biological processes to the changes of pCO_2 using the Olsen et al. (2008) method (suggested by the reviewer 3). This quantification appears in the Material and methods (Line 174-191) and Discussion sections (Line 374-391) and a new figure has been added (Fig. 7).

The Discussion section has been modified following your suggestions. Firstly, some Discussion paragraphs are moved to the Results section (Line 223-229 and Line 244-249). Second, in the Discussion, the results are considered in the context of previous studies of the same area (including references to years and seasons) and then in the context of studies of other continental shelf areas. And last, Table 4 has been removed, and Table 5 is now Table 4, in which only studies of the Gulf of Cádiz are included.

- ***Specific comments***

Line 74: If previous studies have already determined the sink strength of the Gulf of Cádiz, seasonally driven by temperature and biology, what is the added value of your study? I am missing a clear motivation for this manuscript in the introduction.

AC: Thank you very much for your suggestion. We have included the following in the text to explain the added value that our study provides:

Line 73-77: "It has also been possible to estimate the influence that various sea surface currents have on pCO_2 variability, since this study considers deeper areas than previous works. Therefore, we can analyse the change that has occurred in relation to the CO_2 uptake capacity in the Gulf of Cádiz in the last 10 years, in comparison with other studies that analyse the seasonal variation underway of pCO_2 in this area (Ribas-Ribas et al., 2011)".

Line 84 / Figure 1: Add bathymetry. Add position of river Guadalete and the tidal creeks and the position of cape San Vicente. You may want to add a circulation scheme here that would help to visualise the surface circulation here.

AC: We followed your suggestions and edited Fig. 1. However the tidal creek named "River San Pedro" could not be added due to its small dimension compared to the rivers Guadalquivir and Guadalete.

Line 110: Do the transects cover different water masses or circulation features?

AC: Yes, the shallower stations of the different transects are influenced by the Gulf of Cádiz Current and the deeper stations (about 300 m approximately) by the Azores Current. In Fig. 1 the circulation scheme of the study area is illustrated.

Line 133: How do you correct the temperature difference?

AC: Corrections between the equilibrator and SST were made following the method of Takahashi et al. (1993). The sentence has been edited in the text.

Line 127-129: "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 ºC".

Line 144: How was the oxygen sensor calibrated? Confusing to first explain how AOU is derived, without a detailed description of how oxygen values were determined.

AC: This point is now clarified and added in the text.

Line 134-138: "Dissolved oxygen values were obtained with the sensor of the rosette (SeaBird 63) pre-calibrated using Winkler titration (±0.1 µmol L^{-1}) of samples collected from several water depths at selected stations (Parsons et al., 1984). Apparent Oxygen Utilization (AOU) was determined as the difference between the solubility calculated applying the expression proposed by Weiss (1974) and the experimental values of dissolved oxygen".

Line 150: Why unit "mile"? Why is exactly 0.5 mile chosen? What is the distance between two stations? Particularly in the SP section, could there be an overlap in pCO_2 data for calculating the mean? If there is a CTD coupled to the rosette-sampler, why are not discrete SST and SSS data used for each station and compared / evaluated to the underway SST / SSS measurements?

AC: We have used the unit “mile” to facilitate our estimation of transit times between the sampling stations.
The mean distance between stations was set at 5 miles from the beginning, and then 0.5 mile constitutes approximately 10% of this distance.
The mean pCO_2 of the study was not calculated using the discrete values, but by the underway measurements. In any case, we have reviewed the manuscript and the data and we have observed that the SP7 station represented in the previous Fig. 1 is not included in the results presented in the Table 2. This station was removed in the new Fig. 1.

SST and SSS data for each station and for the underway measurements were compared and they do not show differences greater than 0.04 ºC and 0.01 units, respectively. This point was clarified and added in the text: Line 146-148: “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 ºC and 0.01 units, respectively”. Moreover, the discrete values obtained through the underway measurements of SST and SSS were used because they are necessary in subsequent calculations.

Line 200: How can there be no spatial and seasonal variation in SSS, when there are freshwater inputs through storms and rivers?

AC: Spatial variation was only observed in the area of the Guadalquivir River related with a storm period that led to very heavy freshwater discharges during December 2014 (Line 230-231).

Line 212: In which zones exactly? If sharp pCO_2 variations are observed that coincide with discrete sampling stations, could that be related to the sampling strategy (e.g. potential sampling of ship exhaust) and not be a real signal? Do you correct for this? How can the sampling time be depth-dependent if only discrete samples were taken at 5m depth (Line 135)?

AC: The sampling time in each station was variable because water samples were taken at different depths of the water column with Niskin bottles, which were mounted on a rosette-sampler, although in this study we use only the “surface” sample at 5 m. In addition, as these cruises were multidisciplinary, the sampling time was dependent on the various activities carried out in each station. For example, at some stations, this activity could take up to 8 hours due to the sampling of zooplankton where a bongo and neuston net and/or multinet was used. Studies such as those of Sierra et al. (2017a, 2017b), González-García et al. (2018) are examples of these cruises and the other activities carried out here.
This sentence is now clarified in the text: Line 239-241: “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 time at these stations, which varied between 2 and 8 hours in function of the depth of the system”.
Additionally, we have observed some instability of the underway measurements of pCO_2 in the areas that coincide with the position of the discrete water samples (Fig. 1), due to changes in the flow pump of the ship when its dynamic positioning was functioning.

Line 220-228: Are there no spatial differences in pH and AOU?

AC: There are some spatial differences in pH and AOU, although a general trend was not observed. They seem related more to the intensity of local processes, such as continental inputs through the River

Guadalquivir, increase of the primary production in coastal areas, influence of the upwelling in Trafalgar and relative change in the intensity of the surface currents.
A short sentence is now added in the text: Line 259: “No general trend in the spatial variations of pH and AOU was found”.

Line 258: Is it truly equivalent? 17.4 µatm C^{-1} divided by 400 µatm results in $0.0435C^{-1}$.

AC: Our apologies, the correct value is 16.9 µatm $ºC^{-1}$. This has been rectified in the manuscript (Line 289). Thank you for drawing this to our attention.

Line 265: It is not clear to me, why table 4 is useful. Clearly, local effects and seasonality impact pCO_2-SST relationships, but they are not discussed or put in perspective with the results of the Gulf of Cádiz.

AC: Yes, you are right. We have removed Table 4, and we have discussed in the text certain relationships and seasonal variations found in other studies.

Line 290: The larger trend in pCO_2 in the ocean than in the atmosphere can be driven by

AC: We are sorry, but we think that this suggestion is not complete. In any case, this sentence has been clarified in the manuscript: Line 311-314: “This suggests a possible increase of the anthropogenic nutrient and C inputs from land (Mackenzie et al., 2004) since the direction and magnitude of estuarine and continental shelf CO_2 exchange with the atmosphere is highly dependent on the terrestrial organic budget and nutrient supplies to the coastal ocean (Borges and Abril, 2011; Cai, 2011)”.

Line 300-305: There is no statistical difference in pCO_2 or temperature with bottom depth, which might be because Figure 5 shows data from all seasons and years.

AC: Yes, you are correct. With this figure, we want to show only the general trend of pCO_2 and SST at different intervals of depth of the water column through offshore areas. Fig. 5 has been modified to Fig. 4, and this paragraph moved to Results, now Line 242-247.

Line 362: You only show the relationship between AOU or pH and pCO_2 but there is no discussion of it. Why is almost the entire study area over different seasons oversaturated in oxygen?

AC: This point is now explained and discussed better in the following paragraph of the text (Line 361-373). The oversaturation in oxygen may be due to the influence of two factors: the first is, greater photosynthetic activity in the area throughout the year (González-García et al., 2018) and the air injection processes responsible for an mean increase of 7µmol L^{-1} in the surface waters of the ocean (Sarmiento and Gruber, 2006).

Line 377: total or mean T/B. The T/B ratios by Ribas-Ribas et al. (2011) and de la Paz et al. (2009) have been estimated for which years or seasons?

AC: It is total T/B. Years and seasons of these studies are included in Table 4, and in the text we have included a notification to refer to this table.

Line 382: How does the DIC flux from the sediment affect T/B?

AC: Benthic DIC flux is another source of inorganic carbon that increases the CO_2 concentration in the water column, which would affect the increase of CO_2 non-thermal.

Line 385: What is the cause for ΔpCO_2bio variations over depth?

AC: The variations of ΔpCO_2bio (now modified to ΔpCO_2 non-thermal) observed with respect to the system depth are due to the influence of several processes. In areas close to the coast there is an increase of ΔpCO_2non-thermal due to continental inputs, greater primary production and the remineralization of the organic matter in the sediment. In the central area, there is a decrease of these 3 processes. And in the deepest areas, there is an increase of ΔpCO_2 non-thermal with the change in the origin of the surface currents.
This point clarified in the text, Line 404-419.

Line 389: If ΔpCO_2temp and bio are calculated as a seasonal amplitude, what temperature and chlorophyll values are used to establish the dependency here? Are these annual means (same for Figure 8 A and B). In any case, I do not understand how the thermal component in relation to temperature and the non-thermal component in relation to chlorophyll confirms the importance of different processes on pCO_2 variation.

AC: Temperature and chlorophyll values used to establish the dependency are the mean values of the 8 cruises for each of the discrete sampling stations.
Following the suggestions of other reviewers, Fig. 8 was removed and the importance of different processes on pCO_2 variation was calculated by a different method (Olsen et al., 2008), (Line 374-391 and Fig. 7).

Line 397: How can the surface chlorophyll and nutrients be constant, when there is a large gradient with distance to the coast (Line 395)?

AC: Thank you for this question. There was a mistake in the text and it has been corrected (Line 410). We wanted say that chlorophyll-a and nutrients concentrations decrease exponentially with the depth system, but their values are relatively constant in waters with bottom-depth higher to 200 m.

Line 405: Are the T/B ratios for the different transects significantly different from each other?

AC: T/B ratios for the different transects are not associated with a standard deviation since they are calculated as total ratios, so is not possible to determine significant differences between transects.

Line 422: Again, why is table 5 helpful? I understand that there are many studies that evaluate shelf area processes in the North Atlantic, but this is not discussed in the manuscript. It appears more as a list of literature than it helps to put you own results in perspective.

AC: Yes, you are right. Table 5 is now Table 4 and following your suggestion it has been modified. In this table only the studies carried out in the Gulf of Cádiz are included, and these are also discussed in the manuscript. Other general studies are also discussed in the text where relevant.

Figure 3: Panels should have the same size; panel B should next to or below panel A. Add linear correlation equation including units for both panels.

AC: Corrected.

Figure 6: Why are there 2 regression lines plotted for AOA-pCO_2?

AC: Corrected.

Figure 7 / 9: What are the uncertainties of the thermal and non-thermal components? Are they significantly different from each other?

AC: T/B is a total ratio, so it is not associated with a standard deviation; nor is it possible to determine significant differences between components either. Figure 9 is now Figure 8.

Figure 10: You could change the colourbar; it is not clear where the border between outgassing and uptake is located.

AC: The border between outgassing and uptake is shown in yellow now (Fig. 10).

You could simply state in section 2.5. that all reported linear correlations are statistical significant with p-values smaller than 0.05 in the entire manuscript unless indicated otherwise. With that, you do not have to report the p-value again. There a numerous linear relationship equations in the manuscript without units. The correlation equations could be plotted within the according figures to increase readability.

AC: Corrected, thank you for your suggestions.
Section 2.5 modified, Line 207-209: "The threshold value for statistical significance was taken as $p < 0.05$. Moreover, all reported linear correlations are type I and they are statistically significant with p-values smaller than 0.05 in the entire manuscript unless indicated otherwise".
Units in the linear relationship are included in the text.
Correlation equations have been plotted within the figures but without units, since there is insufficient space (Fig. 5, 6 and 11).

Please have colour blind people in mind for all figures. It is not possible to differentiate between years with the presently used lighter / darker colours; you could use different symbols as well.

AC: Fig. 5, 6 and 11 have were modified using different symbols.

Abbreviations that are only used in one paragraph only are superfluous; for example EBUS. Consider abbreviating T by SST and and S by SSS for readability.

AC: These suggestions have been considered in the text.

The manuscript will benefit from the input of a native speaker. There is a need to check for incomplete sentences and the use of correct tenses. There should be fewer, but longer paragraphs that consist of more than one or two sentences; while covering the same topic. This will make it easier to follow clear arguments.

AC: A native speaker with experience of scientific papers has revised the manuscript again.

References:

González-García, C., Forja, J., González-Cabrera, M. C., Jiménez, M. P., and Lubián, L. M.: Annual variations of total and fractionated chlorophyll and phytoplankton groups in the Gulf of Cádiz, Sci. Total Environ., 613, 1551–1565, https://doi.org/10.1016/j.scitotenv.2017.08.292, 2018.

Olsen, A., Brown, K. R., Chierici, M., Johannessen, T., Neill, C.: Sea-surface CO_2 fugacity in the subpolar North Atlantic, Biogeosciences, 5, 535-547, https://doi.org/10.5194/bg-5-535-2008, 2008.

Sierra, A., Jiménez-López, D., Ortega, T., Ponce, R., Bellanco, M. J., Sánchez-Leal, R., Gómez-Parra, A., and Forja, J.: Spatial and seasonal variability of CH_4 in the eastern Gulf of Cadiz (SW Iberian Peninsula), Science of the Total Environment, 590, 695-707, 2017a.

Sierra, A., Jiménez-López, D., Ortega, T., Ponce, R., Bellanco, M. J., Sánchez-Leal, R., Gómez-Parra, A., and Forja, J.: Distribution of N_2O in the eastern shelf of the Gulf of Cadiz (SW Iberian Peninsula), Science of the Total Environment, 593, 796-808, http://dx.doi.org/10.1016/j.scitotenv.2017.03.189, 2017b.

