Title: Seasonal variability of surface fCO₂ in the Strait of Gibraltar

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Abstract: From September 2005 to May 2006 four cruises were performed in the Strait of Gibraltar to study the seasonal variability of carbon dioxide surface waters and assess the air-sea CO₂ fluxes. Continuous water measurement of fugacity of CO₂ (fCO₂), temperature and salinity was performed along the longitudinal and latitudinal axes of the Strait. Additionally, discrete surface water samples were taken to measure dissolved inorganic carbon (DIC) and oxygen. The spatial distribution of surface fCO₂ showed low variability compared to the seasonal scale, with fCO₂ values ranging from 329 μatm in March to 387 μatm in September. Seasonal variability of fCO₂ was assessed and discussed in terms of temperature and biology, and the temperature was the main controlling factor. The Strait of Gibraltar is CO₂ undersaturated most of the year, except in September, when the annual average CO₂ uptake equals 0.28 mol C m⁻² yr⁻¹, if behaves as a discreet sink of CO₂ on an annual scale.

INTRODUCTION

Coastal and marginal seas play a key role in the global carbon cycle by linking the terrestrial, oceanic and atmospheric carbon reservoirs. They host strong biological activity and buffer the terrestrial and human impacts before such impacts reach the open ocean systems. In general, the coastal ocean tends to decrease its partial pressure of CO₂ in winter, when the water cools, and in spring, as a consequence of biological processes. In summer and fall, the processes of warming, respiration of marine organisms, and decomposition of organic matter tend to increase the partial pressure of CO₂ in surface waters. Finally, direct and indirect human perturbations to the continental margins (e.g., pollution and eutrophication) are large and have direct consequences for marine ecosystems. The coastal and marginal seas cover only 7% of the world ocean's surface (Gattuso et al., 1998), nevertheless their contribution to the exchange of CO₂ with the atmosphere plays a significant role in the global carbon budget (Chen et al., 2003). Unfortunately, owing to the diversity and complexity of the shelf systems, their precise role in the carbon cycle have not been quantified with any degree of certainty. Seasonal amplitudes in the air-sea CO₂ gradient can easily be on the order of 100 ppm, with continuous undersaturation in the North Sea (Thomas et al., 2004) or even up to 400 ppm in the Baltic Sea (Thomas and Schneider, 1999). In contrast, in the open ocean at of similar latitudes, seasonal amplitudes are only around 40 ppm (Takahashi et al., 2002). This higher air-sea CO₂ disequilibrium causes higher CO₂ uptake from the atmosphere by coastal and continental shelves, and needs to be taken into account in global budgeting efforts.

Several processes transport oceanic properties onto shelves. Coastal upwelling areas are known to show important CO₂ oversaturation of CO₂ with respect to the atmosphere due to the inputs of CO₂-rich deep waters. However, inputs of nutrients from upwelling fuel important primary productions that in turn lower pCO₂ values. Each of these two processes have an antagonistic effect on the gradient of CO₂ across the interface, and so far it has been difficult to assess the role of coastal upwelling areas as sources or sinks of atmospheric CO₂ (Borges and Frankignoulle, 2002). Typical coastal upwelling follows longer periods between upwelling events and relaxation than tidal mixing periods found at the Gibraltar Strait, where the mixing processes occur mainly at the tidal scale. Changes in the biogeochemical parameters of waters interacting through the Strait of Gibraltar are largely controlled by hydrodynamic phenomena. The normal regime in the Strait of Gibraltar consists of two superimposed flows; a shallow Atlantic inflow and a deeper Mediterranean outflow. In turn,

these two water masses show very different biogeochemical properties. Atlantic inflow is characterised by lower dissolved inorganic carbon concentrations, inorganic nutrients and AOU content compared to Mediterranean deep waters (Minas et al., 1991; Santana-Casiano et al., 2002). There also exists a third water mass in the upper layer, the North Atlantic Central Water (NACW) with slightly higher DIC content and lower salinity ($S < 36.2$) than Atlantic waters. The long-term average flow pattern in the Strait of Gibraltar exhibits large fluctuation at different time scales. Seasonal and subinertial fluctuations (meteorologically-induced) are on the order of 40 to 8 times lower than the tidal variability (Garcia-Lafuente et al., 2002). This fact can be explained by the dramatic bottom topography changes between 900 to 300 m depth near the Camarinal Sill. The interaction between mean flows and the topography makes the interface between Atlantic and Mediterranean waters change abruptly, originating internal hydraulic jumps (Armi and Farmer, 1985) or arrested internal waves (Bruno et al., 2002). Such undulatory processes enhance the interfacial mixing and can inject deep Mediterranean water into the upper Atlantic layer. In addition, the intensity of these undulatory phenomena is related to the tidal amplitude, with a maximum mixing and surface nutrient enrichment at spring tides (Macias et al., 2006). Macias et al. (2007) recently developed a model that couples hydrodynamical and biogeochemical factors with the aim to explore the effects of strong advection and mixing processes on biogeochemical exchange and on the pelagic community of the area. These authors found that the short residence times within the channel do not allow phytoplankton communities to grow and proliferate appreciably during their transit. Therefore, all the phenomena co-occurring in the Strait of Gibraltar makes it very difficult to discern between the different biogeochemical driving mechanisms from tidal to seasonal scales.

