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Title: Reconstruction of the seasonal cycle of air-sea CO_2 fluxes in the Strait of Gibraltar

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Abstract:

The present study reports and discusses water surface fCO_2 measurements from 36 cruises in the Strait of Gibraltar made over an eleven-year period (1997 to 2009). Underway measurements of sea surface CO_2 fugacity (fCO_2^{sw}), sea surface temperature (SST) and sea surface salinity (SSS) compiled during the cruises were analysed and integrated into a single data-base which then provided the data resolution/sensitivity required for an examination of the seasonal variability of the fCO_2^{sw}; these data will ultimately allow the reconstruction of the climatological seasonal cycle for the year 2005. The seasonal cycle of both SST and SSS was found to be within the range of the thermohaline signature of the North Atlantic Surface Water, which is the main water mass that flows into the Mediterranean Sea through the Strait of Gibraltar at the surface. The seasonal distribution of CO_2 was characterised by a monthly minimum fCO_2^{2005} value of 334±12 μatm in May, followed by a gradual fCO_2 increase reaching a maximum of 385 μatm during late summer, due to the warming of surface waters. The spatial variability of fCO_2^{sw} observed in the area also indicated that superimposed phenomena, occurring at other scales rather than the seasonal, could affect the dissolved CO_2 distribution. In particular, intense vertical mixing processes generated by internal waves in this region may have a relevant impact on the surface fCO_2^{sw} on a tidal scale. Seasonal CO_2 cycle dynamics indicated that the surface waters of the Strait of Gibraltar acted as an atmospheric CO_2 source during summer and autumn and a CO_2 sink during winter and spring. When these sink/source strengths are considered on an annual basis, the Strait of Gibraltar was close to equilibrium with atmospheric CO_2, resulting in a neutral atmosphere-ocean exchange (-0.06 ± 0.12 mol C m^{-2} yr^{-1}).

Keywords: Carbon dioxide, air-sea CO_2 exchange, Strait of Gibraltar, seasonal variability.

1. Introduction

Over the last 200 years, the ocean has taken up an excess of inorganic carbon from the atmosphere equivalent to approximately 25-30% of the total emission of CO_2 from human activities, specifically fossil-fuel burning, cement manufacturing, and land-use change since the beginning of the industrial revolution (Sabine et al., 2004; Canadell et al., 2007). Improvements in knowledge of the magnitude of this oceanic carbon uptake can be made thanks to an emerging international observation network that will allow routine monitoring of the oceanic CO_2 uptake, on decade and basin scales. However, meaningful projections of future behaviour of the oceanic sink are more challenging. Attempts to set a baseline stabilization target for the atmospheric CO_2 concentration will ultimately depend on an improved understanding of the oceanic mechanism regulating CO_2 uptake and the ability to make useful predictions of this parameter. In particular, predictions are needed of its evolution under a future altered climate and the impacts of climate change trends on air-sea CO_2 fluxes (Doney et al., 2009).

The ~~precise~~ requirements for underway fCO_2 system measurements reflect, in part, the scientific effort made by the research community to constrain regional air-sea CO_2 fluxes to 0.2 Pg C yr^{-1} (Bender et al., 2002). Quantifying the trends in surface-ocean fCO_2 requires robust instrumentation for making high-quality fCO_2 field measurement from various platforms. In order to obtain a comprehensive and accurate quantification of the ocean fCO_2 trends at global scales, a growing international network of underway fCO_2 measurement systems is being deployed on research vessels and commercial voluntary observing ships (VOS). This has provided an unprecedented view of both the spatial pattern of the ocean surface fCO_2 and its temporal variability at different time scales (Doney et al.,2009).

The Strait of Gibraltar ~~constitutes~~ the only connection of the Mediterranean Sea with the Atlantic Ocean. A number of previous studies have highlighted the role played by the Mediterranean in the global circulation of the Atlantic (Hetch et al., 1997; Serra and

Ambar, 2002; Carton et al., 2002), in its biogeochemical inventory (Dafner et al., 2001; Dafner et al., 2003) and in its carbon content (Rios et al., 2001; Alvarez et al., 2005; Ait-Ameur and Goyet, 2006; Huertas et al., 2009). The Strait ~~represents~~ a key area for evaluating the interactions between ~~both~~ Atlantic and Mediterranean water masses in the current context of global climate change. Therefore, under the umbrella of the CARBOOCEAN project, a monitoring program has been established in the region ~~with the objects of assessing~~ the dynamics of the inorganic carbon system in the Strait, and of estimating the transport of both total and anthropogenic carbon between the North Atlantic and the Mediterranean Sea.

The implementation of the measurement program has provided new data on biogeochemical fluxes ~~occurring~~ through the channel and a carbon budget for the whole Mediterranean (Huertas et al., 2009). Despite ~~this~~, CO_2 exchange across the water-atmosphere interface remains uncertain in this region and hence, a thorough examination has been carried out here ~~with the aim of clarifying~~ this important component of the carbon cycle. In this work, underway measurements of fCO_2^{sw}, sea surface temperature (SST) and sea surface salinity (SSS) were compiled during 36 cruises (research ~~cruises and voyages of Mediterranean~~ commercial ~~ships~~) conducted between 1997 and 2009 (Table 1).

2. Material and Methods:

2.1 The study area

The Strait of Gibraltar is located ~~at the~~ south of the Iberian Peninsula and is the principal hydrodynamic connection of the Mediterranean Sea with the Atlantic Ocean. It is a narrow and shallow channel with an east-west orientation. Its minimum width is 14 km at the Tarifa Narrows (Fig. 1). In ~~the context~~ of oceanic circulation, a small net inflow of Atlantic Water (AW) through the Strait occurs to balance the buoyancy losses and the excess ~~of~~ evaporation over precipitation observed in the Mediterranean. Mass and salt conservation forces result in a density-driven baroclinic exchange, in which warm AW of lower salinity (between 36.2-36.4) enters the Mediterranean Basin at the surface, ~~whilst~~ colder Mediterranean Outflow Water of higher salinity (~38.4) flows out at depth (Gascard and Richez, 1985).

The Strait of Gibraltar represents an important boundary condition for dynamic processes in the Mediterranean over a wide range of frequencies, the precise restrictions depending on the time and spatial scale involved. Among these processes, the most energetic are tides within the Strait; the tide generates flow fluctuations whose amplitude can be up to 4 Sv during spring tides, more than four times greater ~~in magnitude~~ than the time-averaged flows (García-Lafuente et al., 2000). Furthermore, resulting from the interaction of tides with the topography of the Strait, large internal waves are generated, especially at the Camarinal Sill (Sanchez-Garrido et al., 2008). ~~However~~, despite the hydrodynamic complexity of the Strait of Gibraltar, the thermohaline properties of surface waters can be approximated to those of the North Atlantic Surface Water (NASW) with the exception of some deeper water "footprint" related to tidally-forced fluctuations occurring at the Camarinal Sill.

2.2. Dataset and methods

Underway measurements of ~~the~~ fCO_2^{sw} ~~and~~ sea surface temperature (SST) and salinity (SSS) were compiled during a total of 36 cruises, all being elements of ~~various~~ different scientific efforts integrated within the framework of the European projects CANIGO (Canary Islands Azores Gibraltar Observations), CAVASSO (Carbon Variability Studies by Ships Of Opportunity) and CARBOOCEAN (Marine Carbon Sources and Sinks Assessment). The tracks ~~of the cruises~~ are shown in Fig. 1 and details about the cruises ~~have been~~ summarised in Table 1.

