

1 Title: Reconstruction of the seasonal cycle of air-sea CO₂ fluxes in the Strait of
2 Gibraltar

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37 **Abstract:**

38 The present study reports and discusses water surface fCO₂ measurements from 36
39 cruises in the Strait of Gibraltar made over an eleven-year period (1997 to 2009).
40 Underway measurements of sea surface CO₂ fugacity (fCO₂^{sw}), sea surface
41 temperature (SST) and sea surface salinity (SSS) compiled during the cruises were
42 analysed and integrated into a single data-base which ~~then~~ provided the ~~data~~
43 resolution/sensitivity required for an examination of the seasonal variability of the
44 fCO₂^{sw}; these data ~~will ultimately~~ allow the reconstruction of the climatological seasonal
45 cycle for the year 2005. The seasonal cycle of both SST and SSS was found to be
46 within the range of the thermohaline signature of the North Atlantic Surface Water,
47 which is the main water mass that flows into the Mediterranean Sea through the Strait
48 of Gibraltar at the surface. The seasonal distribution of CO₂ was characterised by a
49 monthly minimum ~~fCO₂~~²⁰⁰⁵ value of 334±12 µatm in May, followed by a gradual fCO₂
50 increase ~~reaching~~ a maximum of 385 µatm during late summer, due to the warming of
51 surface waters. The spatial variability of fCO₂^{sw} observed in the area also indicated that
52 superimposed phenomena, occurring at ~~other~~ scales ~~rather~~ than ~~the~~ seasonal, could
53 affect the dissolved CO₂ distribution. In particular, intense vertical mixing processes
54 generated by internal waves in this region may have ~~a relevant~~
55 fCO₂^{sw} on a tidal scale. Seasonal CO₂ cycle dynamics indicated that the surface waters
56 of the Strait of Gibraltar acted as an atmospheric CO₂ source during summer and
57 autumn and a CO₂ sink during winter and spring. When these sink/source strengths are
58 ~~considered~~ on an annual basis, the Strait of Gibraltar was close to equilibrium with
59 atmospheric CO₂, resulting in a neutral atmosphere-ocean exchange (-0.06 ± 0.12 mol
60 C m⁻² yr⁻¹).

61 **Keywords:** Carbon dioxide, air-sea CO₂ exchange, Strait of Gibraltar, seasonal
62 variability.

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66 1. Introduction

67 Over the last 200 years, the ocean has taken up an excess of inorganic carbon from
68 the atmosphere equivalent to approximately 25-30% of the total emission of CO₂ from
69 human activities, specifically fossil-fuel burning, cement manufacturing, and land-use
70 change since the beginning of the industrial revolution (Sabine et al., 2004; Canadell et
71 al., 2007). Improvements in knowledge of the magnitude of this oceanic carbon uptake
72 can be made thanks to an emerging international observation network that will allow
73 routine monitoring of the oceanic CO₂ uptake, on decade and basin scales. However,
74 meaningful projections of future behaviour of the oceanic sink are more challenging.
75 Attempts to set a baseline stabilization target for the atmospheric CO₂ concentration
76 will ultimately depend on an improved understanding of the oceanic mechanism
77 regulating CO₂ uptake and the ability to make useful predictions of this parameter. In
78 particular, predictions are needed of its evolution under a future altered climate and the
79 impacts of climate change trends on air-sea CO₂ fluxes (Doney et al., 2009).

80 The ~~precise~~ requirements for underway fCO₂ system measurements reflect, in part, the
81 scientific effort made by the research community to constrain regional air-sea CO₂
82 fluxes to 0.2 Pg C yr⁻¹ (Bender et al., 2002). Quantifying the trends in surface-ocean
83 fCO₂ requires robust instrumentation for making high-quality fCO₂ field measurement
84 from various platforms. In order to obtain a comprehensive and accurate quantification
85 of the ocean fCO₂ trends at global scales, a growing international network of underway
86 fCO₂ measurement systems is being deployed on research vessels and commercial
87 voluntary observing ships (VOS). This has provided an unprecedented view of both the
88 spatial pattern of the ocean surface fCO₂ and its temporal variability at different time
89 scales (Doney et al., 2009).