Sarmiento, J. L., and Gruber, N.: Ocean biogeochemical dynamics. Princeton Univ. Press., 2006.

*** Reviewer 2**

In general, the manuscript is written with too many very short paragraphs.

AC: An experienced native speaker revised the manuscript again to ensure that pargraph lengths are appropriated to the content and style, and generally to improve the manuscript.

The topic of the presented research is interesting and pertinent in the actual context of climate change. The title is very appealing and the reader expects to learn about the processes that control the pCO_2 variability in the eastern Gulf of Cadiz. Unfortunately, the abstract does not reveal any factor controlling the pCO_2 variability. The conclusion indicates that: "temperature and biological activity are the two principal factors that explain the temporal variability of CO_2". This is the case everywhere in the ocean. There is nothing new here! Then (line 470), it is indicated that: ": : : the distribution is principally controlled by the temperature". Here again, there is nothing new and this is normal.

Therefore, I would suggest the authors to change the title of their manuscript to more accurately reflect its content.

AC: Thank for your suggestion. The title has been modified to "pCO_2 variability in surface waters of the eastern Gulf of Cádiz (SW Iberian Peninsula)".

The authors should also precise (and justify) what kind of linear regression (type I, type II, : : :) they did in order to determine the general trends.

AC: We have added the kind of linear regression in the text (type I, Line 208).

They should also detail all their calculations (including simple ones such as the mean capture capacity, : : :).

AC: The mean capture capacity is calculated using the total surface of the study area ($52.8\cdot10^2$ km^2) and the mean annual flux during the 8 cruises (-0.18 mmol m^{-2} d^{-1}). This detail is now added in the manuscript (Line 466-467). Another calculation not indicated in the text and that may be of interest is the mean benthic flux of CO_2 (Line 342), which is calculated making certain assumptions that are stated in the text (Line 343-346).
The last sentence should be re-written to me more precise (what means ": : :variability of CO_2: : :"; is it TCO_2, CO_2 flux, pCO_2???; what means ": : :capacity of CO_2 capture: : :"; surface/depth, on what timescale?). The manuscript will gain in clarity if it were much concise.

AC: This final paragraph has been modified to give more clarity. Line 491-494: "The annual uptake capacity of CO_2 by the surface waters in our study area is 14.9 Gg C $year^{-1}$. The CO_2 fluxes present seasonal variation: these waters act as a source of CO_2 to the atmosphere in summer and autumn and as a sink in winter and spring. 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".

There is a need to remove some of the tables and figures.

AC: Thank you for your suggestion. Fig. 8 and Table 4 have been removed. Table 5 is now Table 4 and only includes studies in the Gulf of Cádiz. Fig. 1 has been improved.

In summary, this manuscript needs a major revision before publishing.

AC: Agreed. We hope the substantial revisions we have made to the manuscript now make the paper suitable for publication.

References:

Olsen, A., Brown, K. R., Chierici, M., Johannessen, T., Neill, C.: Sea-surface CO_2 fugacity in the subpolar North Atlantic, Biogeosciences, 5, 535-547, https://doi.org/10.5194/bg-5-535-2008, 2008.

*** Reviewer 3:**

The authors investigate factors controlling pCO_2 variations in the Gulf of Cadiz. They use high quality data from 8 cruises incorporating underway data of pCO_2, SSS, SST, and wind speed as well as discrete data for pH, AOU, and nutrients taken along three repeat transects during the cruises. They present spatiotemporal distributions of the underway data, the cruise averages of the discrete data, and the seasonal changes of the computed air-sea CO_2 flux. The authors then discuss the factors influencing the pCO_2 variability. Specifically, they quantify thermal/non-thermal controls of pCO_2. They conclude that temperature and biological activity are the two principal factors that explain the temporal variability of pCO_2. They also point out that continental inputs and mixing with water originating from warm ocean currents influence the spatial variability of pCO_2.

The work is OK structured, includes original research based on high quality data, and suits for publication in this journal. However, there are several things that need improvements and/or clarification and I recommend major revision.

- ***General comments***

1- The main subject of the study is the controls of pCO_2 variations. The authors correctly write "In addition to influence of temperature, the spatiotemporal distribution of pCO_2 in surface seawater is affected by the biological utilization of CO_2, the vertical and lateral transport, the sea-air exchange of CO_2 and terrestrial inputs." However, they do not quantify the relative importance of these controls in their data although there are published methods for such quantification (e.g. Olsen et al 2008). Specifically, the importance of fresh water input and air-sea exchange need to be quantified. This should be feasible since they have seasonal data of two parameters of the CO_2-system in addition to SST, SSS, and nutrients.

AC: Thank you very much for your suggestion, which is very interesting. The Olsen et al. (2008) method has been taken into account in the revised manuscript and the contributions of SST, air-sea CO_2 exchange and mixing plus biology on pCO_2 change have been quantified. This method also considers change due to SSS variations but we have not included this quantification, since we do not have available the variations of total alkalinity and dissolved inorganic carbon, and the spatial changes of SSS are only significant near the Guadalquivir River mouth (a point included in the text, Line 186-187).
The manuscript has been edited in Material and methods (Line 174-191) and Discussion sections (Line 374-391) to include this quantification. A new figure has been added (Figure 7).

2- The readability of the manuscript need to be improved. For instance, the study area is quite small, but quite complicated in terms of processes and interactions. Hence, there are a lot of names used in the manuscript (e.g. Gulf of Cadiz Current; AZORES Current; Guadalquivir River; Bay of Cádiz; Cape San Vicente), but locations of these are not shown anywhere in the manuscript. Including these names in the maps/figures would enhance the readability of the manuscript. It is also my opinion that it would be much easier to read the paper if the authors present results in seasonal maps (they do that for CO_2 flux in Fig. 10) and then discuss the controls of pCO_2 changes between seasons and places.

AC: Thank you for your suggestion. Fig. 1 has been edited to add different processes and names used to improve the readability of the manuscript. However, it is not possible to present results in seasonal maps,except for the spatial distribution of CO_2 fluxes, since for example in Fig. 2, the data interpolated in our database for the same season would not be right.

- ***Specific comments***

Line 19, "On the other side" do you mean "on the other hand?"

AC: Corrected.

Line 48, after "all other organisms" please add "which increases the concentration of inorganic carbon"

AC: This point has been added in the text, thank you (Line 46).

Line 50 "generate uncertainty" please replace with "is not clearly defined"

AC: Corrected.

Lines 62-65 I do not understand the sentences between "Finally, the inner.." and ": : :.towards offshore (Walsh 1991)."

AC: These sentences have been modified (Line 57-62). The effect of the continental inputs on pCO_2 variation are explained.

Line 193, "T values were significantly different among all cruises ($p < 0.05$)" why is this important result to mention?

AC: Yes, you are correct. In any case, p-values have been removed from the manuscript and a brief reference has been added to the Statistical analysis section.

Line 207-209: "The threshold value for statistical significance was taken as $p < 0.05$. Moreover, all reported linear correlations are type I and they are statistically significant with p-values smaller than 0.05 in the entire manuscript unless indicated otherwise".

Line 96-97 "Spatially T tended to increase from coastal to offshore areas" during all seasons? Or during winter?

AC: This sentence has been modified in the text. It was not clear in the previous version of the manuscript. Line 217-218: "In general, spatially SST tended to increase from coastal to offshore areas during spring and winter, while in summer and autumn this SST gradient was inverse (Fig. 2A)".

Lines 211-215. I do not understand. Do you mean that both underway and discrete data are shown in Fig 2B? if so please clarify this in the caption and explain more about the reasons for differences between different data.

AC: Fig. 2B only show the underway measurements, but we have observed an increase of these pCO_2 values in the areas that coincide with the position of the discrete water samples (Fig. 1). This sentence has been edited in the manuscript: Line 239-241: "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 time at these stations, which varied between 2 and 8 hours in function of the depth of the system".

Line 238 “TF presented the highest mean concentration for the whole study (0.77 _ 0.76 _mol L-1).” I notice that given the mean PO4 of 0.28 this mean NO3 is much less than what is expected from Redfield, is this typical for the area?

AC: Low N/P relationships are typical for this study area (Anfuso et al., 2010). This information has been added in the text: Line 273-275: “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)”.

Lines 283-291, please state the uncertainty of the implied pCO_2 growth. Please elaborate why you believe the excess pCO_2 growth (over the atmospheric growth) is caused by continental input.

AC: The uncertainty value has been added in the text (Line 309). The pCO_2 growth caused by continental inputs was also found by other authors and this point is included in the text.

Line 311-314: “This suggests a possible increase of the anthropogenic nutrient and C inputs from land (Mackenzie et al., 2004) since the direction and magnitude of estuarine and continental shelf CO_2 exchange with the atmosphere is highly dependent on the terrestrial organic budget and nutrient supplies to the coastal ocean (Borges and Abril, 2011; Cai, 2011)”.

Lines 300-305, can the reason for difference pCO_2 over different depth ranges be due to different TA/DIC ratios in the FW influenced areas and those offshore?

AC: Thank you for your comment. This is a very interesting question. However, at the moment, we do not have available this information needed to answer it.

Line 321, in which form is the CO_2 input?

AC: The form of CO_2 input is inorganic carbon. This sentence has been edited in the text (Line 331-334).

Lines 333-334, How pCO_2 increase can be computed from only F? or do you make more assumptions?

AC: More assumptions are necessary: mean depth of the water column (23 m) and the fact that it is well-mixed; a pH = 8; in the conditions of mean temperature and salinity in the Gulf of Cádiz (18.8 ºC and 36.19, respectively) and using the K1 and K2 acidity constants proposed by Lueker et al. (2000) in the total pH scale (information indicated in the text: Line 341-346).

Lines 335-342, you mention that upwelling systems can be influencing the distribution of pCO_2 in the Gulf of Cadiz. BUT do you have any evidence for such influence in your data? If not why do you mention it here?

AC: There is some evidence in our data for the Trafalgar transect. This point is included in the text: Line 351- 354: “In our database experimental evidence of the upwelling was found only in the TF transect. A local decrease of the mean values of SST (17.4 ºC) and pCO_2 (399.1 µatm) was observed in this coastal area of TF, with respect to the deeper areas (18.8 ºC and 405.1 µatm, respectively) for the whole period”. In addition, in Fig. 10 it can also observed that the areas near to the Trafalgar section show lower values of CO_2 flux during summer and winter.

Figures: Figure 1: show important currents and places mentioned in the text. Figures 2, 3, 5, 6, and 7. Clarify in the caption whether both underway and discrete data are used.

AC: Fig. 1 has been improved and the figure captions have been clarified.

References:

Anfuso, E., Ponce, R., Castro, C. G., and Forja, J. M.: Coupling between the thermohaline, chemical and biological fields during summer 2006 in the northeast continental shelf of the Gulf of Cádiz (SW Iberian Peninsula), 47–56, Sci. Mar., https://doi: 10.3989/scimar.2010.74s1047, 2010.

~~Factors controlling~~ pCO$_2$ variability in the surface waters of the eastern Gulf of Cádiz (SW Iberian Peni~~í~~nsula)

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Abstract

Spatiotemporal variations of the partial pressure of CO$_2$ (pCO$_2$) were studied during 8 oceanographic cruises conducted between March 2014 and February 2016 in surface waters of the eastern shelf of the Gulf of Cádiz (SW Iberian Peni~~í~~nsula) between the Guadalquivir River and Cape Trafalgar. pCO$_2$ presents~~ed~~ a range of variation between 320.6 and 513.6 µatm, with highest values during summer and autumn and lowest during spring and winter. For the whole study, pCO$_2$ shows a linear dependence with temperature, and spatially there is a general decrease from coastal to offshore stations associated with continental inputs and an increase in the zones deeper than 400 m related to the influence of the eastward branch of the Azores Current. ~~, showing a linear dependence between pCO$_2$ and temperature. The distributions of pCO$_2$ were not homogeneous. Spatially, there was a general decrease from coastal to off-shore stations associated with continental inputs and presented an increase in the zones deeper than 400 m due to the influence of the eastward branch of the Azores Current. On the other side, the~~The study area acts~~ed~~ as source of CO$_2$ to the atmosphere during summer and autumn and as a sink in spring and winter, with a mean value for the study period of -0.18 ± 1.32 mmol m^{-2} d^{-1}. In the Guadalquivir and Sancti Petri ~~section~~transects, the CO$_2$ fluxes decrease~~d~~ towards offshore, whereas in the Trafalgar ~~section~~ transect fluxes increase~~d~~ due to the presence of an upwelling. These results highlight~~ed~~ the Gulf of Cádiz as a CO$_2$ sink, with an uptake ~~capture~~ capacity of 14.9 Gg C year^{-1}.

1. Introduction

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

Generally, waters over the continental shelf account for ~15 % of the global ocean CO$_2$ uptake (-2.6 ± 0.5 Pg C yr^{-1}, Le Quéré et al., 2017). Using direct surface ocean CO$_2$ measurements from the global Surface Ocean CO$_2$ Atlas (SOCAT) database, Laruelle et al. (2014) estimated a sea-air exchange of CO_2 in these zones of -0.19 ± 0.05 Pg C yr^{-1}, lower than the estimated in other studies published in the last decade (e.g. Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009; Laruelle et al., 2010; Chen et al., 2013). The discrepancies with respect to this estimation derive from the different definitions of the continental shelf domain and the skewed distribution of local studies~~studies~~ (Laruelle et al., 2010). In several works~~studies~~, it has been observed that the continental shelves present different behaviour~~s~~ according to their latitude: they tend to act as a sink of carbon (-0.33 Pg C yr^{-1}) at high and middle latitudes (30 - 90º) and as a weak source (0.11 Pg C yr^{-1}) at low latitudes (0 - 30º) (Cai et al., 2006; Hofmann et al., 2011; Bauer et al., 2013; Chen et al., 2013; Laruelle et al., 2014, 2017). Laruelle et al. (2010) found differences between the two hemispheres: the continental shelf seas of the Northern Hemisphere are a net sink of CO_2 (-0.24 Pg C yr^{-1}) and those of the Southern Hemisphere are a weak source of CO_2 (0.03 Pg C yr^{-1}).