SSS and SST were recorded using a thermosalinometer and the fCO_2^{sw} was measured by equilibration-infrared absorption analysis with a precision of ±1 μatm. Details of methods identical to those outlined here have been published previously (Santana-Casiano et al., 2002; Rios et al., 2005) ~~and were related~~ to ~~the~~ earlier cruises ~~made~~

within this study (CANIGO 1 and Azores 1). The twelve FICARAM (Air-Sea CO_2 fluxes along a meridional transect in the Atlantic Ocean) cruises included in this study commenced in October 2000 and continued to the present (Padin et al.,2010), and were conducted onboard the Hespérides. The tracks of the courses (headed southward during boreal falls and northward in boreal springs) were framed within the Spanish Antarctic Research Program. An additional project that has contributed since 2007 to the fCO_2^{sw} data-base in the Strait is the ICCABA VOS line which connected the Canary Islands with Italy. In addition to the VOS lines that occasionally pass through the Strait, data collected in the GIFT (Gibraltar Fixed Time Series) section was also included in this study. This time series was established in 2005 with the aim of monitoring the carbon exchange between the Mediterranean and Atlantic basins. During only three of the GIFT cruises were continuous underway fCO_2^{sw} measurements performed (de la Paz et al., 2008). The rest of the GIFT data used in this study were obtained from discrete water samples collected at 5 meter depth at eight stations forming a cross-section of the Strait and in which SST and SSS were taken from the CTD record.

Total Alkalinity (A_T) was measured by potentiometric titration (Mintrop et al., 2000). The accuracy of the A_T determination was assessed by measurement of Certified Material (CRM, supplied by Professor Andrew Dickson, Scripps Institution of Oceanography, La Jolla, CA, USA). From the analysis of 3 CRM batches, an accuracy for A_T of about ±0.8 μmol kg^{-1} was obtained. pH_T was determined at 25 ºC following the spectrophotometric method of Clayton and Byrne (1993) with m-cresol purple as indicator. The pH method had a precision of ±0.003 units.

fCO_2^{sw} was subsequently calculated from these parameters using the carbonic dissociation constant formulated by Mehrbach et al. (1973) and refitted by Dickson and Millero (1987). For these computed values, the estimated precision of the fCO_2^{sw} was ±2.7 μatm (Millero, 2007). More details about the methodology used on the GIFT cruises are given in Huertas et al. (2009). fCO_2^{sw} was measured by equilibration on a total of 23 cruises, whereas it was calculated from pH_T, and A_T, on 15 cruises, with both being simultaneously recorded on two cruises (13th Dec 2005 and 23rd May 2006) for purposes of data comparison (Table 1). The cruise-averaged values obtained for fCO_2^{sw} from both methods were very similar, with average differences in fCO_2^{sw} of ±4 and ±3 μatm for the Dec 2005 and May 2006 cruises respectively. Regardless of the sampling strategy used (continuous underway versus discrete water samples at stations), the differences in SSS and SST were insignificant, less than 1 % of the averaged value. The precision of the fCO_2^{sw} measurements with the equilibration technique is higher than that based on calculations from A_T and pH_T (Millero, 2007). However, the integration of data obtained with the two techniques significantly increased the dataset, which allowed far greater seasonal fCO_2^{sw} coverage, especially when equilibration/infrared absorption measurements were very scarce, such as during summer. Because both techniques produced very similar results when run concomitantly, it is considered that the approach used is fully validated.

FIGURE 1, TABLE 1

Monthly atmospheric CO_2 molar fraction (xCO_2^{atm}) data at the meteorological station of the Azores (Terceira Island, Portugal) were obtained from the Cooperative Air Sampling Network of the NOAA/ESRL Global Monitoring Division. The xCO_2^{atm} was converted to fCO_2^{atm} taking into account the atmospheric pressure, and was expressed in wet air using the water vapour formulation of Weiss and Price (1980) as a function of SSS and SST.

In order to obtain a composite seasonal picture of fCO_2^{sw} behaviour, data gathered in all available years were collated into a single "virtual year". This procedure was based on the assumption that surface waters reflected the atmospheric fCO_2 increase, as proposed by Takahashi et al. (2009) in the most recent global ocean surface CO_2 climatology. For the study case of the Strait of Gibraltar, the validity of this assumption is reinforced by the study of Santana-Casiano et al. (2007) on the time-series obtained at the ESTOC (European Time Series of the Canary Islands) site located in the

Subtropical North Atlantic, where the upper layer shows a very similar biogeochemical signature to that in the Strait of Gibraltar. That study showed that fCO_2^{sw} was strongly correlated with atmospheric CO_2 ~~and followed the same trends~~ in this oceanic region. Thus, each fCO_2^{sw} value observed in a particular year i and in the month j was referenced to its respective month in the year 2005 (an arbitrarily chosen year of reference) according to the following equation:

$$fCO_2^{sw}{}_{2005} = fCO_2^{sw} + (fCO_2^{atm}{}_{2005\ month\ j} - fCO_2^{atm}{}_{year\ I\ month\ j}) \qquad (1)$$

Air –water CO_2 flux was computed as:

$$F = k\alpha\ \Delta\ fCO_2 \qquad (2)$$

where ~~F denotes the air-sea CO_2 flux,~~ k represents the gas transfer velocity, α is the CO_2 solubility coefficient given by Weiss (1974), and ΔfCO_2 is the air-sea fCO_2 gradient. The gas transfer velocity as formulated by Nightingale et al. (2000) was estimated as a function of wind speed corrected to 10 m. The 6-hourly wind speed data were provided by the Spanish *Agencia Estatal de Meteorología* from the station located at Tarifa (Figure 1).

3. Results and discussion:

3.1. Biogeochemical properties in the surface water.

Data gathered between 1997 and 2009 in the Strait are given in Table 1. Seasonal fCO_2^{sw} data from all years was integrated to represent a composite seasonal cycle (Figure 2), referred arbitrarily to the year 2005.

Average in-situ surface water temperature (SST) for cruises varied between 15.6 and 22.8 ºC. Minimum and maximum temperatures were recorded in March and September respectively. This seasonal pattern of temperature was a direct consequence of seasonal heating and cooling of surface waters at these temperate latitudes (Fig. 2a). ~~However~~, SSS did not show such a distinctive seasonal pattern, as its values ranged between 36.06 and 36.55 (Fig. 2b). Data gathered on cruises close to each other in time exhibited an evident scattering, which suggests that the thermohaline properties in the Strait might be also subjected to short-term variability. Nevertheless, the averaged values obtained for SSS in the Strait remain within the range of the haline signature described by Gascard and Richez (1985) for NASW: that is, between 36.2 and 36.4.

FIGURE 2

The most notable feature of the seasonal $fCO_2^{sw}{}_{2005}$ cycle in the Strait of Gibraltar is the decrease detected during spring, attributed to the withdrawal of carbon by biological activity. A minimum of 320 μatm was measured in May (Fig. 2c). $fCO_2^{sw}{}_{2005}$ gradually increased until late summer, which reflected an increase in respiratory processes and is due also to surface warming. Maximum averaged monthly $fCO_2^{sw}{}_{2005}$ values (≈385 μatm) were observed in late summer (August); However, some particular values indicated in Table 1 deviate from this seasonal pattern, the highest averaged value from the cruises being observed in October (396 μatm). It is worth noting that the greatest variability for $fCO_2^{sw}{}_{2005}$ was also observed in October, with values ranging from 339 to 396 μatm. Coincidentally, October is the month when the most sampling cruises took place: 9 out of the total 36 cruises considered were made during this month. For that reason, temporal scales other than seasonal were examined in detail, as described in the next section.

Temperature plays an important role in determining the pattern of surface water fCO_2^{sw} by controlling the thermodynamic equilibrium of the inorganic carbon system. To remove the temperature effect, fCO_2^{sw} needs to be normalized to a common temperature, using the temperature dependence of fCO_2 in isochemical conditions ($\delta \ln fCO_2/\delta\ SST$) which is equal to 4.23 % ·ºC^{-1} (Takahashi et al. 1993). After removing the thermal effect induced by seasonal SST changes, the composite annual cycle for

fCO_2^{sw} ($fCO_{2@2005@Tmean}$) was estimated. In essence, $fCO_{2@2005@Tmean}$ represents the added effects of biological processes, vertical mixing and air-water CO_2 exchange on fCO_2. The $fCO_{2@2005@Tmean}$ distribution mirrors that observed for the SST, with the minimum and maximum values being observed during late summer and winter, respectively (Fig. 2d).