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

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

102 The implementation of the measurement program has provided new data on
103 biogeochemical fluxes ~~occurring~~ through the channel and a carbon budget for the
104 whole Mediterranean (Huertas et al., 2009). Despite ~~this~~, CO₂ exchange across the
105 water-atmosphere interface remains uncertain in this region and hence, a thorough
106 examination has been carried out here ~~with the aim of clarifying~~ this important
107 component of the carbon cycle. In this work, underway measurements of fCO₂^{sw}, sea
108 surface temperature (SST) and sea surface salinity (SSS) were compiled during 36
109 cruises (~~research cruises and voyages of Mediterranean commercial ships~~) conducted
110 between 1997 and 2009 (Table 1).

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112 2. Material and Methods:

113 2.1 The study area

114 The Strait of Gibraltar is located ~~at the~~ south of the Iberian Peninsula and is the
115 principal hydrodynamic connection of the Mediterranean Sea with the Atlantic Ocean. It
116 is a narrow and shallow channel with an east-west orientation. Its minimum width is 14
117 km at the Tarifa Narrows (Fig. 1). In ~~the context~~ of oceanic circulation, a small net
118 inflow of Atlantic Water (AW) through the Strait occurs to balance the buoyancy losses
119 and the excess ~~of~~ evaporation over precipitation observed in the Mediterranean. Mass
120 and salt conservation forces result in a density-driven baroclinic exchange, in which

121 warm AW of lower salinity (between 36.2-36.4) enters the Mediterranean Basin at the
122 surface, whilst colder Mediterranean Outflow Water of higher salinity (~38.4) flows out
123 at depth (Gascard and Richez, 1985).

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

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137 2.2. Dataset and methods

138 Underway measurements of the $f\text{CO}_2^{\text{sw}}$ and sea surface temperature (SST) and salinity
139 (SSS) were compiled during a total of 36 cruises, all being elements of various different
140 scientific efforts integrated within the framework of the European projects CANIGO
141 (Canary Islands Azores Gibraltar Observations), CAVASSO (Carbon Variability Studies
142 by Ships Of Opportunity) and CARBOOCEAN (Marine Carbon Sources and Sinks
143 Assessment). The tracks of the cruises are shown in Fig. 1 and details about the
144 cruises have been summarised in Table 1.

145 SSS and SST were recorded using a thermosalinometer and the $f\text{CO}_2^{\text{sw}}$ was measured
146 by equilibration-infrared absorption analysis with a precision of $\pm 1 \mu\text{atm}$. Details of
147 methods identical to those outlined here have been published previously (Santana-
148 Casiano et al., 2002; Rios et al., 2005) and were related to the earlier cruises made

149 within this study (CANIGO 1 and Azores 1). The twelve FICARAM (Air-Sea CO₂ fluxes
150 along a meridional transect in the Atlantic Ocean) cruises included in this study
151 ~~commenced~~ in October 2000 and continued ~~to the present~~ (Padin et al., 2010), and
152 were conducted onboard the Hespérides. The ~~tracks of the courses~~ (headed southward
153 during boreal falls and northward in boreal springs) were ~~framed~~ within the Spanish
154 Antarctic Research Program. An additional project that ~~has~~ contributed since 2007 to
155 the fCO₂^{sw} data-base in the Strait is the ICCABA VOS line which connected the Canary
156 Islands with Italy. In addition to the VOS lines that occasionally pass through the Strait,
157 data collected in the GIFT (Gibraltar Fixed Time Series) section was also included in
158 this study. This time series was established in 2005 with the ~~aim~~ of monitoring the
159 carbon exchange between the Mediterranean and Atlantic basins. During only three of
160 the GIFT cruises were continuous underway fCO₂^{sw} measurements performed (de la
161 Paz et al., 2008). The rest of the GIFT data used in this study were obtained from
162 discrete water samples collected at 5 meter ~~depth~~ at eight stations forming a cross-
163 section of the Strait and in which SST and SSS were taken from the CTD record.
164 Total Alkalinity (A_T) was measured by potentiometric titration (Mintrop et al., 2000). The
165 accuracy of the A_T determination was assessed by measurement of Certified Material
166 (CRM, supplied by Professor Andrew Dickson, Scripps Institution of Oceanography, La
167 Jolla, CA, USA). From the analysis of 3 CRM batches, **an accuracy for A_T of about ±0.8**
168 μmol kg⁻¹ was obtained. pH_T was determined at 25 °C following the spectrophotometric
169 method of Clayton and Byrne (1993) with m-cresol purple as indicator. The pH method
170 had a precision of ±0.003 units.
171 fCO₂^{sw} was subsequently calculated from these parameters using the carbonic
172 dissociation constant ~~formulated~~ by Mehrbach et al. (1973) and refitted by Dickson and
173 Millero (1987). For these computed values, the estimated precision of the fCO₂^{sw} was
174 ±2.7 μatm (Millero, 2007). More details about the methodology used on the GIFT
175 cruises are given in Huertas et al. (2009). fCO₂^{sw} was measured by equilibration on a
176 total of 23 cruises, whereas it was calculated from pH_T and A_T on 15 cruises, with both