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

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

~~(depth less than 40 m) also presents greater seasonal variability of temperature than the outer platform, and consequently the effect of temperature on pCO_2 will be greater in the inner platform (Chen et al., 2013).~~

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

In~~ the study reported in~~ this paper~~, the main objective is to~~ we evaluate the spatial and seasonal variation of the sea-surface pCO_2 on the eastern shelf of the Gulf of Cádiz. In addition, w~~w~~e aim to assess the relative contribution of the ~~temperature~~ thermal and non-~~temperature~~ thermal effects to p~~to the total~~ CO_2 ~~concentration~~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 of pCO_2 in this area (Ribas-Ribas et al., 2011). In this work~~To do this, we have~~ we have analysed a surface measurement database of >26000 values of pCO_2 obtained during cruises made between 2014 and 2016 and covering an area of 0.8º x 1.3º~~ area~~ of the Gulf of Cádiz.

2. Material and methods

2.1. Study area

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

The Gulf of Cádiz is part of one of the four major Eastern Boundary Upwelling System~~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 system~~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 Eastern Boundary Upwelling System~~EBUS~~ phenomena, and the bilayer flow through the Strait of Gibraltar, are two factors that complicate the simple Eastern Boundary Upwelling System~~EBUS~~ conceptual model (Arístegui et al., 2009; Peliz et al., 2009).

In addition, the surface circulation in the Gulf of Cádiz is characterised by several different processes. These are: ~~first~~ the presence of an anticyclonic water flow towards the east over the shelf edge as far south as the Strait of Gibraltar, known as the Gulf of Cádiz Current (Sánchez and Relvas, 2003; Peliz et al., 2007); ~~second,~~ an upwelling process occurs in the Trafalgar area ~~an upwelling process occurs~~, produced by tidal interaction with the topography of the zone; and ~~third,~~ the mixing of surface layers induced by the wind (Vargas-Yáñez et al., 2002~~; Sánchez and Relvas, 2003~~; Peliz et al., 2009; Sala et al., 2018). ~~In addition, t~~The centre of the Gulf is also under the influence of the eastern-end branch of the Azores Current, producing a front subjected to a mesoscale variability (Johnson and Stevens, 2000; García-Lafuente and Ruiz, 2007; Peliz et al., 2007; Sala et al., 2013) (Fig. 1).~~.~~

2.2. Field sampling and analysis

The database for this study has been obtained following two different sampling strategies. The first ~~one~~ consisted of~~n~~ taking sea surface measurements while underway. T ~~Meanwhile, t~~he second strategy was to obtain ~~one acquired the~~ measurements at several discrete surface stations along three transects at right angles ~~perpendicular~~ to the coastline: the Guadalquivir transect (GD), the Sancti Petri transect (SP) and the Trafalgar transect (TF) (Fig. 1). Data was ~~re~~collected during 8 cruises carried out with a seasonal frequency (spring: ST1 and ST5; summer: ST2 and ST6; autumn: ST3 and ST7; winter: ST4 and ST8) during 2014, 2015 and 2016 (~~precise dates are indicated in~~ Table 1). All the cruises were ~~were carried out~~made~~realised~~ on ~~board~~ the R/V Ángeles Alvariño, except the ~~one of~~ summer 2015 cruise (ST6) that was undertaken~~carried out~~~~completed~~ on ~~board~~ the R/V Ramón Margalef. The study area is located between 35.4 and 36.7º N and 6.0 and 7.2º W (52.8·10^2 k~~K~~m^2).

2.2.1. Underway measurements

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

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

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

2.2.2. Fixed stations

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

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

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

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

The corresponding data of SST, SSS and pCO$_2$ for the fixed stations were obtained by the underway measurements averaging data corresponding to 0.5 mile around the location of the fixed stations. SST and SSS data were compared with the values collected with the CTD coupled to the rosette-sampler and they do not show differences ~~high~~greater than 0.04 ºC and 0.01 units, respectively.

2.3. ~~Temperature~~ Thermal and non-thermal~~biological~~ effects on pCO$_2$ calculations

To determine the relative importance of the thermal~~temperature~~ and non-thermal~~biological~~ effects on the changes of pCO$_2$ in sea-water (e.g., Landschützer et al., 2015; Reimer et al., 2017), we follow the method proposed by Takahashi et al. (2002). To remove the thermal~~emperature~~ effect from the observed pCO$_2$, the data were normalized to a constant temperature, the mean in situ SST depending on the focus considered, according to Eq. (1).

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

(1)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

where the superscript “i” refers to the mean value between consecutives cruises for all variables~~.~~; $d\,pCO_2^{sw,i}$ is the observed change in pCO_2~~,~~; $d_{SST}pCO_2^{sw,i}$ is the change due to SST changes~~,~~; $d_{AS}pCO_2^{sw,i}$ is the change due to air-sea exchange~~,~~;

$d_{SSS}pCO_2^{sw,i}$ is the change due to salinity variations; and $d_{MB}pCO_2^{sw,i}$ is the change due to mixing plus biology. At the same time, each process is calculated with the following~~next~~ equations (Olsen et al., 2008):

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

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

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

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

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

2.4. Estimation of CO_2 fluxes

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

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

(~~6~~9)

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

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

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

(~~7~~10)

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

2.5. Statistical analysis

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

3. Results

3.1. Underway variables

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

SST- values ~~were significantly different among all cruises (p < 0.05),~~ vary~~ing~~ between 14.3 and 23.4 ºC~~ among all cruises~~. T~~In general, t~~he samplings made during 2014 presented ~~temperatures~~ SST values higher than those in 2015 and 2016 (Table 1). For the whole period, the averaged values for both seasons were highest during summer (21.0~~2~~ ± 0.8~~1.3~~ ºC) and autumn (21.1~~0~~ ± 1.2~~0.8~~ ºC), with the lowest values during spring (15.5 ± 0.5 ºC) and ~~. During winter, T showed~~ an intermediate value ~~of 17.6 ± 0.9 ºC~~during winter (17.5 ± 0.6 ºC). In general, ~~. S~~spatially SST tended to increase from coastal to offshore areas during spring and winter, while in summer and autumn this SST gradient was inverse (Fig. 2A).~~,~~ ~~with a difference of ~11.8 ºC (Fig. 2A).~~ No substantial differences were found between the three transects studied (GD, SP and TF)~~ in terms of temperature data.~~, although ~~The lowest values of T were detected~~ near the Guadalquivir River mouth and Cape Trafalgar (36.19º N, 6.03º W) ~~were detected~~ ~~,~~ the lowest values of SST due to freshwater inputs and the frequent upwelled waters, respectively,~~.~~ were detected.

Since the cruises were carried out at the beginning of each meteorological season, it is appropriate to analyse how representative is the range of temperatures that has been obtained. Figure ~~4~~3 shows the mean value over~~f~~ the last 10 years of~~for~~ the maximum and minimum temperatures in the Gulf of Cádiz acquired by a oceanographic buoy~~mooring~~ (bottom-mounted at 36.48° N - 6.96° W; Puertos del Estado; http://www.puertos.es/es-es/oceanografia/Paginas/portus.aspx, last access: 12 July 2018);~~, and~~ the mean values and standard deviations of the 8 cruises are superimposed. It can be observed that the mean values for each cruise are within the range~~s~~ of variation of the typical temperature in the Gulf of Cádiz, and the mean temperature found, 18.8 ºC, is very close~~similar~~ to the mean value obtained at the oceanographic buoy~~mooring~~ (19.2 ºC, Fig. ~~4~~3).~~). If the dependence of pCO_2 with temperature is taken to be 4.80 µatm ºC^{-1}, one would expect that the mean values of pCO_2 obtained in this study would be approximately 2 µatm higher.~~

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

During our study period, pCO_2 values ranged from 320.6 to 513.6 µatm. Highest values were recorded during summer and autumn of 2014 and 2015 (Table 1), with a similar mean value~~ found for both seasons~~, 411.6~~7~~ ± 13.~~3~~2 µatm and 410.6~~1.3~~ ± 10.5~~7~~ µatm~~,~~ respectively, found for both seasons. The ~~low~~lowest ~~st er~~ mean value ~~(382.5390.3 ± 16.95.2 µatm)~~ was logged during spring (382.5 ± 16.9 µatm)~~winter~~, while~~ and~~ winter presented an intermediate value~~the lowest mean value~~ (390.8~~83.9~~

± 15.4~~22.1~~ µatm)~~ during spring~~. In general, the pCO_2 tended to decrease with the distance to the coast (Fig. 2B). Comparing these values with pCO_2 values in the atmosphere, ~~it was observed~~ an undersaturation of CO_2 was observed during spring and winter (15.3 ± 15.7 and 18.0 ± 11.4 µatm, respectively) and an oversaturation in summer and autumn (-20.4 ± 24.6 and -8.0 ± 15.3 µatm, respectively)~~ΔpCO_2 values ranged between -37.5 ± 14.9 µatm during March 2015, and 16.5 ± 9.5 µatm during October 2014. Moreover, an oversaturation relative to the atmosphere was evidenced during spring and winter for both years~~. In Fig. 2~~B~~ a sharp~~ly~~ variation of SST and pCO_2 can be observed in~~at~~ some zones that~~. These~~ coincides with the~~ose~~ stations where discrete water samples were taken. This may be due to the different sampling time at~~in~~ these stations, which varied between 2 and 8 hours in function of the depth of the system.

~~daily variation (day/night) presented by pCO_2, since the sampling procedure did not take the same amount of time at each station – it varied in function of the depth of the system in each zone. It is possible that during the daytime, the pCO_2 values were higher than at night.~~The database of this study includes the transition from coastal zones~~,~~ with depths of the order of ~~15 –~~20 m~~,~~ to distal shelf waters with depths greater than 800 m.~~.~~ Figure ~~5~~4 shows the general trend of the mean values of pCO_2 and ~~temperature~~SST for different intervals of depth of the water column based on the information obtained in the 8 cruises. There is no statistical difference in pCO_2 or SST with bottom depth. I~~, i~~t can be observed that the highest values of pCO_2 (408.3 ± 26.7 µatm) correspond to the coastal zone (< 50 m), and that values decrease down to a depth of 100 - 200 m~~ of depth~~ (396.1 ± 23 µatm). In addition, towards open waters (> 600 m) there is a progressive increase of pCO_2 and ~~temperature~~SST (404.3 ± 16.5 µatm and 20.1 ± 2.4 ºC, respectively)~~.~~.

3.2. Discrete surface variables

Table 2 shows the average~~average~~ values and standard deviation for the underway averaged measurements of ~~temperature~~SST and ~~, salinity~~SSS, and for the discrete samples of ~~,~~ pH, AOU, chlorophyll-a, nitrate and phosphate~~ measured~~ at fixed stations along the three transects during the 8 cruises.

The pH presented significant differences among the cruises ~~($p < 0.05$),~~ with a range of variation from 7.84 to 8.34. Lowest mean values were found during summer (8.00 ± 0.04) and autumn (7.96 ± 0.05) of 2014~~ (8.00 ± 0.04)~~ and 2015 ~~(7.96 ± 0.05)~~ (Table 2), coinciding with the highest average values of pCO_2~~ were~~ recorded (Table 1). The ~~minimum value of~~ pH values for spring and winter were equal practically for both years (8.08 ± 0.08 and 8.07 ± 0.05, respectively).~~were found in September 2015 (7.49 ± 0.03) and the maximum in March 2015 (8.09 ± 0.12).~~

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

Chlorophyll-a values presented significant differences among the cruises and between the same seasons of each year~~ ($p <$ 0.05)~~. This parameter varied from 0.02 to 2.37 µg L^{-1}, with the highest mean value measured in March 2015 (0.76 ± 0.55 µg

L^{-1}), which coincides with the lowest (negative) mean value of AOU (Table 2). The lowest mean value was in June 2014 (0.18 ± 0.14 µg L^{-1}). With reference to the seasons of both years, the highest value was in spring (0.71~~2~~ ± 0.46 µg L^{-1}), followed by winter (0.~~47~~58 ± 0.33~~1~~ µg L^{-1}), autumn (0.26~~8~~ ± 0.30~~30~~ µg L^{-1}) and the lowest value in summer (0.23~~2~~ ± 0.25~~6~~ µg L^{-1}). The SP transect presented the ~~mean~~ lowest mean value of the whole study (0.33 ± 0.31 µg L^{-1}), and the TF zone the highest (0.49 ± 0.37 µg L^{-1}).

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

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

3.3. Air-sea CO$_2$ exchange

Table 3 summarizes the mean values and standard deviation for atmospheric pCO$_2$, wind speed, gas transfer velocity and the air-sea CO$_2$ fluxes measured in this study.

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

There was a clear seasonal variability in the dataset of CO$_2$ fluxes ~~($p < 0.05$)~~. The study area acted as source of CO$_2$ to the atmosphere during summer and autumn (0.7 ± 1.5~~0.3~~ mmol m^{-2} d^{-1} and 1.2 ± 0.9~~4~~ mmol m^{-2} d^{-1}, respectively) and as a sink in spring and winter (-1.3 ± 1.6~~4~~ mmol m^{-2} d^{-1} and -1.3 ± 1.6~~0.01~~ mmol m^{-2} d^{-1}, respectively).