The goal of this work is to evaluate the seasonal variability of the sea-surface CO_2 and to assess the relative contribution of physical and biological processes affecting the CO_2 concentration. Finally, we evaluate the air-sea CO_2 exchanges on an annual scale.

MATERIAL AND METHODS

The data were obtained during four cruises in the Strait of Gibraltar carried out on board the R/V “Amir Moulay Abdellah”, covering all seasons in a consecutive order (7-8 September 2005, 12-13 December 2005, 20-21 March 2006, and 22-23 May 2006). The ship tracks and sampling stations are shown in

figure 1. Two crossed tracks were performed during each cruise, one covering the West-East surface distribution including three discrete sampling stations (G1 to G3), and a second North-South track at the Camarinal Section comprising five sampling stations (C1 to C5). In addition to the continuous surface water sampling of the temperature, salinity and $p\text{CO}_2$, discrete samples were taken to measure pH, total Alkalinity (TA) and dissolved oxygen at each station with the exception of March, when only discrete samples were taken. Continuous parameters were sampled at a 30 second frequency from the surface seawater supply of the ship (pump inlet at 3m depth). Salinity and temperature were measured with a Seabird thermosalinograph (SBE-45-MicroTSG) before entry into the gas equilibrator. The equilibrator design is a combination of a shower and bubble type similar to the system described by Köertzinger et al. (1996). The CO_2 molar fraction ($x\text{CO}_2$) was detected by means of a non-dispersive infrared gas analyzer (Li-Cor 6262), which was calibrated twice per day with CO_2 free synthetic air and a second standard of 523 ppm molar fraction made and certified by Air Liquide (France).

The water saturated CO_2 fugacity ($f\text{CO}_2$) in the equilibrator was calculated from the $x\text{CO}_2$ in dry air, atmospheric pressure and equilibrium water vapour, according to the protocol described in DOE (1994). The formulation proposed by Takahashi et al. (1993) was employed for the partial pressure corrections to in situ water temperature. The atmospheric $p\text{CO}_2$ data were obtained from the data measured at Tenerife Atmospheric Observatory (Spain) taken from the World Data Centre for Greenhouse Gases (WDCGS/WMO) air sampling network (available at <http://gaw.kishou.go.jp/wdcgg.html>). These atmospheric molar fraction CO_2 values were converted to wet air fugacity.

The pH was measured with a glass combined electrode (Methrom) calibrated in the Free pH Scale (Zeebe and Wolf-Gladrow, 2001). Alkalinity computation was made from the titration curve by means of the Gran Function and taking into account the correction for sulphate and fluoride interaction using the constants proposed by Dickson (1990) and by Dickson and Riley (1979), respectively. Dissolved inorganic carbon (DIC) was calculated from $p\text{CO}_2$ and TA using the K_1 and K_2 acidity constants proposed by Lueker et al. (2000) in the Total pH Scale. For the cruise performed in March, in the absence of CO_2 continuous data, pH and TA were used for DIC calculations. The method was validated with reference standards obtained from A. Dickson (Scripps Institution of Oceanography, San Diego, USA) to an accuracy of $\pm 2 \mu\text{mol kg}^{-1}$.

Oxygen was fixed in a sealed flask and stored in darkness for 24 h as described by the Winkler method, for later analysis by potentiometric titration (Metrohm 670 Titroprocessor). The Apparent Oxygen Utilization (AOU) is defined as departure of oxygen from an O_2 concentration in equilibrium with the atmosphere calculated from the Benson and Krause (1984) solubility equation. Measurements for TA and oxygen were accomplished within 24-48 hours after sampling. Wind speed data used for the gas exchange calculation were provided by the regional government (Red de estaciones agroclimáticas de la Junta de Andalucía) for the meteorological station located at Vejer (Cadiz, Spain)

RESULTS AND DISCUSSION

Surface seasonal fCO_2 distribution in the Strait of Gibraltar

Surface water properties in the Strait of Gibraltar during the study period are shown in figure 2. In order to study the spatial distribution of fCO_2 , longitudinal and the latitudinal tracks have been separated. For a given cruise, the East-West variability of surface salinity, temperature, and fCO_2 was slightly higher than the North-South variability. The amplitude of the longitudinal and latitudinal variability for salinity at the water surface is homogeneous both at the spatial scale and the seasonal scale, with values within the range of Surface Atlantic Water (SAW). However, the spatial amplitude for temperature varied between 0.3-3.5°C. These values are between 20 to 0.5 times lower than the seasonal amplitude, which is around 6.5°C, with a minimum temperature reached in March and a temperature maximum recorded in September. The spatial amplitude for fCO_2 ranged between 10-44 μatm , with a maximum recorded in May and with higher variability on the East-West than on the North-South axis. A reproducible seasonal pattern in spatial distribution does not seem noticeable. The fCO_2 variability may be explained on the basis of hydrodynamics in Strait of Gibraltar, considering also the sampling strategy used in this study. Changes in the biogeochemical parameters of water interacting through the Strait of Gibraltar are largely controlled by hydrodynamic phenomena. Undulatory phenomena, such as internal hydraulic jumps or arrested internal waves, enhance the interfacial mixing and can inject deep, DIC and nutrient rich water into the upper layer of the Atlantic water, and eventually the biochemical imprint arrives to the water surface. The higher interface oscillations are