The net annual effect of the temperature control on fCO_2^{sw} can be evaluated using the methods of Takahashi et al. (1993), perturbing the annual mean $fCO_2^{sw}{}_{2005}$ of 360 μatm with an SST seasonal amplitude of 6.6 ºC. Accordingly, the resulting seasonal amplitude of fCO_2^{sw} induced by the seasonal SST cycle is found to be 100 μatm. Apart from temperature variations other effects can be quantified from the seasonal amplitude of the $fCO_{sw@2005@Tmean}$; these additional effects amount to 61 μatm. The ratio between the two amplitudes was 1.6, which indicated that the main mechanism for the observed seasonal variability of fCO_2^{sw} in the Strait was temperature. Other mechanisms, which include tidally-induced vertical mixing, biology and air-water exchange, are also involved in the fCO_2^{sw}. The quantification of these individually is, however, quite complex in this region, owing to the high spatiotemporal variability on a short time-scale. Regarding the contribution of biology, some studies on primary production in the Strait indicate that productivity is significantly low compared to that occurring in the adjacent waters of the Alboran Sea (Macías et al., 2007a, Macías et al., 2009). Macias et al. (2007a) used a set of weekly composite Sea-Wifs images (from 1998 to 2004) and assessed the temporal and spatial variability of the surface chlorophyll distribution in the North-western Alboran Sea, including the study area considered in the present article. These authors found that the lowest mean chlorophyll concentrations of 0.2-0.5 mg m^{-3} were present in the centre of the Strait. This finding has been related to the low residence time of the water in the Strait (Macias et al., 2007b). The coupled physical-biological model formulated by Macias et al. (2007b) found that residence times within the channel are so short that phytoplankton communities cannot grow appreciably during their transit. Thus, water in the central channel of the Strait represented oligotrophic NASW that flowed quickly into the Mediterranean basin.

In order to analyse short-term variability of fCO_2, the longitudinal distribution of the SST, fCO_2^{sw}, and the $fCO_{2@2005@Tmean}$ along the east-west axis was plotted (Fig. 3). October data were selected because this month was sampled more than any other. As for the thermohaline properties, the spatial distribution of surface fCO_2^{sw} values were highly variable, and this resulted in a wide standard deviation associated with the fCO_2^{sw} values (Table 1). The distribution pattern found on the western side of the Strait was typically more homogeneous than that observed on the eastern side for SST, fCO_2^{sw}, and especially in the case of $fCO_{2@2005@Tmean}$, which displayed the most marked east-west variability. This finding is attributed to internal waves and was previously described in the area by Santana-Casiano et al. (2002) and de la Paz et al. (2008a).

The effects of internal waves are related to two different processes responsible for enrichment of the surface layer with inorganic carbon. Firstly, internal wave generation at the Camarinal sill causes surface water enriched with inorganic carbon to be advected subsequently by the water inflow through the Strait. Carbon-enriched water affected by these processes tends to move eastwards at half the speed of observed internal waves. Secondly, the injection process described above continues as the internal waves propagate in an eastwards direction, which then causes the advected water to travel at the wave speed. This phenomenon can be diagnosed from aerial views by changes in the roughness of the sea surface (Bruno et al., 2002, Vazquez et al., 2009). In addition, due to the bathymetry of the channel, the interface between Atlantic and Mediterranean water slopes up toward the east, shifting from approximately 200 m to around 75 m depth (Huertas et al., 2009) from Cape Spartel to Point Almina (Fig. 1). This feature also makes the upwelling of deeper water in the eastern Strait more noticeable.

The detection of surface waters associated with the occurrence of internal waves is difficult if based solely on salinity considerations, because no apparent changes in SSS were evidenced. However, thermal differences are more apparent and the decease of SST clearly demarcates the vertical intrusion of colder water from greater depths (Figure 3). The maximum temperature difference was observed in October 2000 when a decrease in SST of ~3ºC from west to east (Fig 3A) was recorded, accompanied by steep increases in both fCO_2^{sw} and $fCO_{2@2005@Tmean}$ equivalent to ~50 μatm and ~90 μatm, respectively. These increases are greater than the increase expected for fCO_2^{sw} under isochemical conditions (Takahashi et al., 1993).

FIGURE 3.

The tidal-induced variability of the inorganic carbon in the Strait of Gibraltar has been addressed in a previous study (de la Paz et al., 2008a). The fCO_2^{sw} database used in this study included the available fCO_2^{sw} data already published for the Strait, e.g. Santana-Casiano et al. (2002) and de la Paz et al. (2008b). These earlier studies, however, were limited, and seasonal coverage for fCO_2^{sw} was not as consistent as in the present study. In order to obtain more robust seasonal trends of fCO_2^{sw}, the database was integrated into a composite seasonal cycle (Fig. 2). Climatological seasonal cycles of SST, fCO_2^{sw} ,and $fCO_{2@2005@Tmean}$ were obtained by fitting averaged cruise values to a harmonic function in the form of:

$$y = b_0 + b_1 \sin [(x-\varphi_1)2\pi/365] + b_2 \sin [(x-\varphi_2)4\pi/365] \qquad (3)$$

where y is either SST, fCO_2^{sw}, and $fCO_{2@2005@Tmean}$, x represents the time expressed in Julian days, and b_0, b_1, and b_2 , φ_1 and φ_2 are fitted constants. The resulting plots of the fitted equations indicated in Table 2 are shown in Fig. 2. The estimated values closely follow the seasonal pattern of the actual data and statistical analysis shows that this is significant ($p < 0.05$) and characterized by relatively strong regression coefficients ($0.6 < r < 0.86$).

TABLE 2

A study was made of deviations from the expected seasonal patterns, taken as the difference between the averaged cruise value and the predicted value obtained by applying equation (3) to each variable. The ~~object~~ of investigating these anomalies is to ~~understand~~ the ~~potential~~ mechanisms responsible for the fCO_2^{sw} ~~Observed~~. The only statistically significant relationship between anomalies was a negative one (r^2=-0.5) between SST and $fCO_{2@2005@Tmean}$ (Fig. 4). This is consistent with the hypothesis that CO_2-enriched colder water is brought to the surface via upwelling ~~processes~~. In contrast, no relationship was observed between $fCO_{2@2005@Tmean}$ and the SSS anomalies. Positive and negative anomalies for SST and $fCO_{2@2005@Tmean}$ were distributed throughout the year with no apparent pattern, which implies that upwelling is not seasonally dependent in this area. This distribution is different from that observed in other oceanic regions, e.g. the southern waters of Tasmania where reported SST anomalies were associated with negative $fCO_{2@2005@Tmean}$ anomalies (Borges et al, 2008). The correlation observed there was attributed to a reduced input of dissolved inorganic carbon during the fall-winter period, which coincided with phases of positive SST anomalies related to changes in wind regimes and shifts in the mixed layer depth.

FIGURE 4.

To assess the inter-annual variability, the mean rate of change ~~for~~ fCO_2^{sw} was estimated by linear regression of the de-seasonalized monthly values. These were computed as the difference between observations and averaged monthly values for all cruise data. No significant inter-annual trends in SST and $fCO_2^{sw}{}_{2005}$ were found.