4. Discussion

4.1. ~~General trends~~Thermal influence in pCO$_2$

Numerous research studies have determined that temperature is one of the most important factors that control the variability of pCO$_2$ in the ocean (e.g. Millero, 1995; Bates et al., 2000; Takahashi et al., 2002; Carvalho et al., 2017), as a consequence of the dependence of the solubility of CO$_2$ with the temperature (Weiss, 1974; Woolf et al., 2016). When pCO$_2$ is affected only by the temperature, Takahashi et al. (1993) determined a relative variation of pCO$_2$ of 0.0423 ºC^{-1}, equivalent to 16.9~~7.4~~ µatm ºC^{-1} for experimental pCO$_2$ of 400 µatm. In our study ~~was observed~~ a seasonal variation was observed with a linear increase of the values of pCO$_2$ with SST for the entire database ($r^2 = 0.37$, Fig. 5A). This relationship becomes more significant when it is obtained from the mean values of pCO$_2$ and SST of each cruise ($r^2 = 0.71$, Fig. 5B). The slope, 4.80 µatm ºC^{-1}, is lower than the thermal effect on pCO_2 described by Takahashi et al. (1993), and indicates the influence of other non-thermal processes on the distribution of pCO_2 in this zone of the Gulf of Cádiz.

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

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

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

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

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

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

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

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

4.2. Non-thermal factors controlling pCO_2

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

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

~~systems such as, for example, in the southern part of the Yellow Sea (Qu et al., 2014), in the southwestern part of the Atlantic Ocean (Arruda et al., 2015), in the North Sea (Clargo et al., 2015), and on the continental shelf of Maranhense (Lefèvre et al., 2017).~~

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

~~.~~

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

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

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

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

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

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

~~4.2. Control factors affecting pCO_2~~

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

With the object of investigating the influence of the biological utilization of CO_2~~activity~~ on the variations of pCO_2, Fig. 6 shows the dependence between the mean values of pCO_2~~ at the fixed stations,~~ and~~ the temperature,~~ pH, AOU and the concentration of chlorophyll-a at the fixed stations (n = 126). AOU presents a positive relationship (pCO_2 (µatm) = 410 + 1.1 AOU (µmol L^{-1}), $r^2 = 0.21$), with a slope close to what would be obtained taking into account the processes of formation/oxidation of the organic matter phytoplankton considering a Redfield-~~-~~type relationship. Inverse relationships between pCO_2 and dissolved oxygen ~~also~~ were also found in other studies of continental shelf (Zhai et al., 2009; de la Paz et al., 2010; Xue et al., 2012, 2016). However, pCO_2 and pH presents an inverse relationship (pCO_2 (µatm) = 1710 - 162.8 pH, $r^2 = 0.34$), due to the effect of the uptake or production of CO_2 on the~~about~~ pH (Tsunogai et al., 1997; Shaw et al., 2014). ~~The~~

~~thermal effect on pCO_2 is more intense when the discrete database ($pCO_2 = 297 + 5.7$ T, $r^2 = 0.48$; $p < 0.0001$) is considered in comparison to the effect obtained using the whole database.~~ The variation of pCO_2 with ~~pH ($pCO_2 = 1710 - 162.8$ pH, $r^2 = 0.34$; $p < 0.0001$), AOU ($pCO_2 = 410 + 1.1$ AOU, $r^2 = 0.21$; $p < 0.0001$), and~~ chlorophyll-a (pCO_2 (µatm) = 413 - 20.8 [chlorophyll-a~~Chl-a~~] (µg L^{-1}), $r^2 = 0.14$~~; $p < 0.0001$~~) also show the influence of the~~e~~ processes of photosynthesis and respiration ~~of photosynthesis and respiration on the variations of pCO_2~~(e.g. Cai et al., 2011; Clargo et al., 2015), with a ~~similar~~ slope value similar to thate obtained in the study of ~~found.~~ Huertas et al. (2005), (pCO_2 (µatm) = 274 - 19.6 [chlorophyll-a] (µg L^{-1}), $r^2 = 0.32$; n = 28). ~~For the Gulf of Cádiz, Huertas et al. (2005) found a linear relationship between pCO_2 and chlorophyll-a with a slope similar to that obtained in this study ($pCO_2 = 274 - 19.6$ [Chl-a], $r^2 = 0.32$; $p < 0.0001$; n = 28).~~ Other authors have also described the interrelationships existing between pCO_2 and chlorophyll-a in other coastal areas (Borges and Frankignoulle, 1999; Tseng et al., 2011; Zhang et al., 2012; Qin et al., 2014; Litt et al., 2018). ~~Inverse relationships between pCO_2 and dissolved oxygen as a consequence of the balance between the processes of photosynthesis and respiration have been found in other studies (Zhai et al., 2009; de la Paz et al., 2010; Xue et al., 2012; Xue et al., 2016).~~

In ~~A~~accordance with~~ing to~~ Olsen et al. (2008), Fig. 10 shows the decomposition of the variations of pCO_2 between cruises due to changes in SST, in air-sea CO_2 exchange and in combined mixing and biology, in distal and coastal areas. In general, the variations are greater than those found in other works (Olsen et al., 2008; Omar et al., 2010) because this study considers seasonal changes against the monthly change analysed in previous applications. $dpCO_2^{sw}$ presents practically the same temporal trend in deep and coastal areas ~~practically~~, but with a global behaviour different since the distal zones act a sink of CO_2 of the system (mean $dpCO_2^{sw}$ = -3.4 ± 28.9 µatm) and the shallower areas as a source of CO_2 (mean $dpCO_2^{sw}$ = 0.2 ± 22.7 µatm). In distal areas (Fig. 10), pCO_2 changes are mainly brought about by SST (-58.4 - 106.2 µatm) together with mixing and biology processes (-90.8 - 36.2 µatm). ~~It observed an~~An inverse coupling is observed between $d_{SST}pCO_2^{sw}$ and $d_{MB}pCO_2^{sw}$, since with the increase of 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 ~~it happens in the works~~ of Olsen et al. (2008) and Omar et al. (2010), the change produced by the air-sea CO_2 exchange is lower. Instead, in coastal areas (Fig. 10), the dominant~~te~~ effects on~~about~~ pCO_2 changes are produced by air-sea CO_2 exchange (-196.2 - 103.4 µatm) and mixing plus biology (-101.1 - 198.5 µatm). A relative inverse coupling ~~inverse~~ between the ~~both~~two factors was also observed;~~, a de~~outgassing is produced (decrease $d_{AS}pCO_2^{sw}$) when the system receives greater inputs/production of CO_2 (increase $d_{MB}pCO_2^{sw}$). There is a different behaviour between the transition from ~~of~~ spring to ~~and~~ summer of 2014 (ST1 and ST2) and 2015 (ST5 and ST6) for $d_{MB}pCO_2^{sw}$, which ~~can~~may be due to a greater quantity of continental inputs, as reflected in the Guadalquivir river flow rate in these periods (85.1 ± 75.4 $m^3 s^{-1}$ and 25.3 ± 10.2 $m^3 s^{-1}$, respectively). A larger effect of the air-sea CO_2 exchange on ~~about~~ pCO_2 variation is observed in the shallower mixed layers, as also described by Olsen et al. (2008) in the subpolar North Atlantic.

4.3. T/B ratio

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

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

Figure ~~7~~ 8 presents the values of the T/B ratio grouped in different bottom-depth intervals of the water column in the system. The variations of ΔpCO_2 ~~bio~~ non-thermal and ΔpCO_2 ~~temp~~ thermal found have been superimposed. In the coastal zone (depth < 50 m), the T/B ratio is below 1 (0.9), and increases to values of 1.3 in the central zone of the Gulf of Cádiz, at depths ranging from 100 to 400 m. However, in the deepest zone (depth > 600 m), a progressive decrease to values of 1.1 is found. -Qu et al. (2014) also ~~described~~reported the variation i~~o~~n the values of the T/B ratio with the distance from~~to~~ the coast in the southern Yellow Sea, between 0.4 - 0.6 in the nearshore area (depth < 50 m) to more than 1 (up to 2.4) in the offshore area (depth > 50 m).

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

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

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

~~However, the concentrations of chlorophyll-a and nutrients are relatively constant in waters with bottom-depth to 200 m, and do not explain the decrease of the T/B ratio and the increase of ΔpCO_2 bio in waters with bottom-depth higher than 400 m. These variations have been associated with the change in the origin of the surface water masses. Thus, in the central zone of~~

~~the Gulf of Cádiz, the origin of the surface waters is a branch of the larger-scale Portuguese-Canary eastern boundary current that circulates around a cyclonic eddy off Cape San Vicente and veers eastward into the Gulf of Cádiz (García-Lafuente et al., 2006). While the deepest zone is under the influence of a branch of the Azores current, which in addition to being a warmer stream that could lead to an increase in primary production, it is the northern border of the subtropical gyre (Klein and Siedler, 1989), thus favour the accumulation of CO_2 in this area as convergence zone (Ríos et al., 2005).~~~~Qu et al. (2014) have described the variation on the values of the T/B ratio with the distance to the coast, between 0.4 - 0.6 in the nearshore area (depth < 50 m) to more than 1 (up to 2.4) in the offshore sand (depth > 50 m), in the southern Yellow Sea.~~

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

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

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

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

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

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

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

5. Conclusions

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

The total T/B ratio (1.15) suggests that the distribution is principally controlled by the temperature. However, there is ~~llows the adequately identification of the factors that control the variability of pCO_2 in the Gulf of Cádiz. Its mean value (1.15) suggests that the distribution is principally controlled by the temperature. Although~~ a different behaviour in this ratio if it is determined by bottom-depth intervals, ~~decrease of the ratio has been found,~~ related to the existence of non-thermal processes~~,~~

~~mainly taking place close to the coast (at depths of 100 m or less)~~. In the proximity of the Guadalquivir estuary the ratio takes a value of 0.93 due to the continental inputs of C and nutrients, and in the zone around the coastal upwelling off Cape Trafalgar the ratio is 1.09. Furthermore, the actual characteristics of the surface water mass that originates under the influence of a branch of the Azores current also produce a decrease of the T/B ratio in the deeper zone studied (1.05 for depths > 600 m). In contrast, the highest T/B ratio values have been found in the S~~ancti ~~P~~etri~~ ~~section~~transect, where values of up to 1.54 are obtained for depths greater than 100 m.

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

~~Au~~Author contributions

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

Competing interests

The authors declare that they have no conflict of interest.

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Tables

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

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

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

Cruise	n	~~Temperature~~ SST (ºC)	~~Salinity~~SSS	pH	AOU (µmol L^{-1})	Chlorophyll-a ~~-~~(µg L^{-1})*	Nitrate (µmol L^{-1})	Phosphate (µmol L^{-1})
ST1	17~~8~~	15.2~~3~~ ± 0.5	36.05~~08~~ ± 0.13~~4~~	8.06 ± 0.03	-3.6 ± 8.4	0.65 ± 0.37	0.96 ± 1.01	0.14 ± 0.06
ST2	16	~~21.0~~21.0 ± 1.3	36.11~~11~~ ± 0.11~~1~~	7.97 ± 0.03	-10.3 ± 5.7	0.18 ± 0.14	0.42 ± 0.60	0.12 ± 0.04
ST3	17	21.6~~7~~ ± 0.7	36.09~~11~~ ± 0.28~~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~~7~~ ± 0.7	36.0~~2~~3~~6~~ ± 0.13~~27~~	8.05 ± 0.05	7.7 ± 2.1	0.46 ± 0.33	1.05 ± 1.96	0.23 ± 0.09
ST5	16	15.4~~5~~ ± 0.3	36.03~~3~~ ± 0.13~~3~~	8.09 ± 0.12	-19.1 ± 9.4	0.76 ± 0.55	0.68 ± 1.17	0.17 ± 0.09
ST6	16	21.1~~1.1~~ ± 1.0~~1.0~~	36.37~~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~~2~~	35.63~~5.63~~ ± 0.03~~2~~	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~~3	36.44~~5~~ ± 0.04~~5~~	8.09 ± 0.05	-5.1 ± 3.1	0.69 ± 0.32	0.41 ± 0.31	0.14 ± 0.11

*González-García et al. (2018).

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

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

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

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

Table 4~~5~~: Mean ~~average~~ and range of pCO_2 and CO_2 fluxes (FCO_2) found in different ~~shelf~~ areas of the ~~North Atlantic~~Gulf of Cádiz.