normally found during high tide along the Camarinal Sill (Gascard and Richez, 1985). In this study, the North-South axis was always sampled during low tide, when the interface occurs at the deepest position along the Camarinal Sill. This timing avoids the tidal variability and explains the lower variability in comparison to the one observed along the East-West axis, which was sampled without taking into account the tidal stage. In May, and throughout the Camarinal Sill, a high increase of surface fCO_2 from 336 μatm up to 375 μatm was accompanied by a temperature decrease (from 18.5°C to 15.9°C) as a consequence of the maximum upwelling of deeper water in that area during high tide, coinciding with the sampling time at that particular station.

In order to achieve a better understanding of the fCO_2 variability for each cruise, the thermodynamic effects of temperature on fCO_2 have been corrected from the in-situ temperature to the annual average temperature measured in the Strait of Gibraltar (18.5°C) using the expression proposed by Takahashi et al. (1993):

$$fCO_{2\ T_{mean}} = fCO_{2\ obs} \exp [0.0423 (T_{mean} - T_{obs})] \quad (1)$$

Where T is temperature in °C and the subscripts “mean” and “obs ” indicate the annual average and observed values, respectively. The fCO_2 at the mean temperature will be named hereinafter $fCO_{2\ T_{mean}}$. The relationship between $fCO_{2\ T_{mean}}$ versus temperature and salinity for the continuous data was statistically tested by linear regression: a high correlation for $fCO_{2\ T_{mean}}$ versus temperature was found for each cruise, with r^2 varying from 0.87-0.86 in May and September, respectively, and 0.4 in December (in all cases $p < 0.01$). The $fCO_{2\ T_{mean}}$ versus salinity only showed a good fit in September with an $r^2 = 0.74$ ($p < 0.01$), while for the remaining cruises the relationship was not significant. The $fCO_{2\ T_{mean}}$ versus temperature exhibited a negative slope. Since the thermodynamic effects are corrected for this variable and colder waters are linked to higher fCO_2 , it suggests that the surface CO_2 variability is related to the influence of deeper water by the hydrodynamic processes explained above. The fact that no correlation between fCO_2 and salinity was found, can be justified considering the origin and thermal characteristics of the water. The observed occurrence of colder water was accompanied by a rise in fCO_2 , water that could have diverse origins, i.e., NACW (characterised by both lower salinity and temperature and higher fCO_2), the Mediterranean flow, upwelled interface consequence of the Atlantic flow divergence at the Camarinal sill, coastal water inputs as well as the surface signal of propagated internal waves on the eastern section of the Strait (Macias et al., 2007). The presence of these surface fCO_2 peaks seems to be in agreement with previous observations

reported by Santana-Casiano et al. (2002) in the Strait of Gibraltar in September 1997, who also found episodic upwelling coinciding with high $f\text{CO}_2$ in surface waters along the Camarinal Sill and on the eastern section of the Strait, being especially evident at the main sill.

Longitudinal and latitudinal variations in DIC in surface waters are plotted in figure 3. The differences observed in the surface DIC concentration are similar to those measured for salinity and temperature, being highly affected by the different mixing and upwelling phenomena, and thereby directly related to the tidal stage at each station during sampling. Maximum DIC values were recorded along the Camarinal Sill (during high tide) in March with $2140.9 \mu\text{mol kg}^{-1}$ and a minimum was recorded in the same location in May during low tide, with a value of $2044.6 \mu\text{mol kg}^{-1}$. There exists slightly higher DIC concentration on the southern side of the Strait than in the northern side, with the longitudinal DIC amplitude ranging from $10\text{--}55 \mu\text{mol kg}^{-1}$. Although the stations on the Camarinal section showed a deeper bathymetry than the 100 m isobath, these DIC differences could suggest the possible influence of coastal inputs enriched in DIC towards the south. The DIC amplitude found for each cruise was between 25 and $55 \mu\text{mol kg}^{-1}$, and is in the same range as the seasonal DIC amplitude of $48 \mu\text{mol kg}^{-1}$. The DIC values obtained in this study are in agreement to those measured previously in surface Atlantic waters in the Strait of Gibraltar (Dafner et al., 2001; Santana-Casiano et al., 2002). de la Paz et al. (2008) developed a study that focused on tidal-induced inorganic carbon dynamics in the Strait of Gibraltar during November 2003. They observed that the consequence of tidal variations is the upwelling of deep water on the Camarinal Sill at high water that causes an increase in DIC and AOU in the upper water column; this water is subsequently advected to the eastern section and causes higher DIC content in the eastern area. These previous studies focused on the characterization of the water column variability. They coincided that most of the variability in the biogeochemical parameters in the water column is controlled by the complex hydrodynamics of the Strait and is related to the short residence time of water in the channel (12 hours in the surface layer).