Taking into account that $fCO_2^{sw}{}_{2005}$ compilation (see Section 2.2: eq .1) assumes that surface water tracks the atmospheric CO_2 increase (~1.5 μatm yr^{-1}), the resulting long-term rate of fCO_2^{sw} would match the atmospheric rate. The high fCO_2^{sw} variability observed in this system on the seasonal (~70 μatm) and tidal (~50 μatm) time-scales ~~obstruct~~ the observation of any other inter-annual CO_2 trend that may be statistically significant and distinct from the atmospheric trend. This finding is in agreement with the results obtained at the ESTOC site and in other subtropical regions (Bates, 2007; Santana-Casiano et al., 2007).

3.2. Seasonal cycle of the air-water CO_2 exchange in the Strait

The calculation and interpretation of instantaneous CO_2 fluxes from short-term cruise data can provide a process-level understanding of hourly trends and patterns, but this assessment reveals little about the overall status of the Strait as a CO_2 source-sink. Atmospheric conditions (wind, atmospheric pressure) change rapidly, whereas oceanic conditions (SST, salinity, fCO_2^{sw}) generally vary much more slowly (Else et al., 2008). In our analysis, conditions of slow oceanic change were considered to ~~compute the most representative~~ estimate ~~of~~ the integrated annual flux of CO_2 along the Strait of Gibraltar.

The air-water CO_2 fluxes were calculated using equation 2, where the air-water fCO_2 gradient was estimated from the difference between the monthly atmospheric fCO_2 value in 2005, and the monthly fCO_2^{sw} in surface waters. The last term was computed from the $fCO_{2@2005@Tmean}$ obtained by applying equation (3), which was subsequently corrected to the SST in 2005 (equation 3) and the expression proposed by Takahashi et al. (1993). The gas transfer velocity (k) was computed using the monthly climatological wind speed.

In the assessment of the air-water CO_2 fluxes, the greatest uncertainty is often associated with the parameterization of k and, hence, ~~some discrepancies~~ frequently ~~arise about~~ the expression ~~that~~ should be selected to calculate it. In the present study, we applied the wind-driven, air-sea exchange parameterization proposed by Nightingale et al. (2000) to derive k~~; however, in order to compare results,~~ fluxes were also computed using the k value calculated using the method of Wanninkhof (1992). ~~This~~ has previously been applied widely in all oceanic environments, and was previously used to estimate the air-sea CO_2 exchange in the Strait of Gibraltar (Santana-Casiano et al., 2002; de la Paz et al., 2008b). Data obtained using the Wanninkhof coefficient are hereafter shown in parentheses and ~~indicated with~~ the acronym W92.

FIGURE 5

Results show that surface waters of the Strait of Gibraltar behave as a CO_2 source during summer and autumn whereas, during winter and spring, they ~~shift and~~ act as a CO_2 sink. The maximum absorption of atmospheric CO_2 occurs in late spring, with ~~values~~ of -1.60 mmol $m^{-2}d^{-1}$ (W92: -1.56). The most under-saturated ~~CO_2 values of~~ ΔfCO_2–(~-21 μatm) were observed at the same time. After this minimum, ΔfCO_2 progressively increases throughout the summer months and ~~results in the air-sea CO_2 exchange status~~ changing from sink to source. The magnitude of this source reaches its maximum in August, with estimated CO_2 fluxes from surface waters of 1.68 mmol $m^{-2}d^{-1}$ (W92: 2.2) and a ΔfCO_2 of ~ 25 μatm.

The wind regime in the Strait of Gibraltar is characterised by a major zonal component mainly resulting from the orography of the Strait (Dorman et al., 1995), causing the predominance of intense easterlies in the area especially during summer. ~~However,~~ ~~figure 5 shows that~~ the climatological seasonal cycle for wind speed exhibits a relatively small range throughout the year (4.7 - 5.9 m s^{-1})~~; and~~ consequently the monthly k values are similar ~7.8 to 12.5 cm h^{-1} (W92: 8 to 12.5 cm h^{-1})~~. Thus, although~~

~~wind speed is a relevant pumping mechanism driving CO_2 exchange,~~ the strength of the Strait as a CO_2 sink/source is determined by the seasonal carbon dynamics.

When considered on an annual basis, the Strait of Gibraltar is nearly in equilibrium with the atmospheric CO_2~~; however,~~ the CO_2 sink in spring/autumn months ~~has a~~ slightly ~~predominance over~~ the source. Consequently, the calculated air-sea CO_2 flux for 2005 was -0.06 ± 0.12 mol m^{-2} yr^{-1} (W92: -0.02±0.13) mol m^{-2} yr^{-1}.

The formulation of k is ~~wind dependent with~~ a non-linear ~~fit~~. Hence, the effect of short-term wind speed variability on an annual scale was evaluated by calculating k from the climatological daily wind speed data. The CO_2 flux values derived using this approach are identical to those derived using mean monthly wind speeds i.e. -0.06 ± 0.18 mol m^{-2} yr^{-1} (W92: -0.02± 0.19 mol m^{-2} yr^{-1}). These data indicate that short-term variability of the wind speed is not a significant uncertainty on annual times scales for air-sea CO_2 exchange in the Strait. In order to test the effect of wind speed variability on calculated annual CO_2 fluxes, a constant value of k (9.9 cm h^{-1}), which represents the annual mean, was applied. This resulted in a ~50% decrease (-0.03 ± 0.15 mol m^{-2} yr^{-1}) in CO_2 fluxes compared to the values derived using either daily or monthly integrated wind speeds. Daily and monthly wind speeds are considered more representative of seasonal wind speeds, which are higher in the summer months (Figure 5)~~,~~ when the Strait typically behaves as a CO_2 source. Therefore although the Strait acts as a sink ~~of CO_2~~ for a longer period than it does as a CO_2 source ~~during the year~~ (Figure 5), this is counterbalanced by relatively high emissions of CO_2 in summer because of higher observed wind speeds. ~~As a consequence,~~ on an annual basis the Strait remains close to equilibrium with atmospheric CO_2. Furthermore, the discrepancies derived from the use of k computations given by Nightingale et al (2000) or Wanninkhof (1992) are ~~minimum~~ and not relevant ~~for~~ the status as a source or sink that can be attributed to the Strait of Gibraltar. Thus, although wind speeds ~~and k computations~~ play an important role in regulating CO_2 fluxes, the CO_2 source/sink status of the Strait of Gibraltar is mainly dependent on seasonal carbon dynamics.

Previous estimates of air-sea CO_2 fluxes in the Strait of Gibraltar have also reported that the area behaves as an atmospheric sink of CO_2 on an annual basis. Santana-Casiano et al. (2002) described the Strait as a source of CO_2 in summer and a sink during the winter, and provided a net annual flux estimation by averaging the CO_2 fluxes obtained during September and February (1997/1998). A net CO_2 flux of -2.5 mol m^{-2} yr^{-1} based on Wanninkhof (1992) was estimated, ~5 times the CO_2 sink value reported here. This was possibly the consequence of high winds (8 to 15 m s^{-1}) during a relatively short time period. These data demonstrate how seasonal bias in sampling strategies may result in CO_2 flux overestimations. Other previous studies had more comprehensive seasonal coverage. de la Paz et al. (2008b) considered averaged seasonal CO_2 fluxes for March, May, September and December (2005/2006) for calculating an annual CO_2 flux. Essentially, those results showed the same trends as those presented here, with the Strait acting as a CO_2 sink one order of magnitude larger (-0.28 mol m^{-2} yr^{-1}) than the value calculated in this study. This discrepancy demonstrates the need for high resolution CO_2 data, in both time and space, to produce accurate annual flux estimates in any area.