Site	ºE	ºN	Date	pCO_2 (µatm)	FCO_2 (mmol m^{-2} d^{-1})*	Reference
~~North Eastern Atlantic Ocean~~	~~-11.0~~	~~40.0 - 43.0~~	~~May, November, December 1993; July, August 1994~~	~~320 - 430~~	~~-0.47^{a}~~	~~Pérez et al. (1999)~~
~~Upwelling system off the Galician coast~~	~~-9.3 - -10.1~~	~~42.1 - 43.2~~	~~June, July 1997; January, June, July, August, December 1998; January, August, September 1999~~	~~265 - 415~~	~~-4.7 - -2.3^{b}~~	~~Borges and Frankignoulle (2002)~~
Strait of Gibraltar~~US Middle Atlantic Bight~~	-5.5 - -5.2~~-76.0 - -69.0~~	35.6 - 36.0~~35.0 - 42.0~~	September 1997~~February, March, May, June, October 1996~~	339 - 381~~220 - 560~~	3 ± 8^{a}~~-4.4 - -1.9^{b}~~	Santana-Casiano et al. (2002)~~DeGranpre et al. (2002)~~
~~Strait of Gibraltar~~	~~-5.5 - -5.2~~	~~35.6 - 36.0~~	~~September 1997; February 1998; May 1999~~	~~350 - 354~~	~~-6.9^{b}~~	~~Santana-Casiano et al. (2002)~~
~~English Channel~~	~~-6.0 - -4.0~~	~~47.5 - 51.5~~	~~March, September 1995; May, June, July 1997; January, June, July, November 1998; August, September 1999~~	~~200 - 500~~	~~-20.0 - 12.0^{c}~~	~~Borges and Frankignoulle (2003)~~
Gulf of Cádiz~~Ría de Vigo~~	-7.0 - -6.5~~-8.9 - -8.6~~	36.3 - 36.7~~42.1 - 42.3~~	February 1998~~April, July, September, October, November, December 1997~~	334 - 416~~285 - 615~~	-19.5 ± 3.5^{a}~~-1.5 - 1.8^{a}~~	González-Dávila et al. (2003)~~Gago et al. (2003)~~
~~Gulf of Cádiz~~	~~-7.0 - -6.5~~	~~36.3 - 36.7~~	~~February 1998~~	~~334 - 416~~	~~-19.5 ± 3.5^{b}~~	~~González-Dávila et al. (2003)~~
~~Northern and central North Sea~~	~~-3.0 - 10.0~~	~~50.0 - 62.0~~	~~August, September, November 2001; February, March, May 2002~~		~~4.6^{b}~~	~~Thomas et al. (2004)~~
Gulf of Cádiz~~North Sea~~	-8.3 - -6.0~~-3.0 - 10.0~~	33.5 - 37.0~~50.0 - 61.0~~	July 2002~~August, September 2001~~	300 - 450~~220 - 490~~	18.6 ± 4^{a}~~-3.4^{b}~~	Aït-Ameur and Goyet (2006)~~Bozec et al. (2005)~~
Northeastern shelf of the Gulf of Cádiz~~Gulf of Cádiz~~	-7.5 - -6.3~~-8.3 - -6.0~~	36.6 - 37.3~~33.5 - 37.0~~	March 2003 to March 2004~~July 2002~~	130 - 650	-2.5 - 1.0^{a}~~18.6 ± 4^{b}~~	Huertas et al. (2006)~~Aït-Ameur and Goyet (2006)~~
~~Northeastern shelf of the Gulf of Cádiz~~	~~-7.5 - -6.3~~	~~36.6 - 37.3~~	~~March 2003 to March 2004~~	~~196 - 650~~	~~-2.5 - 1.0^{b}~~	~~Huertas et al. (2006)~~
~~Southern North Sea~~	~~0.5 - 4.5~~	~~50.0 - 53.0~~	~~February, March, April, June, August, September, October 2001; February, April, June, August, September, October 2002; August, December 2003; February, May 2004~~	~~149 - 479~~	~~-23.7 - 6.7^{b}~~	~~Schiettecatte et al. (2007)~~

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

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

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

Figures

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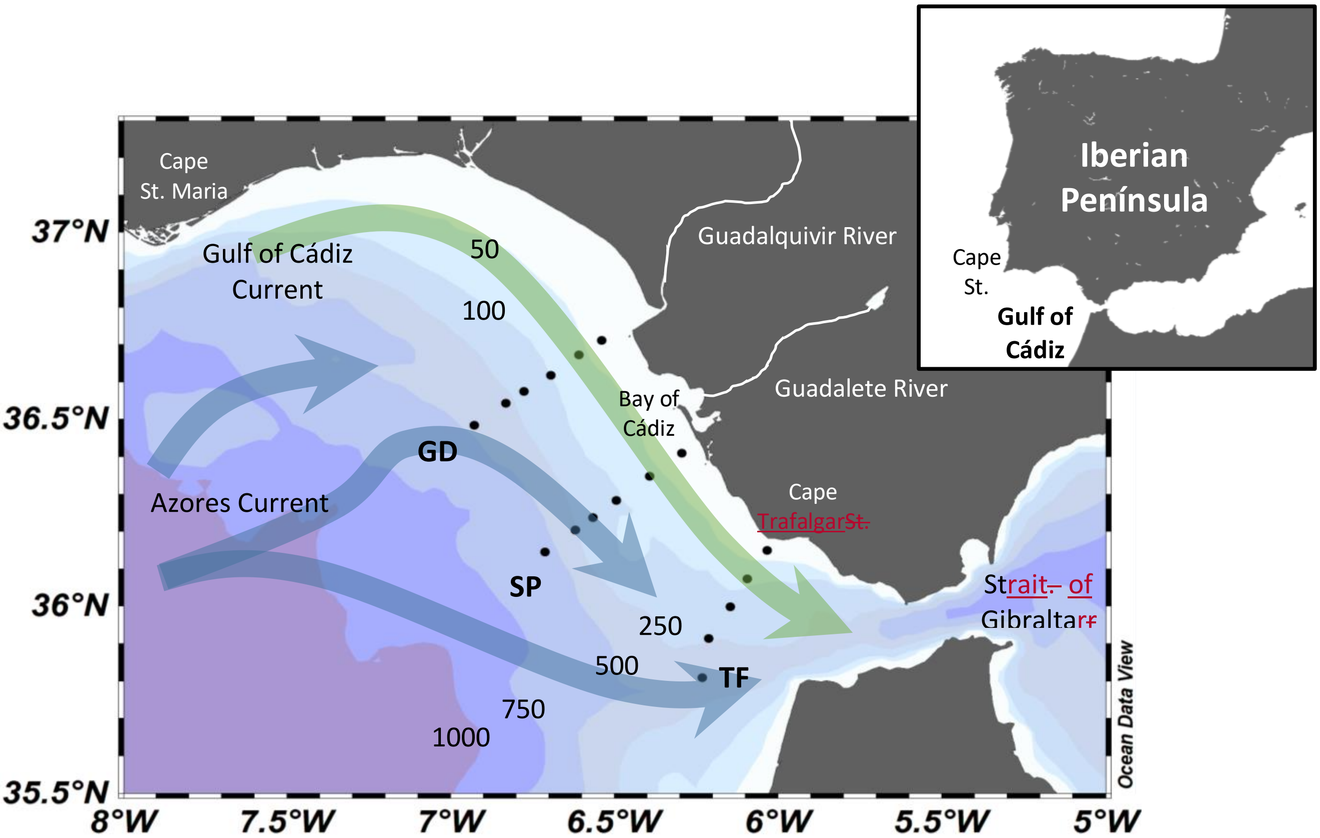


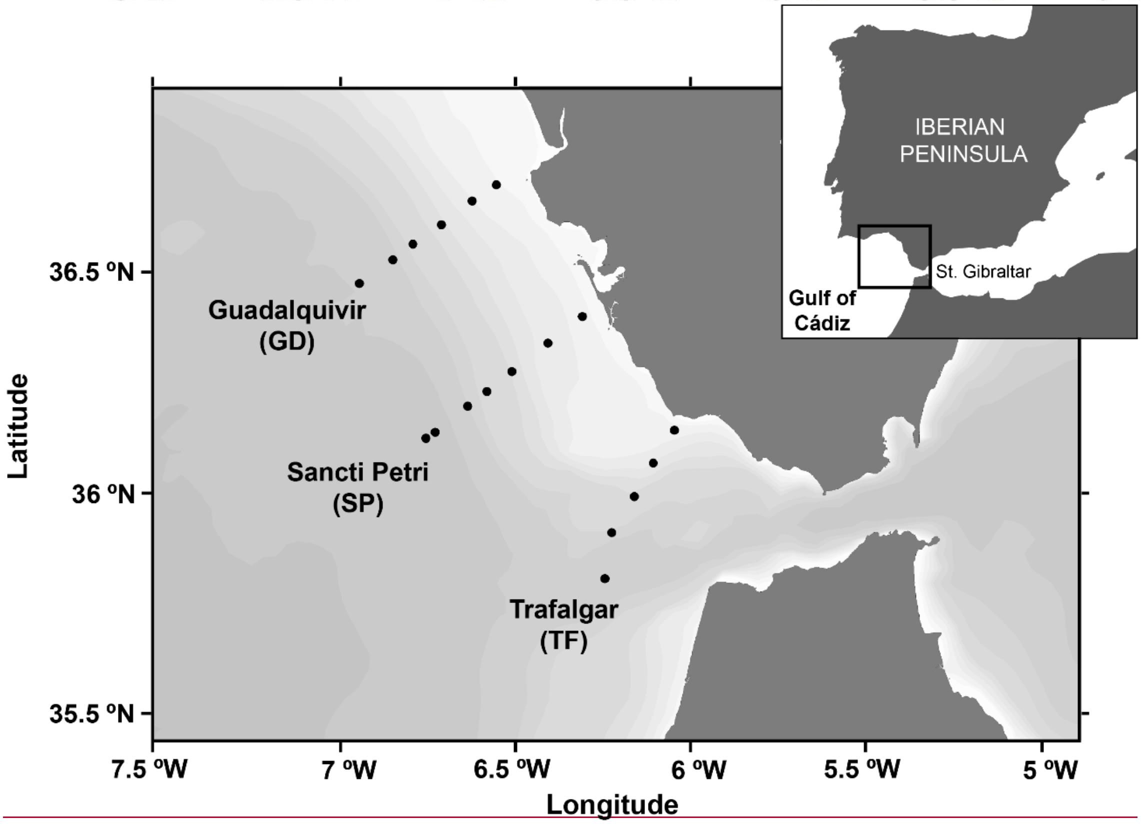


Figure 1: Map of the eastern shelf of the Gulf of Cádiz showing the location of the fixed stations located on 3 transects at right-angles to the coastline: Guadalquivir (GD), Sancti Petri (SP) and Trafalgar (TF). The location of the principal surface currents, rivers and capes of the study area are also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

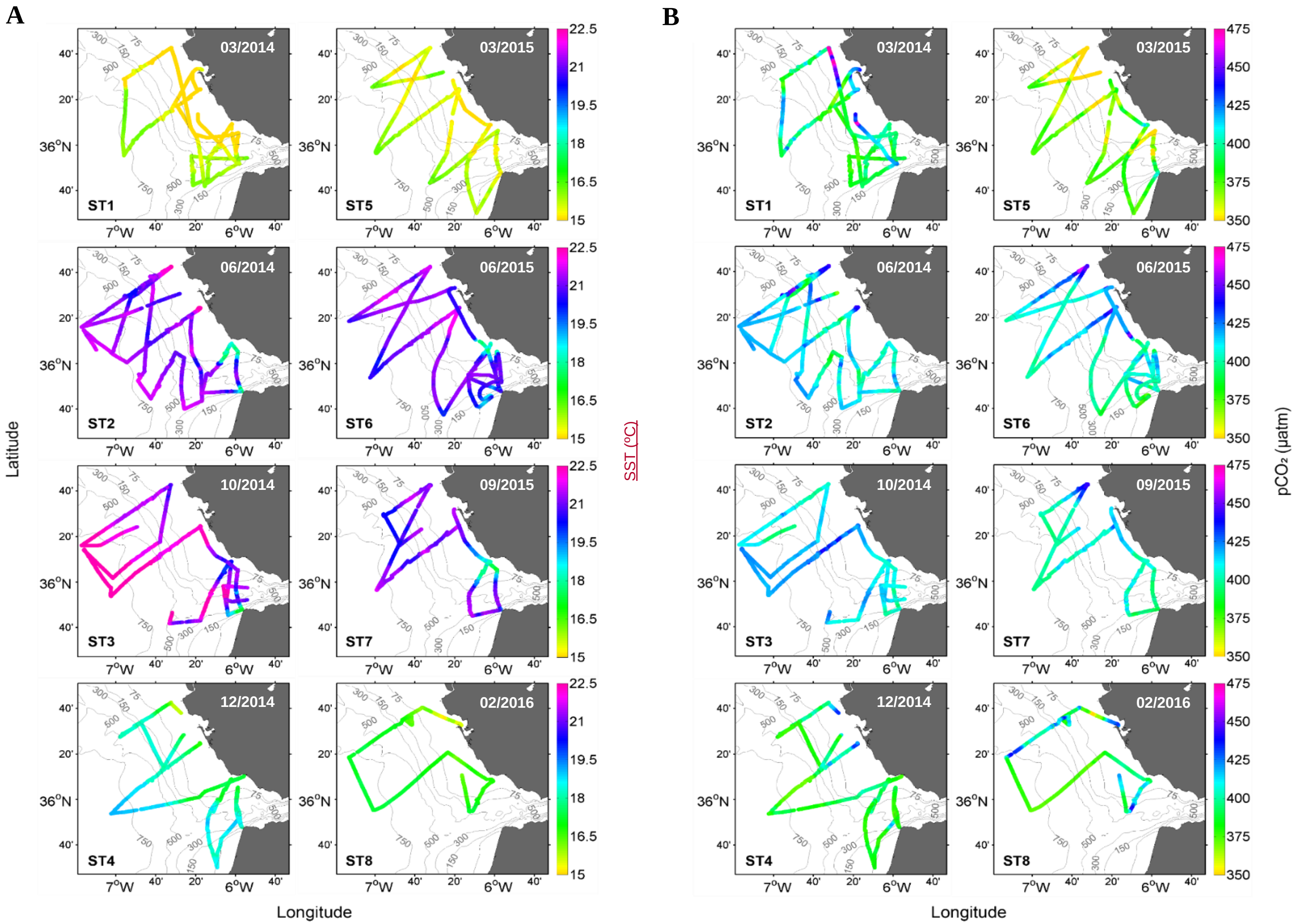


Figure 2: Underway ~~D~~distribution of sea surface temperature (SST, A) and pCO$_2$ (B) during the 8 cruises in the Gulf of Cádiz: March 2014 (ST1), June 2014 (ST2), October 2014 (ST3), December 2014 (ST4), March 2015 (ST5), June 2015 (ST6), September 2015 (ST7) and February 2016 (ST8).