Due to this high variability in both Mediterranean and Atlantic flows at a tidal time scale in the Strait of Gibraltar, seasonal signals of DIC are significantly difficult to assess and also no studies have been seasonally addressed in this area. Previous seasonal hydrodynamic works carried out by Garcia-Lafuente et al. (2002), showed the existence of an annual cycle of the inflow that peaks in late summer. Its amplitude is 10 % of the mean flow, being related to the annual cycle of the density differences between inflowing and outflowing waters (following the seasonal warming of the Atlantic

Water since Mediterranean outflowing water is not exposed to solar heating). In addition, the interface between both water bodies exhibit an annual cycle that places it deepest position in summer, and shallow in late winter (February – March). The cycle of the position of the interface explains 30% of the annual signal of the inflow. The remaining percentage is accounted for by the velocity variations linked to the annual cycle in density differences. On the other hand, the simultaneous sinking of the interface and development of a seasonal thermocline hinders the pumping of nutrients and other particles in the upper layer (Echevarría et al., 2002). These counteracting influences would probably obscure the biological cycle itself, and any reliable description of the seasonal cycle needs more in-situ data. In the present study, shallower position of the interface in the end of winter may explain the maximum surface DIC concentration ($2118 \mu\text{mol kg}^{-1}$) recorded in March when the vertical DIC advection was expected to be maximum. In the proximal waters of the Strait, there exists a clear relationship between zonal winds and upwelling episodes in the Gulf of Cadiz (Huertas et al., 2006) and in the Alboran Sea (Macias et al., 2006). Nevertheless, these wind-induced upwellings are not expected to be relevant in the channel of the Strait due to the orientation of geographical borders and to the mainly one-dimensional character of the flow in the Strait of Gibraltar, being characterized by very high advection velocities.

Temperature versus biological control on $f\text{CO}_2$

To identify and quantify the temperature and “net biology” effects on surface $f\text{CO}_2$ variability, the method proposed by Takahashi et al. (2002) was applied, which assumes $f\text{CO}_2$ is controlled by temperature and biological drawdown. As defined by these authors, the “net biology effect” includes all the biogeochemical processes acting on net CO_2 utilization (primary production, respiration), and other processes governing CO_2 such as riverine inputs, changes in DIC by advection or air-sea CO_2 fluxes that are inherently attributed to the biological signal. The effect of biology on surface water $f\text{CO}_2$ in a given area $(\Delta f\text{CO}_2)_{\text{bio}}$, is represented by the seasonal amplitude of $f\text{CO}_2$ values normalised to the mean annual temperature ($f\text{CO}_2$ at T_{mean}), values computed using equation (1).

$$(\Delta f\text{CO}_2)_{\text{bio}} = (f\text{CO}_2 T_{\text{mean}})_{\text{max}} - (f\text{CO}_2 T_{\text{mean}})_{\text{min}} \quad (2)$$

where the subscripts “max” and “min” indicate the seasonal maximum and minimum values.

The effects of temperature change on mean annual $f\text{CO}_2$ value (equals $352 \mu\text{atm}$ in the Strait of Gibraltar) $(\Delta f\text{CO}_2)_{\text{temp}}$, is represented by the seasonal amplitude of $f\text{CO}_2$ at T_{obs} values computed using the equation:

$$f\text{CO}_{2\ T_{\text{obs}}} = \text{mean annual } f\text{CO}_2 * \exp [0.0423 (T_{\text{obs}} - T_{\text{mean}})] \quad (3)$$

where the mean annual temperature of 18.5°C was used. The changes in $f\text{CO}_2$ related to temperature effects follow then as:

$$(\Delta f\text{CO}_2)_{\text{temp}} = (f\text{CO}_{2\ T_{\text{obs}}})_{\text{max}} - (f\text{CO}_{2\ T_{\text{obs}}})_{\text{min}} \quad (4)$$

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

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

In areas with high seasonal variability in biological activity, the ratio (T/B) would be < 1.0 , whereas in regions with weaker or annually rather constant biology, the (T/B) ratio would be > 1.0 . This method has been widely used by other authors to assess the role of temperature versus biological control in continental shelves (Thomas et al., 2005; Padin et al., 2007; Schiettecatte et al., 2007).

Figure 4 shows the seasonal variations in experimental $f\text{CO}_2$ and the biological and temperature effects represented by $f\text{CO}_{2\ T_{\text{mean}}}$ and $f\text{CO}_{2\ T_{\text{obs}}}$. The seasonal evolution of the observed $f\text{CO}_2$ exhibited a minimum in March and progressively increased during summer to subsequently decrease in early winter. This $f\text{CO}_2$ followed the same pattern as temperature and $f\text{CO}_{2\ T_{\text{obs}}}$, which had minimum values in March and maximum in September, corresponding with minimum (15.5°C) and maximum (21.7°C) temperatures, respectively. May and December are nearly in equilibrium, with the observed $f\text{CO}_2$ values similar to the annual average concentration ($352 \mu\text{atm}$).