Based on an estimated area of 1500 km^2 defined by the Strait's western and eastern limits at Cape Spartel and Point Almina respectively (Fig. 1), the total amount of CO_2 taken up by waters in the Strait is $1.1 \pm 2.2 \cdot 10^{-3}$ Tg C yr^{-1}. ($0.1 \pm 0.2 \cdot 10^{-3}$ Tmol C yr^{-1}). It is instructive to quantify this in the context of the amount of carbon that is exchanged between the Atlantic Ocean and the Mediterranean Sea through the Strait of Gibraltar (Dafner et al., 2001; Ait-Ameur and Goyet, 2006; de la Paz et al., 2008a; Huertas et al., 2009). The most recent estimation by Huertas et al. (2009) reported a net carbon export from the Mediterranean to the Atlantic equivalent to 2.11 TmolC yr^{-1}. Thus carbon transport through the water column is more than one order of magnitude higher than the net annual CO_2 transfer across the air-water interface. Nonetheless, it is still relevant to elucidate what role is played by the air-sea CO_2 exchange in the overall picture of the carbon cycle in the Strait of Gibraltar. Therefore, the results presented in this study, based on a comprehensive analysis of a database compiled with 12 years of data, contribute to completing the carbon budget in this key oceanic region.

The relevance of coastal areas in the global carbon cycle has recently been highlighted by Chen and Borges (2009), who performed the scaling of the air-water CO_2 fluxes using the present database available for the coastal ocean. These authors estimated that the world's continental shelves are responsible for the absorption of atmospheric CO_2 in the range of 0.33 to 0.36 PgC yr^{-1}, which corresponds to an additional sink of 27% to 30% of the CO_2 taken up by the open ocean based on the recent fCO_2 climatology given by Takahashi et al. (2009). The net annual CO_2 flux obtained in the Strait of Gibraltar falls then within the values reported by these two compilations, being close to the -0.8 mol C m^{-2} yr^{-1} provided by Chen and Borges (2009) for the NE Atlantic continental shelf, and to the -0.6 mol C m^{-2} yr^{-1} computed by Takahashi et al. (2009) for the Eastern North Atlantic Ocean.

4. Summary and Conclusions:

This study reports the variability of fCO_2 in the Strait of Gibraltar on the seasonal scale and analyses the mechanisms regulating this variability. The assessment is based on data gathered in 36 cruises undertaken in the area from 1997 to 2009, and a climatological seasonal cycle has been reconstructed, arbitrarily, for the year 2005. This climatological seasonal cycle for the air-water CO_2 exchange varies throughout the year: the Strait behaves as a CO_2 source during summer and autumn, and as a CO_2 sink during winter and spring. However, on an annual basis, the CO_2 efflux recorded during the months of emission are counterbalanced by the CO_2 influx found during the months of absorption, resulting in a neutral status (-0.06 ± 0.12 mol C m^{-2} yr^{-1}).

This study also demonstrates that processes on a shorter-term time scale, such as the enrichment of fCO_2 in surface waters brought about by the vertical mixing induced by the tidal regime, are difficult to assess in this particular area. These short-term processes hinder an accurate assessment of the carbon budget on longer time scales (e.g. inter-annual and decadal). An accurate assessment of the short-term fCO_2^{sw} variability in the Strait, and the mechanisms involved, would require other observational strategies, such as in-situ continuous monitoring of the fCO_2 and ancillary measurements in surface waters. Such observations would be particularly difficult to perform in this region, not least because of the continuous heavy maritime traffic, and socio-political factors associated with its geographical position.

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Figure captions:

Figure 1. Map of the Strait of Gibraltar and ~~the tracks of the~~ cruises made to obtain data for the analysis of fCO_2 temporal variability.

Figure 2. Climatological seasonal cycles for SST, SSS, fCO_2^{2005} and $fCO_{2@2005@mean}$. The black dotted line in the third graph represents the seasonal variability of the atmospheric fCO_2.. The filled black circles are values obtained from continuous pCO_2 measurements by equilibration/IR absorption. The unfilled circles are values calculated from A_T and pH_T. The grey line denotes the sinusoidal fit of each variable, whose ~~parameters~~ are indicated in Table 2.

Figure 3. Longitudinal variability of the SST, fCO_2 and fCO_2 normalised to a temperature of 18.5 ºC for data collected during cruises ~~made~~ in the month of October in several years.

Figure 4. Monthly anomalies of the fCO_2 normalised to a temperature 18.5 ºC, plotted against monthly anomalies of sea surface temperature (SST). Monthly anomalies ~~have been~~ calculated as the difference between monthly averaged ~~values from~~ observed values and those obtained from the sinusoidal fit indicated in Table 2.

Figure 5. Climatological seasonal cycle of the monthly wind speed, air-water CO_2 gradient and CO_2 fluxes in the Strait of Gibraltar.

Table 1

Scientific Program	Ship	date	SST (ºC)	SSS	fCO_2^{sw} (µatm)	fCO_2^{2005} @18.5 (µatm)	pCO2 method
CANIGO	R/V Thalassa	6-Sep-97	19.02 ± 1.58	36.38±0.17	357±11	366±23	pCO2 underway
AZORES 1	R/V Hespérides	26-Aug-98	20.98 ± 0.63	36.46±0.20	371±4	347±7	pCO2 underway
FICARAM	R/V Hespérides	26-Oct-00	18.45 ± 1.58	36.9	364±7	378±40	pCO2 underway
FICARAM	R/V Hespérides	15-Apr-01	16.46 ± 0.23	36.06±0.23	335±9	373±12	pCO2 underway
FICARAM	R/V Hespérides	28-Oct-01	19.05 ± 0.51	36.22±0.10	354±4	355±6	pCO2 underway
FICARAM	R/V Hespérides	29-Oct-02	18.11 ± 0.62	36.37±0.11	349±6	363±7	pCO2 underway
FICARAM	R/V Hespérides	22-Apr-03	16.14 ± 0.39	36.37±0.15	330±11	368±13	pCO2 underway
FICARAM	R/V Hespérides	22-Oct-04	20.80 ± 0.79	36.15±0.10	357±4	328±12	pCO2 underway
GIFT	R/V "Amir Moulay Abdellah"	4-May-05	17.05 ± 0.31	36.33±0.03	320±7	340±11	Alk and pH
GIFT	R/V García del Cid	10-Jun-05	16.87 ± 0.73	36.29±0.06	369±18	395±30	Alk and pH
GIFT	R/V "Amir Moulay Abdellah"	8-Sep-05	22.85 ± 0.70	36.25±0.04	389±6	324±6	pCO2 underway
FICARAM	R/V Hespérides	19-Oct-05	18.61 ± 0.79	36.43±0.11	372±3	371±14	pCO2 underway
GIFT	R/V "Amir Moulay Abdellah"	13-Dec-05	17.60 ± 0.40	36.54±0.04	355±7	368±7	Alk and pH
***GIFT	R/V "Amir Moulay Abdellah"	13-Dec-05	17.86 ± 0.09	36.40±0.03	351±4	361±5	pCO2 underway
GIFT	R/V "Amir Moulay Abdellah"	21-Mar-06	15.55 ± 0.16	36.25±0.02	354±8	400±9	Alk and pH
GIFT	R/V "Amir Moulay Abdellah"	23-May-06	18.15 ± 0.61	36.34±0.02	346±0	352±28	Alk and pH
***GIFT	R/V "Amir Moulay Abdellah"	23-May-06	18.18 ± 0.77	36.24±0.03	343±10	347±20	pCO2 underway
FICARAM	R/V Las Palmas	26-Sep-06	21.47 ± 0.62	36.43±0.05	362±7	318±4	pCO2 underway
GIFT	R/V García del Cid	23-Nov-06	19.27 ± 0.83	36.49±0.06	358±6	347±18	Alk and pH
GIFT	R/V "Amir Moulay Abdellah"	14-Dec-06	17.82 ± 0.37	36.48±0.06	358±15	368±19	Alk and pH
FICARAM	R/V Las Palmas	30-Apr-07	16.78 ± 0.62	36.55±0.36	346±7	371±13	pCO2 underway
GIFT	R/V "Amir Moulay Abdellah	8-May-07	16.74 ± 0.40	36.23±0.10	328±11	353±17	Alk and pH
GIFT	R/V "Amir Moulay Abdellah	5-Jul-07	18.65 ± 0.73	36.34±0.11	360±20	358±13	Alk and pH
FICARAM	R/V Las Palmas	8-Oct-07	21.90 ± 0.54	36.46±0.15	396±5	342±4	pCO2 underway
GIFT	R/V "Amir Moulay Abdellah	6-Nov-07	16.69 ± 0.86	36.37±0.14	376±18	406±30	Alk and pH
ICCABA	MSC Benedetta	18-Nov-07	17.80 ± 0.66	36.42±0.05	340±6	351±7	pCO2 underway
ICCABA	MSC Benedetta	25-Nov-07	18.13 ± 0.60	36.50±0.04	347±3	354±11	pCO2 underway
ICCABA	MSC Benedetta	26-Feb-08	16.74 ± 0.17	36.41±0.03	365±4	388±6	pCO2 underway
GIFT	R/V Regina Maris	13-Apr-08	16.72 ± 0.17	36.47±0.06	353±9	380±7	Alk and pH
FICARAM	R/V Las Palmas	25-Apr-08	16.88 ± 0.31	36.37±0.07	382±12	406±12	pCO2 underway
GIFT	R/V Regina Maris	27-Jul-08	21.10 ± 1.69	36.34±0.10	393±26	353±4	Alk and pH
GIFT	V García del Cid	26-Sep-08	20.35 ± 0.74	36.49±0.12	373±1	346±10	Alk and pH
FICARAM	R/V Las Palmas	9-Oct-08	19.88 ± 0.81	36.49±0.08	341±6	320±8	pCO2 underway
GIFT	R/V Hespérides	12-Oct-08	18.37 ± 1.23	36.47±0.15	352±20	354±3	Alk and pH
GIFT	R/V Hespérides	21-Oct-08	19.80 ± 1.55	36.54±0.09	392±10	373±34	Alk and pH
ICCABA	MSC-Marta	13-Dec-08	16.69 ± 0.16	36.47±0.02	366±11	390±13	pCO2 underway
ICCABA	MSC-Marta	29-Dec-08	16.16 ± 0.27	36.30±0.00	365±5	398±8	pCO2 underway
ICCABA	MSC-Marta	9-Jan-09	16.19 ± 0.38	36.42±0.08	364±6	393±9	pCO2 underway