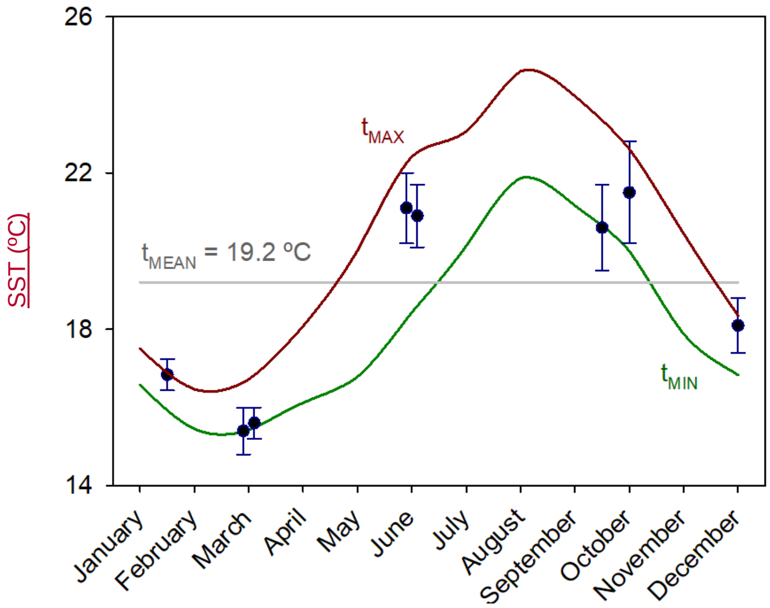
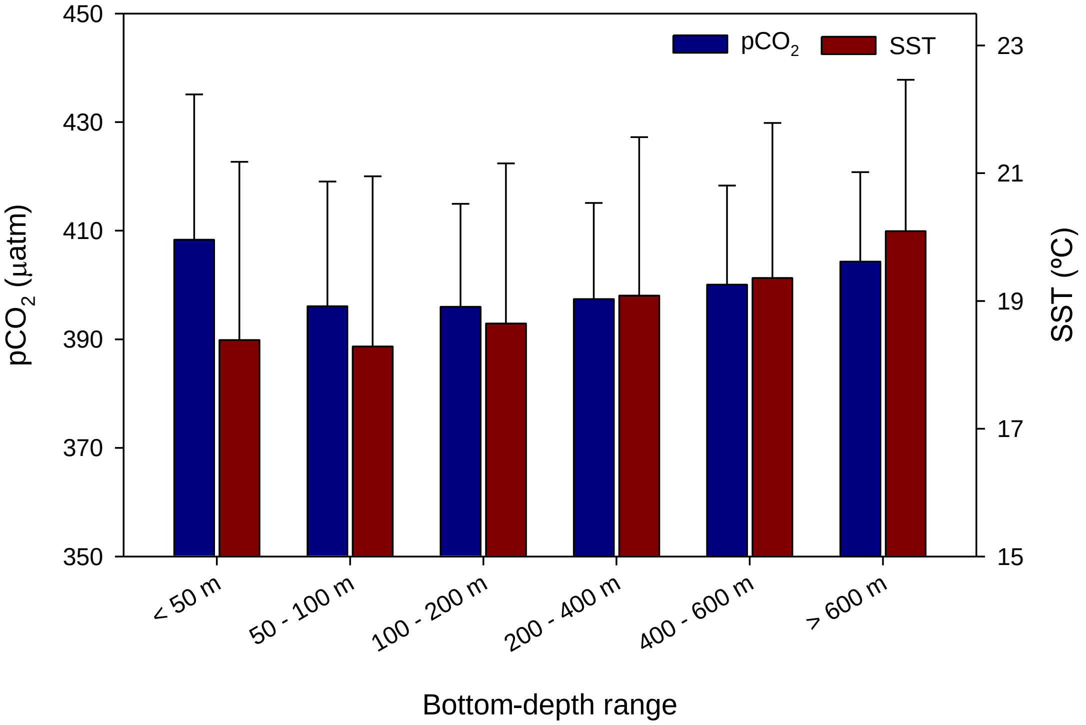


Figure 3: Maximum and minimum sea surface temperature (SST) variation during a 10-year period recorded by an oceanographic buoy located in the Gulf of Cádiz (36.48°N - 6.96°W). The red line shows maximum SST variation. The green line shows minimum SST variation. The grey line shows the average temperature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



2055 **Figure 4: Underway variation of pCO_2 and sea surface temperature (SST) at different bottom-depth ranges of the water column (m) during the 8 cruises. The mean values and standard deviations of pCO_2 (blue) and SST (red) for each range of depth are represented.**

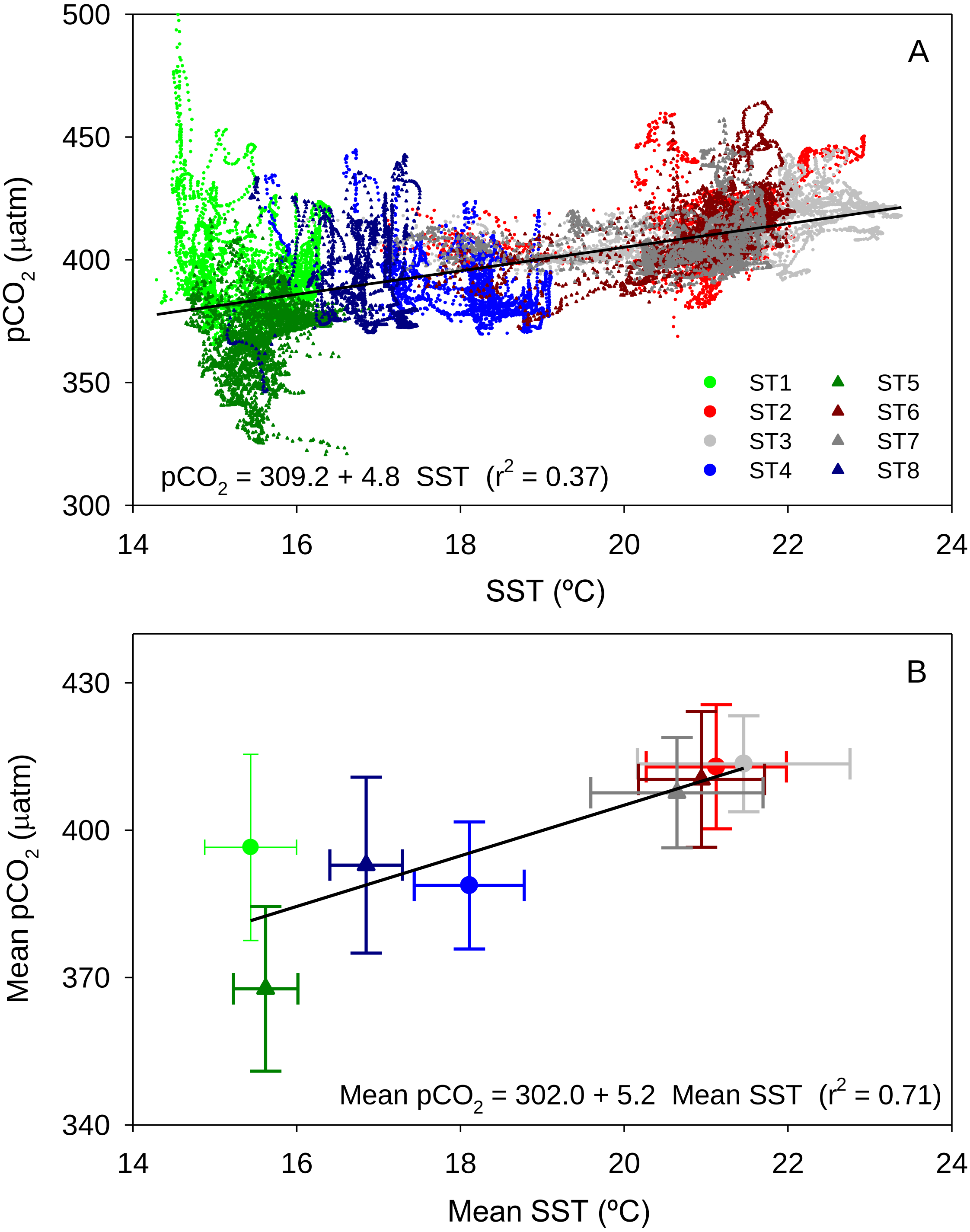
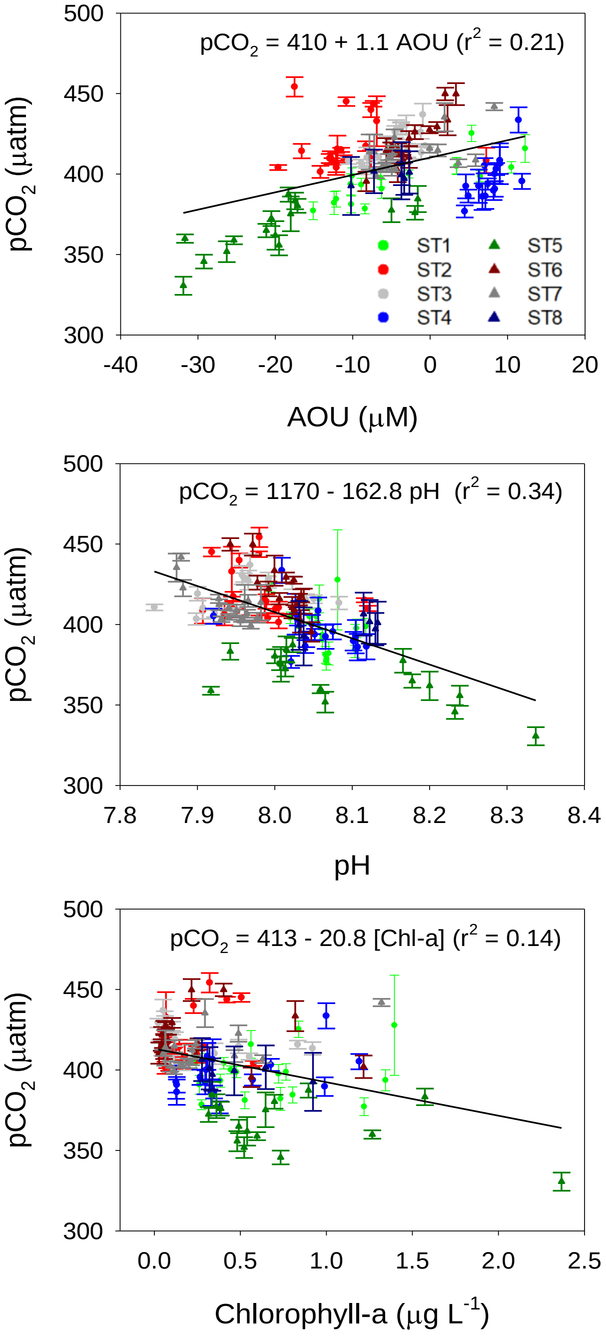
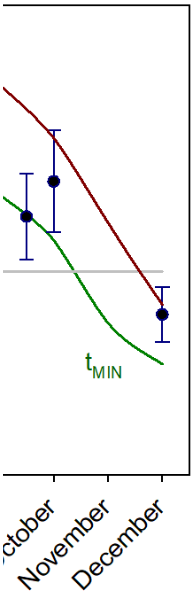
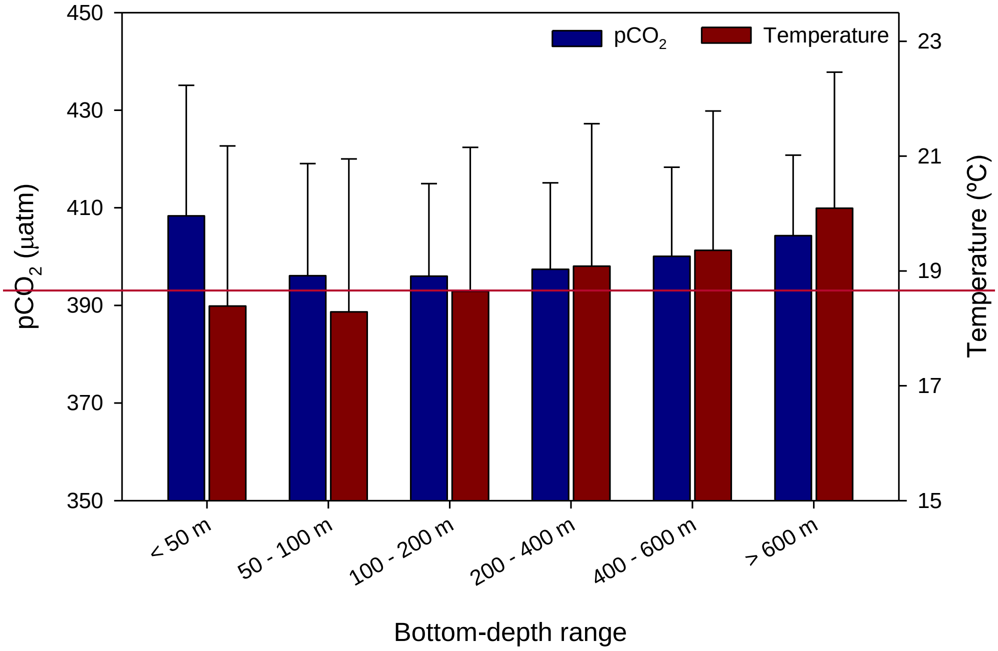


Figure ~~3~~5: Dependence of pCO_2 with sea surface temperature (SST) for the complete underway database during all the cruises (A) and for the mean values of pCO_2 and ~~temperature~~ SST for each cruise showing their standard deviations (B). The solid line shows the linear correlation.