The $f\text{CO}_2$ differences encountered between the observed $f\text{CO}_2$ and the $f\text{CO}_{2\ T_{\text{obs}}}$ are counterbalanced by the biology effect ($f\text{CO}_{2\ T_{\text{mean}}}$), which decreases towards spring and summer. Unlike the temperature effect, the seasonal amplitude is significantly lower. Taking into account the data base, the annual ratio T/B is equal to 2.4, indicating that temperature is the main controlling factor in seasonal $f\text{CO}_2$ variability, with an amplitude $(\Delta f\text{CO}_2)_{\text{temp}}$ of $105 \mu\text{atm}$. Regarding the net biological effects on the seasonal cycle of $f\text{CO}_2$, the amplitude of the $(\Delta f\text{CO}_2)_{\text{bio}}$ is $43 \mu\text{atm}$, which is relatively low in relation to other European continental shelves studied by Borges et al. (2006).

As mentioned above, the method used assumes the vertical mixing processes and lateral inputs to be inherently included into the biological signal. To achieve a better understanding of seasonality on the biological signal, the AOU values were considered. Figure 5a shows the relationship found between DIC and AOU for all the discrete sample data. It can be observed that negative AOU values corresponded to March, possibly as a consequence of a higher biological primary production in the area, whereas maximum positive AOU values were reached in September, and most likely due to organic matter remineralization processes. The negative relationship between DIC and AOU may indicate that the DIC seasonal variability is more related to vertical mixing inputs than to the net biological effect. In fact, a DIC versus observed $f\text{CO}_2$ graph (Fig. 5b) does not match the expected positive relationship, since on a seasonal scale and as mentioned above, $f\text{CO}_2$ is controlled by the temperature annual cycle. Hence, the minimum $f\text{CO}_2$ observed in March can be a combination of a temperature decrease and to a lesser extent biological consumption. During this month the $f\text{CO}_2 \text{ } T_{\text{mean}}$ was maximum, although this could be probably overestimated because of maximum DIC inputs by vertical mixing, which can be inherently attributed to the biological signal computed by the method. The AOU values above zero observed in December and May also match with the equilibrium situations between temperature and biological effects accounted by the method of Takahashi et al. (2002).

Assuming that TA is affected neither by seasonal change of temperature nor biology, and considering that biological change on DIC follows the Redfield ratio proposed by Laws (1991), equal to $-\Delta\text{O}_2 : \Delta \text{DIC} = 1.4$, it is possible to reevaluate the seasonal amplitude of $f\text{CO}_2$ due to net biological processes. The seasonal amplitude for AOU is $49.2 \mu\text{molO}_2 \text{ kg}^{-1}$, which is equivalent to $35.1 \mu\text{molC kg}^{-1}$. Using the k_1 and k_2 dissociation constant proposed by Luecker et al. (2000), this change in DIC yields a change in $f\text{CO}_2$ equal to $58.7 \mu\text{atm}$. This evaluation for $(\Delta f\text{CO}_2)_{\text{bio}}$ in essence is based on the Revelle factor. The Revelle factor relates the relative change in $f\text{CO}_2$ to a given relative change in DIC and is equal to 10.6. Such a change in $f\text{CO}_2$ due to biological processes is larger than the resulting amplitude of $f\text{CO}_2 \text{ } T_{\text{mean}}$ obtained by the Takahashi et al (2002) method. Furthermore, if the ratio T/B is recalculated using this new $(\Delta f\text{CO}_2)_{\text{bio}}$, the resulting value is 1.8. Considering this new T/B ratio, temperature continues being the key factor controlling $f\text{CO}_2$ seasonality, although to a much lesser extent.

Other surface $f\text{CO}_2$ values found in the area are those determined by Santana-Casiano et al. (2002) in February, March and September, with a very similar range to the ones reported in this study. To compare the CO_2 seasonal cycle from this study with previous ones, $f\text{CO}_2$ measurements made during different years were normalised for the annual increase in atmospheric CO_2 , and thus referred to the year of the present study (2005/2006). The CO_2 data have been corrected using a surface water increase of $1.8 \mu\text{atm yr}^{-1}$ following Lefevre et al. (2004). Santana-Casiano et al. (2002) observed in May 1999 an average $f\text{CO}_2$ value equal to $327.6 \mu\text{atm}$ (at 17.4°C), which after the correction by the atmospheric $f\text{CO}_2$ increase, is equal to $340.2 \mu\text{atm}$, very similar to $341.7 \mu\text{atm}$ (at 18.7°C) obtained in this study. Nevertheless, the greatest differences between both studies were found in September 1997, since the previous study showed an average surface $f\text{CO}_2$ of $356.6 \mu\text{atm}$, equal to $371 \mu\text{atm}$ after CO_2 atmospheric increase normalization, which is lower in comparison to $387.5 \mu\text{atm}$ observed in our study at similar temperature (21.7°C).