Table 1: Cruises / research program, ships, dates (dd-mmm-yy) and averaged values for SST, SSS, fCO_2^{sw} (µatm), $fCO_{2@2005@18,5}$ (µatm) and the technique used for the fCO_2^{sw} measurements. *** mark the two cruises where both analytical techniques were employed (See section 2).

Table 2

	b_0	b_1	φ_1	b_2	φ_2	r
SST	18,2	-2,31	-31,75	0,55	12,23	0,86
$fCO_{2\ sw}$	361,31	-10,74	-8,77	-11,47	-97,20	0,60
$fCO_{2\ sw\ @2005@\ 18.5}$	364,91	22,88	-407,8	-	-	0,58

Table 2. Fitting ~~parameter~~ of the wave function used for the climatologycal seasonal cycles of SST, $fCO_{sw,}$ and $fCO_{sw@2005@Tmean}$.

Figure 1

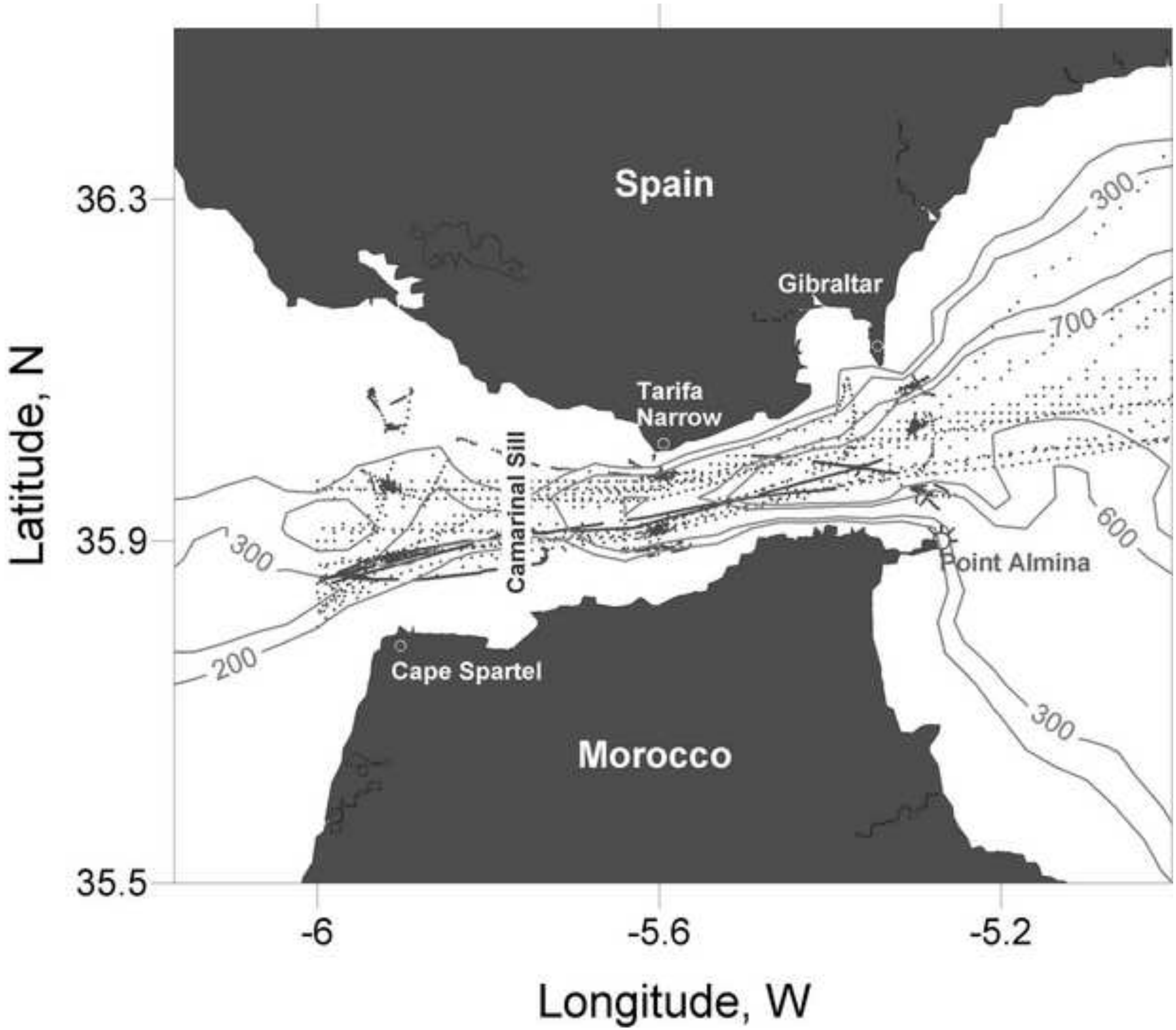
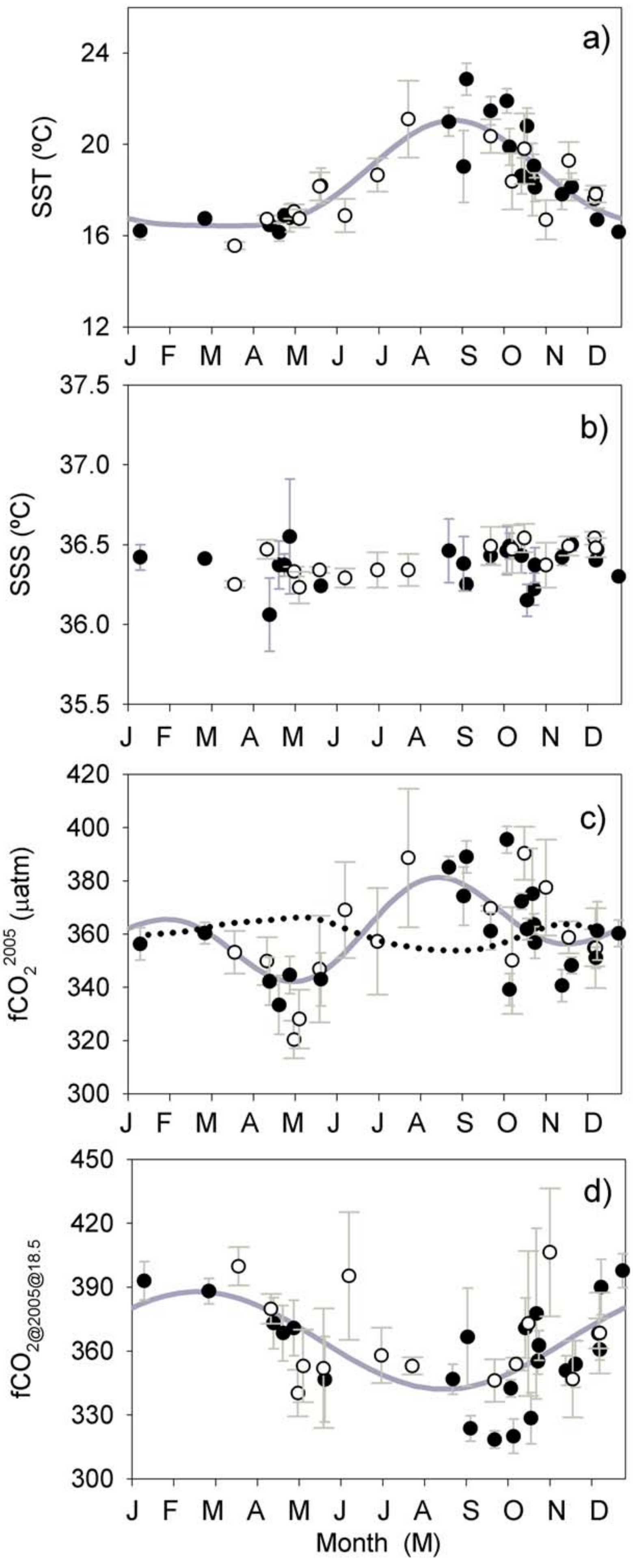