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



~~**Figure 5: Variation of pCO$_2$ (µatm) and temperature (ºC) at different bottom-depth ranges of the water column (m) during the 8 cruises. The mean values and standard deviations of pCO$_2$ (blue) and temperature (red) for each range of depth are represented.**~~

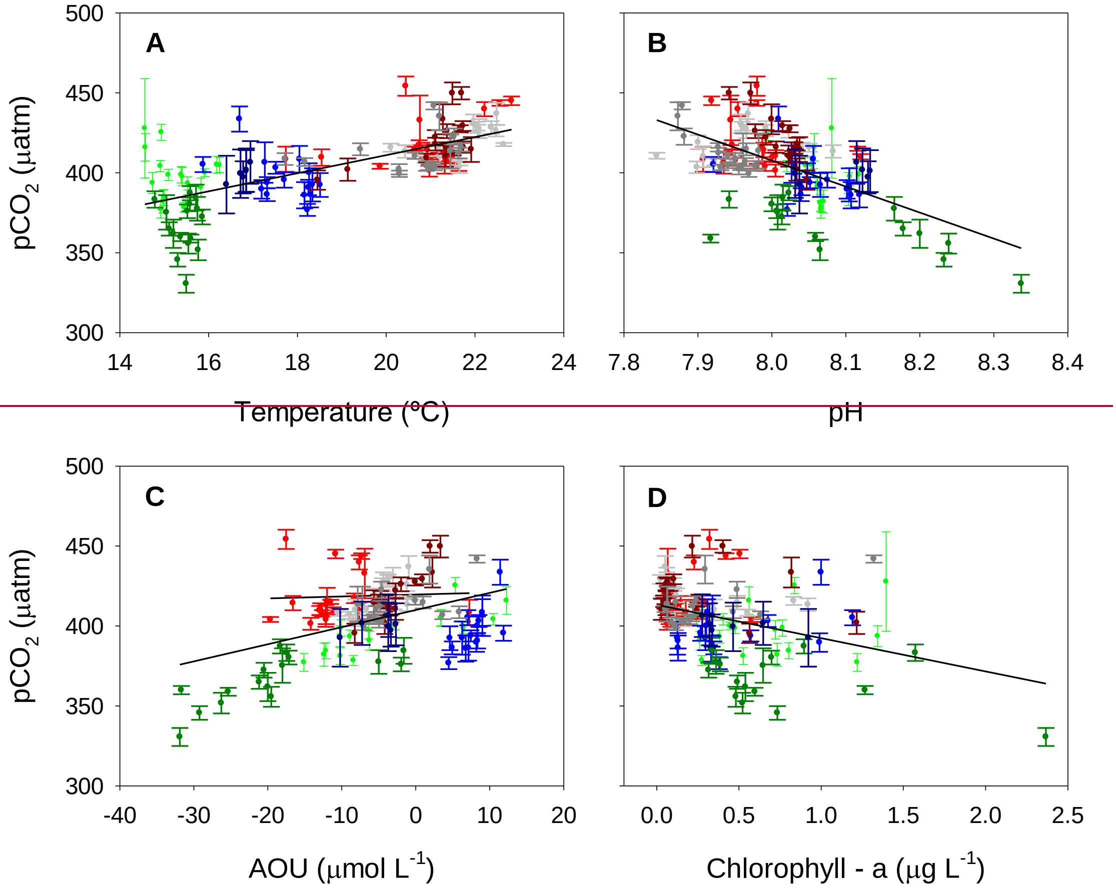

A
B
C
D
pCO$_2$ (µatm)
500
450
400
350
300
14
16
18
20
22
24
Temperature (°C)
7.8
7.9
8.0
8.1
8.2
8.3
8.4
pH
-40
-30
-20
-10
0
10
20
AOU (µmol L^{-1})
0.0
0.5
1.0
1.5
2.0
2.5
Chlorophyll - a (µg L^{-1})

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

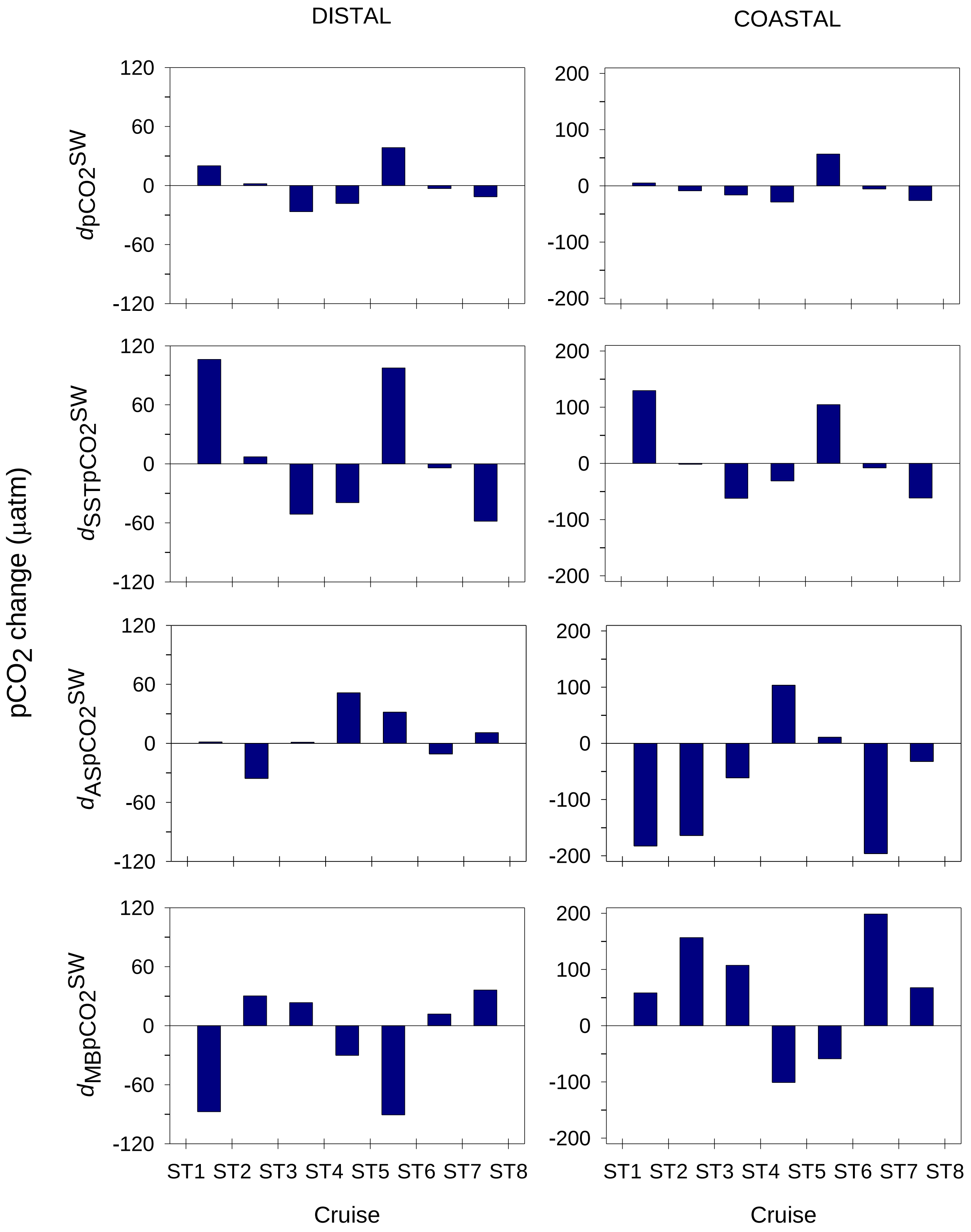


Figure 7: Observed changes in pCO_2 (first row) and expected due to: SST changes (second row), air-sea CO_2 exchange (third row) and biology plus mixing (last row) in the distal (left column) and coastal areas (right column) between the 2145 periods of each cruise: ST1 (March 2014), ST2 (June 2014), ST3 (October 2014), ST4 (December 2014), ST5 (March 2015), ST6 (June 2015), ST7 (September 2015) and ST8 (February 2016).

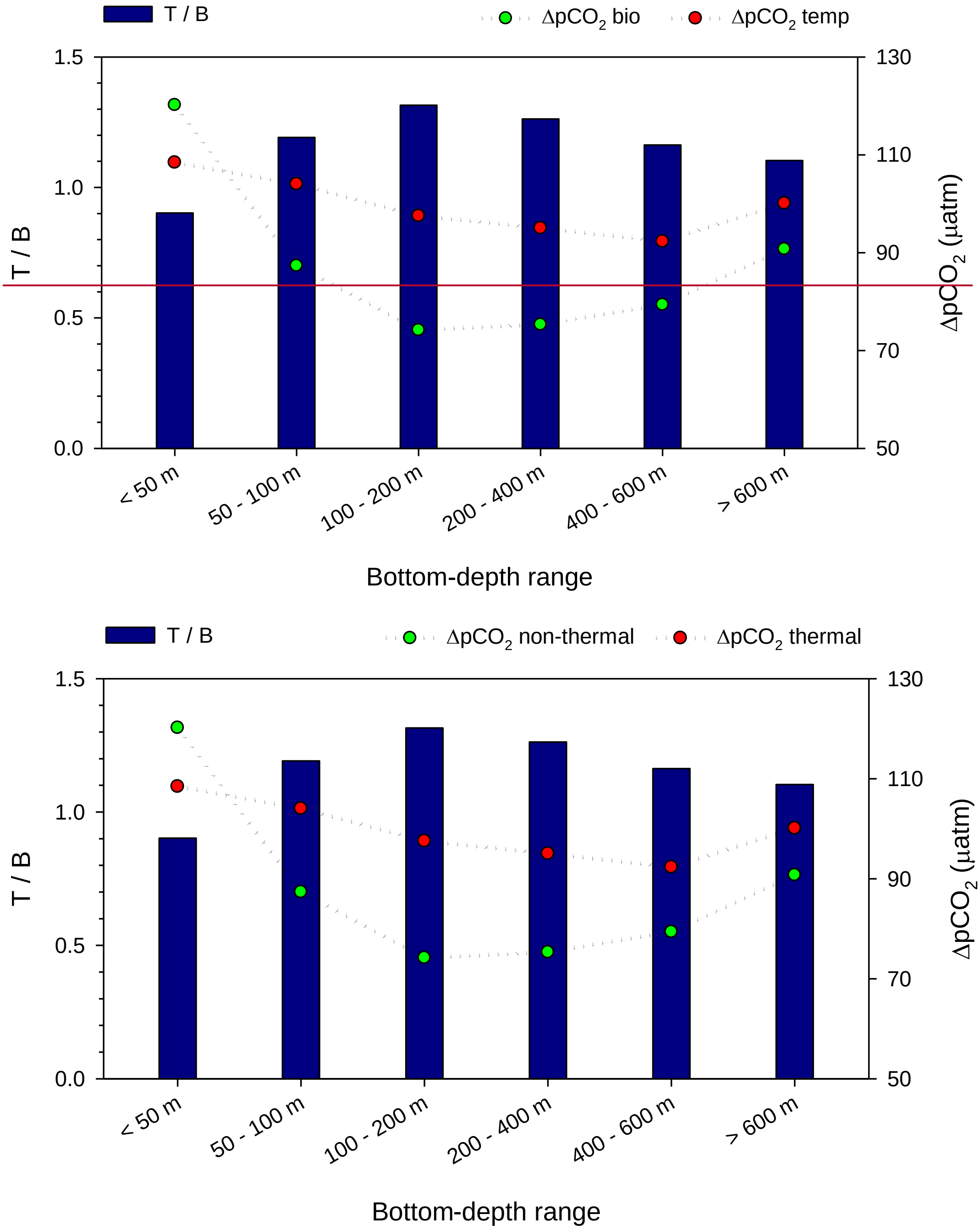
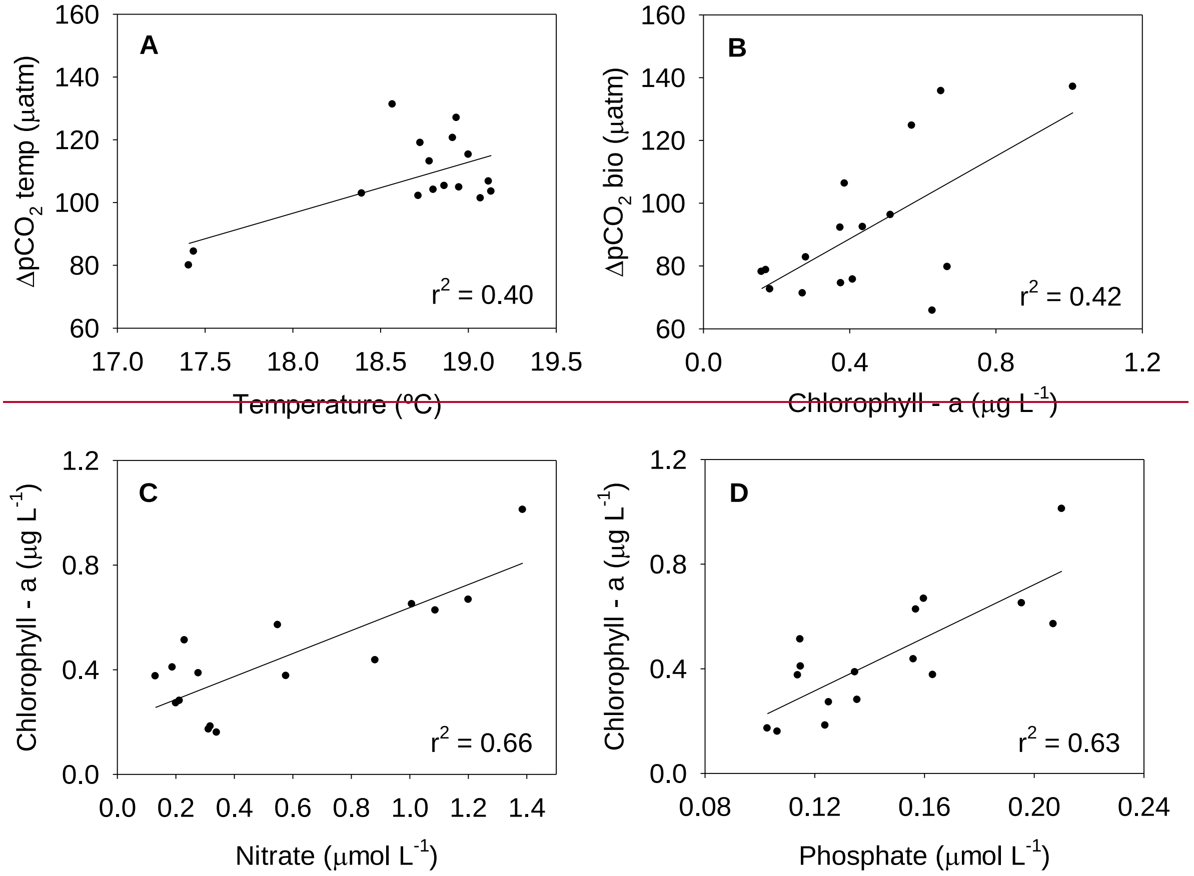


Figure ~~7~~8: Variation of the T/B ratio (blue bar), ΔpCO_2 ~~bio~~ non-thermal (green point) and ΔpCO_2 thermal~~emp~~ (red point) at different bottom-depth ranges of the water column (m) for the 8 cruises.