Borges et al. (2006), in a recent review of the European coastal waters comparing the seasonal cycle of five temperate European continental shelves, encountered that four of them, meso- and eutrophic ecosystems, exhibited a springtime decrease in $f\text{CO}_{2 \text{ obs}} - f\text{CO}_{2 \text{ T mean}}$ due to phytoplankton spring blooms and then a decrease in late summer or early autumn when heterotrophic processes increase $f\text{CO}_2$. The exception to this seasonal biology control is the oligotrophic Bay of Angels in the Mediterranean Sea, where the $f\text{CO}_2$ followed the annual temperature cycle with a progressive rise in $f\text{CO}_2$ towards the summer months and a subsequent $f\text{CO}_2$ decrease as winter cooling begins. The net biological effect ($\Delta f\text{CO}_{2 \text{ bio}}$) accounted in these continental shelves ranges from $569 \mu\text{atm}$ in the Gotland Sea to $68 \mu\text{atm}$ achieved in the Bay of Angels, which is the one showing more similarities in seasonality of $f\text{CO}_2$ to the Strait of Gibraltar, where the amplitude of the net biological effects is $63 \mu\text{atm}$.

Air-sea CO_2 exchange

The air-sea CO_2 exchange ($F \text{ CO}_2$) was calculated using the equation:

$$F \text{ CO}_2 = k S (f\text{CO}_{2 \text{ sea}} - f\text{CO}_{2 \text{ air}}) \quad (6)$$

where k is the gas transfer velocity, S is the CO_2 solubility and $f\text{CO}_{2\text{ sea}}$ and $f\text{CO}_{2\text{ air}}$ are the seawater and atmospheric CO_2 fugacity. Seawater solubility has been calculated using the expression proposed by Weiss (1974). The k was computed using the k parameterization for long-term wind speed given by Wanninkhof (1992) and monthly average wind speed data. Negative fluxes indicate air to sea gas transfer.

Figure 6 shows the seasonal variability in air-sea CO_2 fluxes. The CO_2 fluxes ranged from -1.9 to $1.9 \text{ mmol m}^{-2} \text{ d}^{-1}$, with maximum uptake in March and maximum outgassing in September. The calculated fluxes showed a clear seasonality following the CO_2 air-sea gradient ($\Delta f\text{CO}_2$) seasonal variability. Wind speed average values used for the k calculations were homogeneous, ranging from 3.7 to 5.1 m s^{-1} in March and September, respectively. According to these data, during most of the year, the Strait of Gibraltar behaves as a moderate sink for atmospheric CO_2 except in summer, following the temperature and biology cycle described in the previous section. The resulting mean annual CO_2 flux in the Strait of Gibraltar was $-0.28 \text{ mol m}^{-2} \text{ yr}^{-1}$ ($-0.76 \text{ mmol m}^{-2} \text{ d}^{-1}$), indicating that the area acts as a net sink on an annual basis. This sink behaviour is in agreement with the results obtained by Santana-Casiano et al. (2002), who estimated an annual average CO_2 flux of $-2.5 \text{ mmol m}^{-2} \text{ yr}^{-1}$, and considering only the September and February CO_2 data as extreme seasonal situations. The differences in the magnitude of the uptake, besides the shorter temporal coverage, may be derived mainly from the wind speed used for the k calculations, which were systematically much greater in the study of Santana-Casiano et al. (2002), with wind speeds ranging from 8 to 15 m s^{-1} . These high wind speeds yield a CO_2 flux of $-19 \text{ mmol m}^{-2} \text{ d}^{-1}$ in February and $-5.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ in May, up to three times higher than the one obtained in this study.

Seasonal studies of surface water CO_2 dynamics and air-sea CO_2 fluxes are rather scarce in the Strait as well as in adjacent waters. Huertas et al. (2006) carried out a 12 month study on the inorganic carbon dynamics in the Gulf of Cadiz, concluding that the annual cycle of phytoplankton biomass, riverine nutrients inputs and the fluctuation in local temperature (influenced by coastal wind-induced upwellings) control surface pCO_2 variability. The Gulf of Cadiz remains CO_2 undersaturated most of the year with respect to atmospheric equilibrium, except the oversaturation observed in late summer, behaving as a net CO_2 sink of atmospheric CO_2 on an annual scale, with fluxes ranging between $0.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ in summer and $-2.0 \text{ mmol m}^{-2} \text{ d}^{-1}$ in October. The mean annual air-sea CO_2 flux in the Gulf of Cadiz is about $-0.4 \text{ mmol C m}^{-2} \text{ yr}^{-1}$ (Borges et al., 2006 based on data of Huertas et

al., 2006), slightly higher than the net annual CO₂ flux -0.28 mmol C m⁻² yr⁻¹ obtained in this study for the Strait of Gibraltar, indicating a slightly higher uptake capacity than the adjacent Strait of Gibraltar. Taking into consideration that the total surface area of the Strait of Gibraltar delimited by Cape Spartel to the West and Point Almina to the East, is around 1500 km², the total CO₂ uptake by the Strait of Gibraltar would be 0.5 10⁻³ TgC yr⁻¹ (4.2 10⁸ mol C yr⁻¹), an amount that can be integrated into the total uptake estimated by Borges et al. (2006) for European continental shelves of -68.1 TgC yr⁻¹, which constitutes a high significant CO₂ sink equivalent to the carbon sink of the terrestrial biosphere.