Spain
Gibraltar
Tarifa Narrow
Camarinal Sill
Cape Spartel
Point Almina
Morocco
300
700
600
300
300
200
36.3
35.9
35.5
-6
-5.6
-5.2
Latitude, N
Longitude, W

Figure 2



a)
SST (ºC)
24
20
16
12
J F M A M J J A S O N D
b)
SSS (ºC)
37.5
37.0
36.5
36.0
35.5
J F M A M J J A S O N D
c)
fCO_2^{2005} (μatm)
420
400
380
360
340
320
300
J F M A M J J A S O N D
d)
$fCO_{2@2005@18.5}$
450
420
390
360
330
300
J F M A M J J A S O N D
Month (M)

Figure 3
Click here to download high resolution image

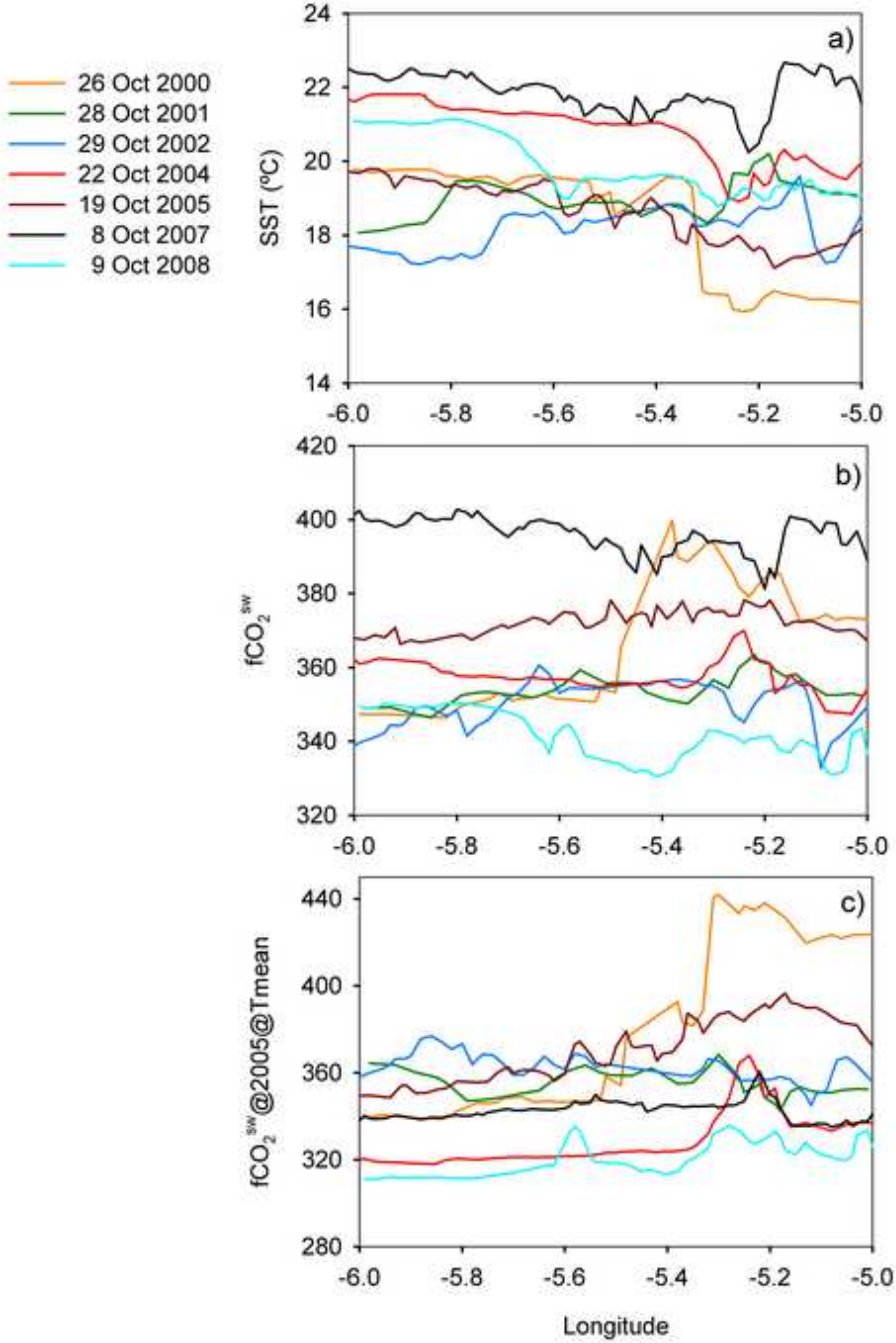
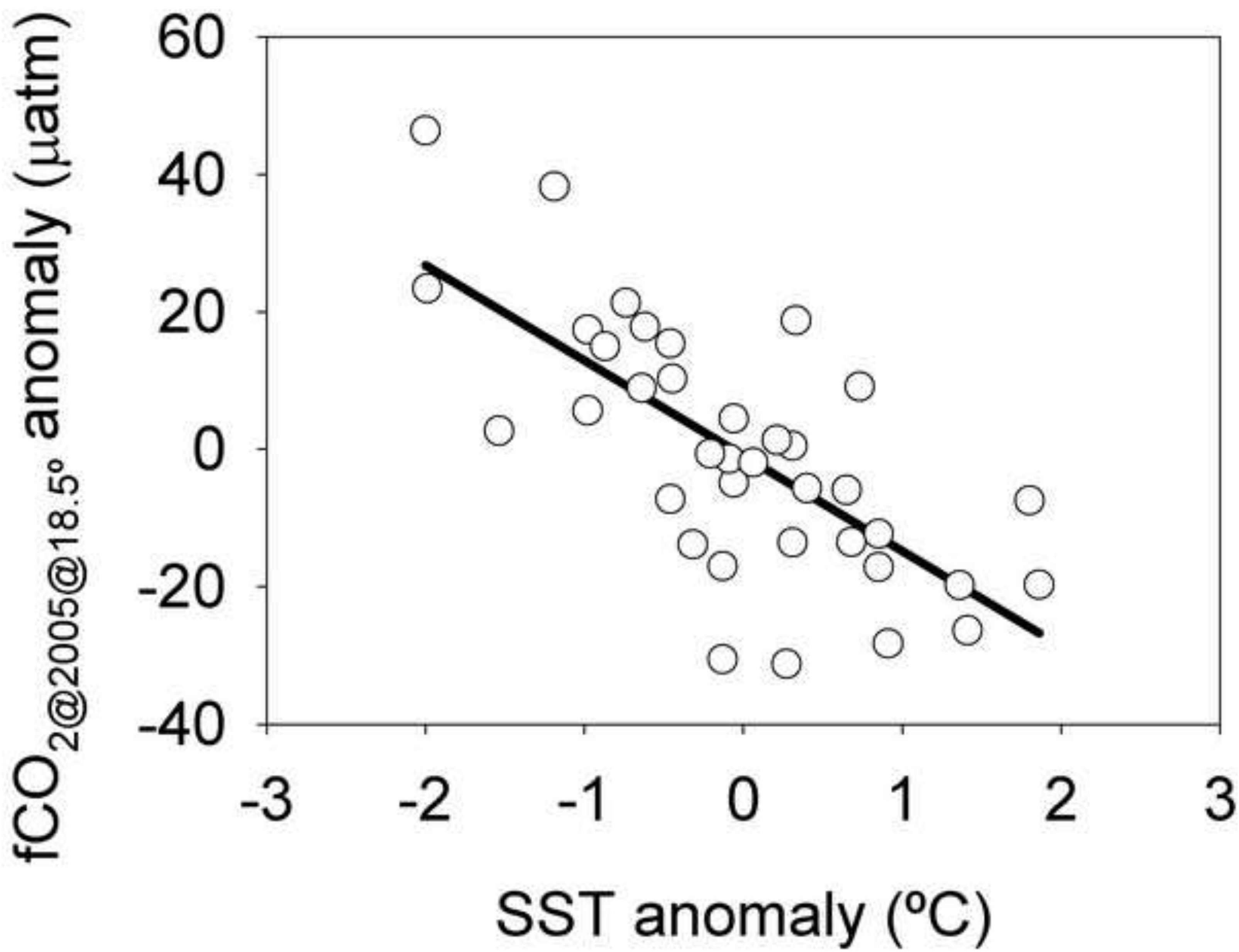