~~**Figure 8: Correlations between A) ΔpCO$_2$ temp and temperature, B) ΔpCO$_2$ bio and chlorophyll-a, C) chlorophyll-a and nitrate and D) chlorophyll-a and phosphate for the mean values at the 16 discrete stations during the 8 cruises.**~~

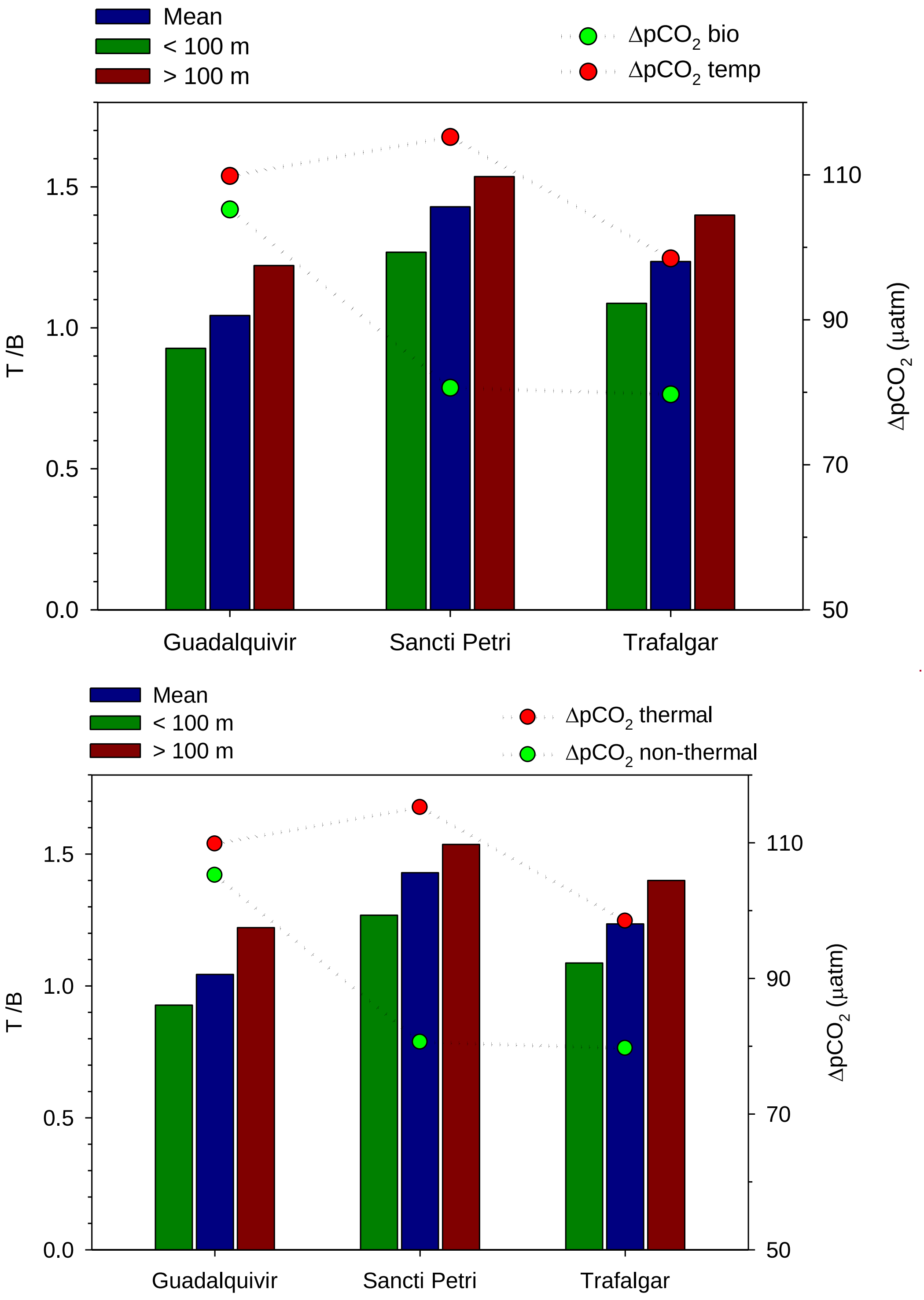


Figure 9~~9~~: Variation of the ~~mean~~ T/B ratio (blue bar), the ~~mean~~ T/B ratio at depths < 100 m (green bar), the~~ mean~~ T/B ratio at depths > 100 m (red bar), ΔpCO_2 non-thermal~~bio~~ (green point) and ΔpCO_2 thermal~~emp~~ (red point) on the ~~various~~3 transects of the study (Guadalquivir, Sancti Petri and Trafalgar) during the 8 cruises.

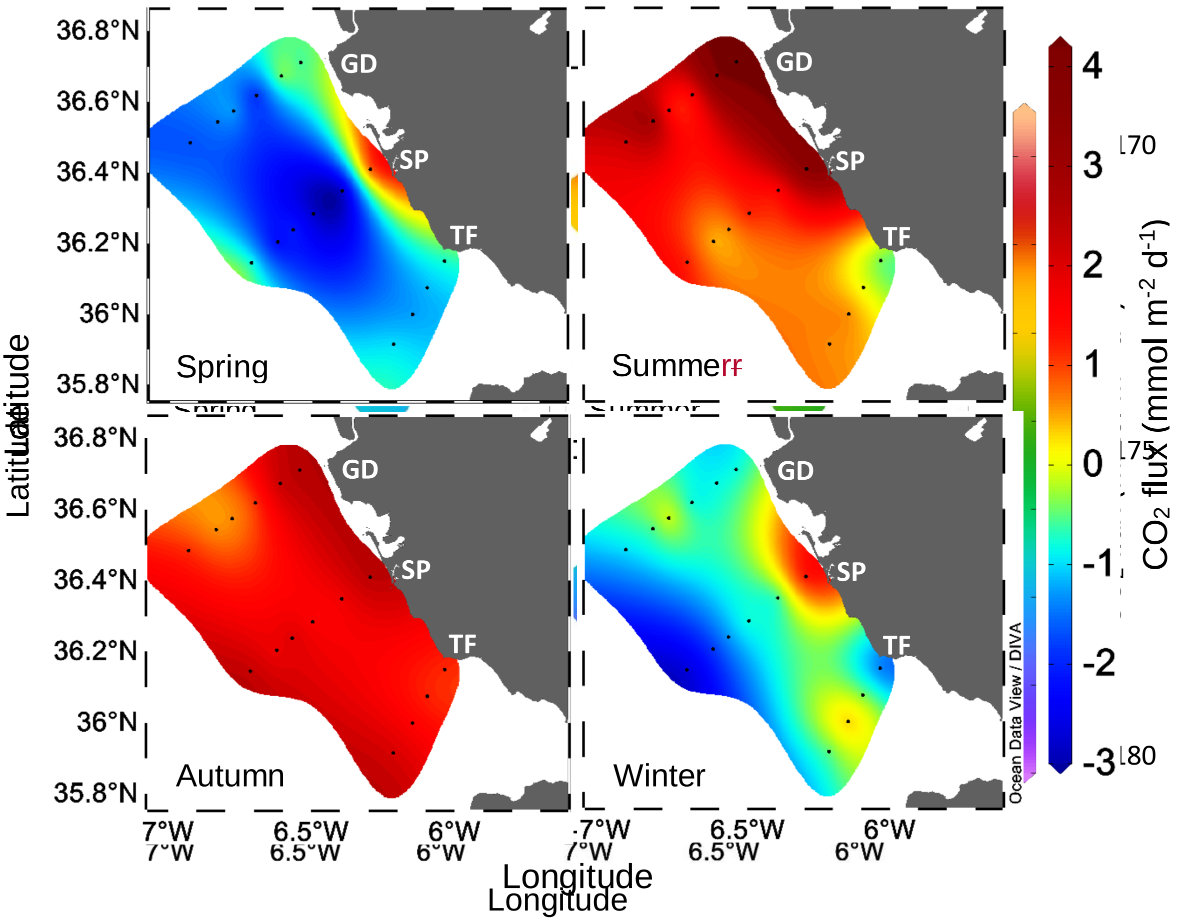


Figure 10~~10~~: Spatial distribution of mean values of CO_2 fluxes in the eastern shelf of the Gulf of ~~Cádiz~~ Cádiz at the 16 discrete stations during spring (ST1, ST5), summer (ST2, ST6), autumn (ST3, ST7) and winter (ST4, ST8).

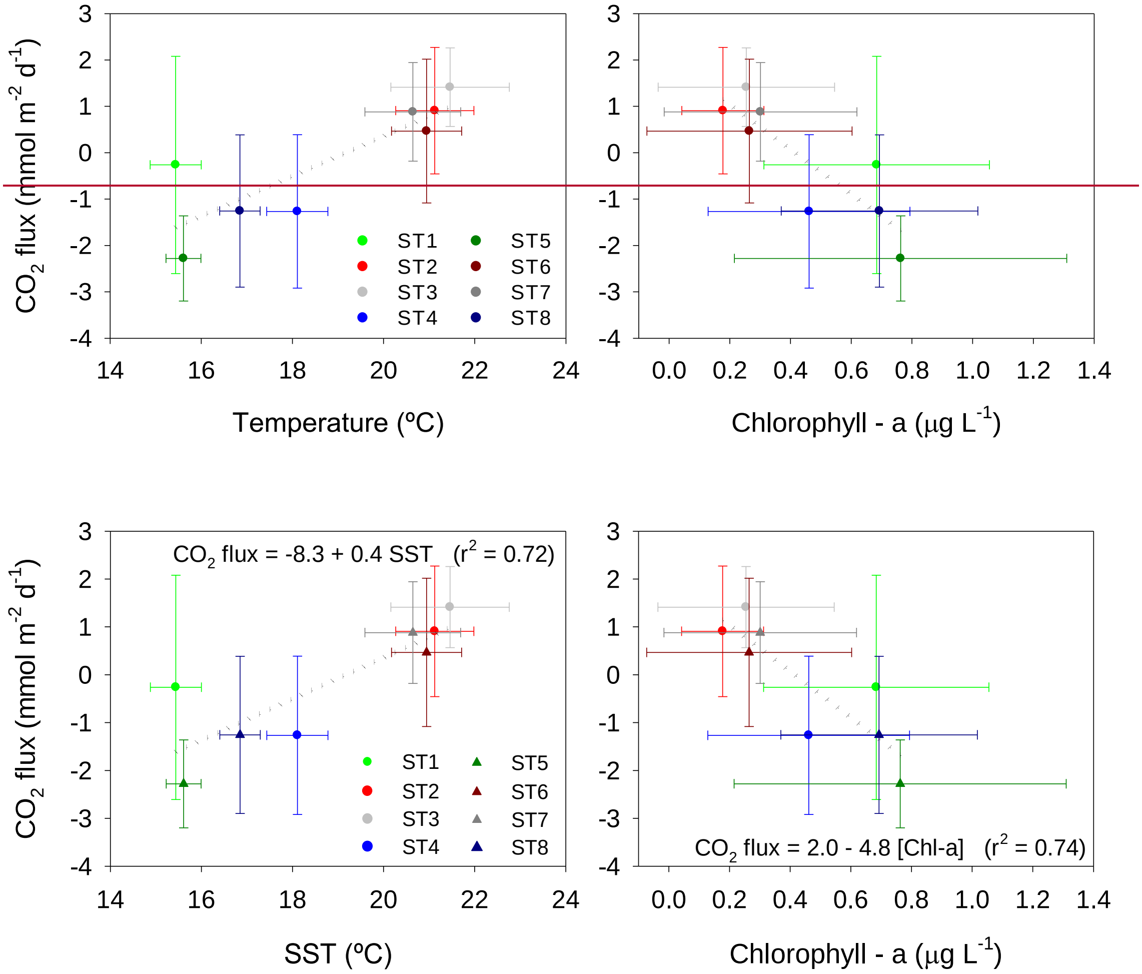


Figure 11~~1~~: Correlations between the mean values of CO_2 fluxes and sea surface temperature (SST) fo~~o~~r the underway database (left~~, $r^2 = 0.72$~~), and the CO_2 fluxes and chlorophyll-a (Chl-a) at the 16 discrete surface stations (right~~, $r^2 = 0.74$~~) for each cruise and showing the standard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