In summary, the present study reports and discusses surface fCO₂ data obtained in surface waters of the Strait of Gibraltar, whose seasonal sequence is characterised by a minimum concentration observed in March 2006 equal to 329 µatm and a progressive increase in concentration caused by water warming until reaching a maximum concentration in September, coinciding with the maximum temperature of the system. Surface waters in the Strait remain undersaturated most of the year, except in September when the warming of surface waters leads to oversaturation in CO₂. The study area behaves as a discrete net sink on annual scale. The high intensity of mixing processes at a tidal scale, masks the seasonal variability in DIC and the assessment of the biological seasonal cycle in the Strait.

REFERENCES:

- Armi, L. and D., Farmer, 1985. The internal hydraulics of the Strait of Gibraltar and associated sill and narrows. *Oceanologica Acta* 8 (1): 37– 46.
- Benson, B. B., and J.R. Krause, 1984. The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with atmosphere. *Limnology and Oceanography* 29: 620–632.
- Borges, A.V. and M. Frankignoulle, 2002. Distribution of surface carbon dioxide and air sea exchange in the upwelling system off the Galician coast. *Global Biogeochemical Cycles* 16 (2): 1020. doi:10.1029/2000 GB001385.
- Borges, A.V., L.-S., Schiettecatte, G., Abril, B., Delille and F., Gazeau, 2006. Carbon dioxide in European coastal waters. *Estuarine Coastal and Shelf Science* 70(3): 375-387.

389 Bruno, M., J.J., Alonso, A., Cózar, J., Vidal, A., Ruiz-Cañavate, F., Echevarría and J., Ruiz, 2002. The
 390 boiling-water phenomena at Camarinal Sill, the strait of Gibraltar. *Deep-Sea Research II* 49:
 391 4097–4113.

392 Chen, C.T.A., K.K., Liu, R., Macdonald, 2003. Continental margin exchanges. In: M.J.R. Fasham,
 393 (eds.), *Ocean Biogeochemistry: A Synthesis of the Joint Global Ocean Flux Study (JGOFS)*.
 394 Springer-Verlag, Berlin, pp. 53-97.

395 de la Paz, M., B., Debelius, D., Macias, A., Vázquez, A., Gómez-Parra, and J.M. , Forja, JM., (2008).
 396 Tidal-induced inorganic carbon dynamics in the Strait of Gibraltar. *Continental Shelf Research*,
 397 28: 1827-1837.

398 Dafner, E.V., M., González-Dávila, J.M., Santana-Casiano, R. and Sempere, 2001. Total organic and
 399 inorganic carbon exchange through the Strait of Gibraltar in September 1997. *Deep-Sea*
 400 *Research II* 48: 1217–1235.

401 Dickson, A.G., 1990. Standard potential of the reaction: $\text{AgCl(s)} + \frac{1}{2} \text{H}_2(\text{g}) = \text{Ag(s)} + \text{HCl(aq)}$, and the
 402 standard acidity constant of the ion HSO_4^{4-} in synthetic seawater from 273.15–318.15 K.
 403 *Journal of Chemical Thermodynamics* 22: 113–127.

404 Dickson, A.G. and J.P., Riley, 1979. The estimation of acid dissociation constants in seawater media
 405 from potentiometric titrations with strong base. I. The ionic product of water — KW. *Marine*
 406 *Chemistry* 7:89–99.

407 DOE, 1994. Handbook of methods for the analysis of various parameters of carbon dioxide in
 408 seawater; version 2. In: Dickson, A.G., Goyet, C. (Eds.), ORNL/CDIAC-74.

409 Echevarría, F., J., García-Lafuente, M., Bruno, G., Gorsky, M., Goutx, N., González, C.M., García, F.,
 410 Gómez, J.M., Vargas, M., Picheral, L., Striby, M., Varela, J.J., Alonso, A., Reul, A., Cózar,
 411 L., Prieto, T., Sarhan, F., Plaza and F., Jiménez-Gómez, 2002. Physical biological coupling in
 412 the Strait of Gibraltar. *Deep-Sea Research II* 49 (19): 4115–4130.

413 García-Lafuente, J., J., Delgado, J. M., Vargas, M., Vargas, F., Plaza and T. Sarhan, 2002. Low
 414 frequency variability of the exchanged flows 646 through the Strait of Gibraltar during
 415 CANIGO. *Deep-Sea Research II* 49 (19): 4051–4067.

416 Gascard, J.C. and C., Richez, 1985. Water masses and circulation in the Western Alboran Sea and in
 417 the Strait of Gibraltar. *Progress in Oceanography* 15: 157–216.

418 Gattuso, J.-P., M., Frankignoulle, and R., Wollast, 1998. Carbon and carbonate metabolism in coastal
 419 aquatic ecosystems. *Annual Review Ecology Systematics* 29: 405-433.

420 Huertas, E., G., Navarro, S. Rodríguez-Galvez, and L.M., Lubián, 2006. Temporal patterns of carbon
 421 dioxide in relation to hydrological conditions and primary production in the northeastern shelf
 422 of the Gulf of Cadiz (SW Spain). *Deep-Sea Res. PT II*, 53:1344-1362.

423 Körtzinger, A., H., Thomas, B., Schneider, N., Gronau, L., Mintrop, J.C. and Duinker, 1996. At-sea
 424 intercomparison of two newly designed underway pCO₂ systems - Encouraging results.
 425 *Marine Chemistry* 52:133-145.