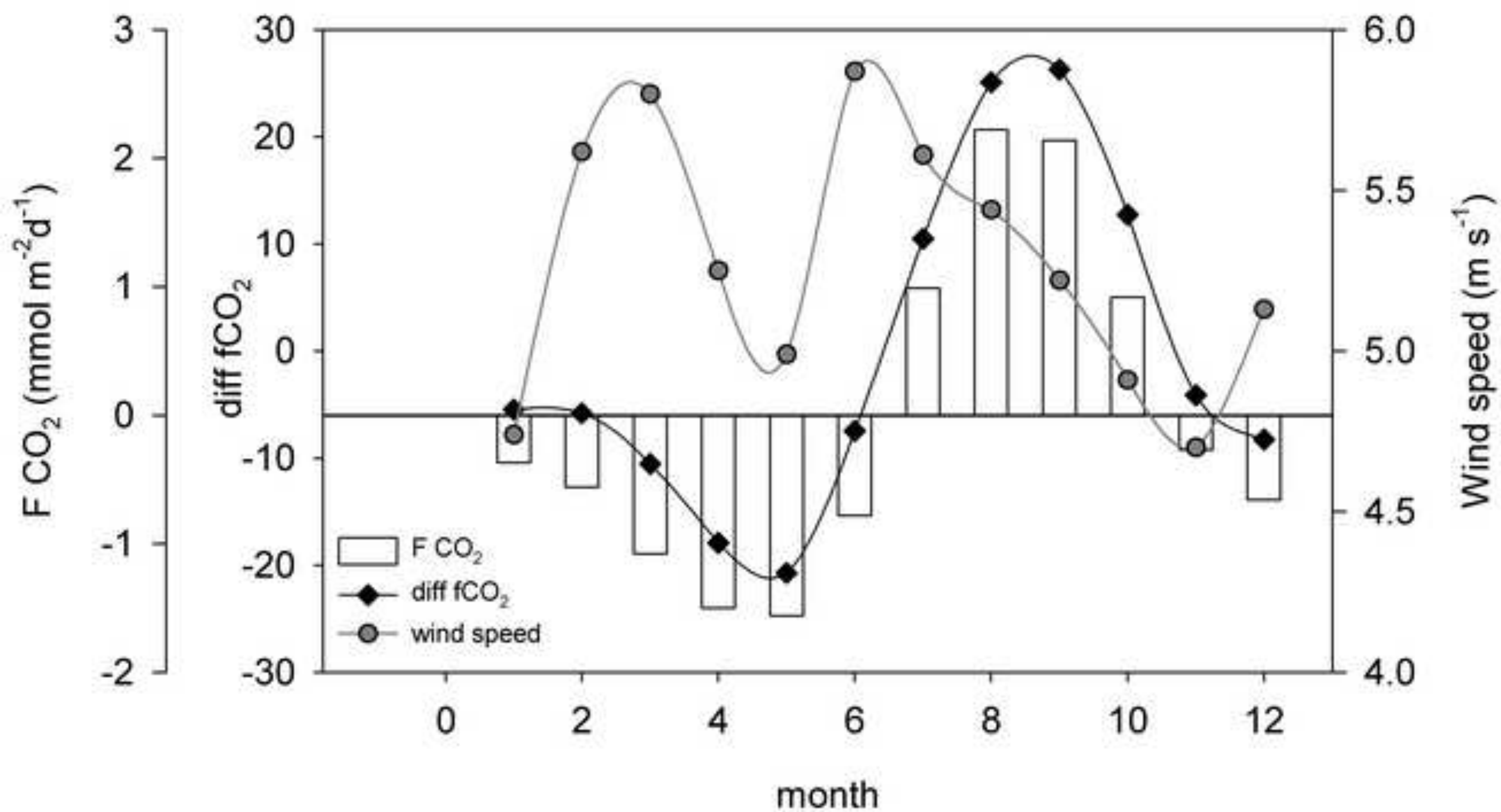


Figure 4



60
40
20
0
-20
-40
-3
-2
-1
0
1
2
3
fCO2@2005@18.5° anomaly (µatm)
SST anomaly (ºC)

Figure 5



F CO2 (mmol m-2d-1)
3
2
1
0
-1
-2
diff fCO2
30
20
10
0
-10
-20
-30
Wind speed (m s-1)
6.0
5.5
5.0
4.5
4.0
F CO2
diff fCO2
wind speed
0
2
4
6
8
10
12
month

***Research Highlights**

- We study the seasonal variability of air-water CO_2 fluxes in the Strait of Gibraltar
- >The water temperature was is the main controlling mechanism of fCO_2 seasonality
- On annual basis, the Strait was almost in equilibrium with the atmosphere