426 Laws, E.A., 1991. Photosynthetic quotients, new production and net community production in the open
 427 ocean. *Deep-Sea Research* 38 (1): 143-167.

428 Lefevre, N., Watson, A.J., Olsen, A., Rios, A.F., Perez, F.F., and Johannessen, T., 2004. A decrease
 429 in the sink for atmospheric CO₂ in the North Atlantic. *Geophysical Research Letters* 31-
 430 L07306

431 Lueker, T.J., A.G., Dickson, and, C.D., Keeling, 2000. Ocean pCO₂ calculated from dissolved
 432 inorganic carbon, alkalinity, and equations for K₁ and K₂ : validation based on laboratory
 433 measurements of CO₂ in gas and seawater at equilibrium. *Marine Chemistry* 90: 105-119

434 Macías, D., C.M., García, F., Echevarría, A., Vázquez-Escobar and M., Bruno, 2006. Tidal induced
 435 variability of mixing processes on Camarinal Sill (Strait of Gibraltar): A pulsating event. *Journal*
 436 *of Marine Systems* 60: 177–192.

437 Macías, D. , A.P., Martín, J., García-Lafuente , C.M.,García , A., Yool , M.,Bruno, A., Vázquez-
 438 Escobar , A. Izquierdo, D.V., Sein and F, Echevarría, 2007. Analysis of mixing and
 439 biogeochemical effects induced by tides on the Atlantic–Mediterranean flow in the Strait of
 440 Gibraltar through a physical–biological coupled model. *Progress in Oceanography* 74: 252-
 441 272.

442 Minas, H.J., B., Coste, P., Le Corre, M., Minas and P., Raimbault, 1991. Biological and geochemical
 443 signatures associated with the water circulation through the Strait of Gibraltar and in the
 444 Western Alboran Sea. *Journal of Geophysical Research* 96: 8755–8771.

445 Padin, X.A., M., Vázquez-Rodríguez, A.F., Ríos and F.F, Pérez, 2007. Surface CO₂ measurements in
 446 the English Channel and Southern Bight of North Sea using voluntary observing ships. *Journal*
 447 *of Marine Systems* 66:297-308.

- Santana-Casiano, J.M., M., González-Dávila, L.M. and Laglera, 2002. The carbon dioxide system in the Strait of Gibraltar. *Deep-Sea Research II* 49: 4145–4161.
- Schiettecatte L-S., H., Thomas, Y., Bozec, A.V. and Borges, 2007. High temporal coverage of carbon dioxide measurements in the Southern Bight of the North Sea. *Marine Chemistry* 106:106-173.
- Takahashi, T., J., Olafsson, J., Goddard, D.W., Chipman and S.C., Sutherland, 1993. Seasonal variation of CO₂ and nutrients in the high latitude surface oceans: a comparative study. *Global Biogeochemical Cycles* 7: 843–878.
- Takahashi, T., S.C., Sutherland, C., Sweeney, A., Poisson, N., Metzl, B., Tilbrook, N., Bates, R., Wanninkhof, R.A., Feely, C., Sabine, J., Olafsson and Y., Nojiri, 2002. Global sea–air CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects. *Deep-Sea Research II* 49: 1601–1622.
- Thomas, H., B. and Schneider, 1999. The seasonal cycle of carbon dioxide in Baltic Sea surface waters. *Journal of Marine Systems* 22 (1): 53-67.
- Thomas, H., Y., Bozec, K., Elkalay, H. and De Baar, 2004. Enhanced open ocean storage of CO₂ from shelf sea pumping. *Science* 304: 1005–1008.
- Thomas, H., Y., Bozec, H.J.W., De Baar, K., Elkalay, M., Frankignoulle, L.-S., Schiettecatte and A.V., Borges, 2005. The carbon budget of the North Sea. *Biogeosciences* 2 (1): 87-96.
- Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical research* 97 (C5): 7373-7382.
- Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry* 2:203–215.
- Zeebe, R. E., and D. A. Wolf-Gladrow, 2001. CO₂ in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier Sciences., New York, 346 pp.,

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Figure captions:

Figure 1. Map of the sampling stations and ship-track for the continuous measurements.

Figure 2. Longitudinal and latitudinal variations in salinity, temperature and $f\text{CO}_2$ in surface waters for the four samplings performed on 7-8 September 2005, 12-13 December 2005, 20-21 March 2006 and 22-23 May 2006.

Figure 3. Longitudinal and latitudinal variations in DIC concentrations in the Strait of Gibraltar for each cruise.

Figure 4. Seasonal variations in observed $f\text{CO}_{2\text{ obs}}$, and the biological and temperature effects represented in $f\text{CO}_{2\text{ T mean}}$ and $f\text{CO}_{2\text{ T obs}}$, respectively.

Figure 5. DIC vs AOU and $f\text{CO}_2$ vs AOU for all the stations and cruises. The dashed line in figure a) represents the theoretic relationship for DIC vs AOU following the Redfield ratio proposed by Laws (1991).

Figure 6. Seasonal variability in air-sea CO_2 fluxes

Figure 1

517

518 Figure 2

Figure 4

525

526 Figure 6

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