177 being simultaneously recorded on two cruises (13th Dec 2005 and 23rd May 2006) for
178 purposes of data comparison (Table 1). The cruise-averaged values obtained for
179 $f\text{CO}_2^{\text{sw}}$ from both methods were very similar, with average differences in $f\text{CO}_2^{\text{sw}}$ of ± 4
180 and $\pm 3 \mu\text{atm}$ for the Dec 2005 and May 2006 cruises respectively. Regardless of the
181 sampling strategy used (continuous underway versus discrete water samples at
182 stations), the differences in SSS and SST were insignificant, less than 1 % of the
183 averaged value. The precision of the $f\text{CO}_2^{\text{sw}}$ measurements with the equilibration
184 technique is higher than that based on calculations from A_T and pH_T (Millero, 2007).
185 However, the integration of data obtained with the two techniques significantly
186 increased the dataset, which allowed far greater seasonal $f\text{CO}_2^{\text{sw}}$ coverage, especially
187 when equilibration/infrared absorption measurements were very scarce, such as during
188 summer. Because both techniques produced very similar results when run
189 concomitantly, it is considered that the approach used is fully validated.

FIGURE 1, TABLE 1

192 Monthly atmospheric CO_2 molar fraction ($x\text{CO}_2^{\text{atm}}$) data at the meteorological station of
193 the Azores (Terceira Island, Portugal) were obtained from the Cooperative Air
194 Sampling Network of the NOAA/ESRL Global Monitoring Division. The $x\text{CO}_2^{\text{atm}}$ was
195 converted to $f\text{CO}_2^{\text{atm}}$ taking into account the atmospheric pressure, and was expressed
196 in wet air using the water vapour formulation of Weiss and Price (1980) as a function of
197 SSS and SST.

198 In order to obtain a composite seasonal picture of $f\text{CO}_2^{\text{sw}}$ behaviour, data gathered in
199 all available years were collated into a single "virtual year". This procedure was based
200 on the assumption that surface waters reflected the atmospheric $f\text{CO}_2$ increase, as
201 proposed by Takahashi et al. (2009) in the most recent global ocean surface CO_2
202 climatology. For the study case of the Strait of Gibraltar, the validity of this assumption
203 is reinforced by the study of Santana-Casiano et al. (2007) on the time-series obtained
204 at the ESTOC (European Time Series of the Canary Islands) site located in the

205 Subtropical North Atlantic, where the upper layer shows a very similar biogeochemical
206 signature to that in the Strait of Gibraltar. That study showed that $f\text{CO}_2^{\text{sw}}$ was strongly
207 correlated with atmospheric CO_2 ~~and followed the same trends~~ in this oceanic region.
208 Thus, each $f\text{CO}_2^{\text{sw}}$ value observed in a particular year i and in the month j was
209 referenced to its respective month in the year 2005 (an arbitrarily chosen year of
210 reference) according to the following equation:

$$f\text{CO}_2^{\text{sw}}_{2005} = f\text{CO}_2^{\text{sw}} + (f\text{CO}_2^{\text{atm}}_{2005 \text{ month } j} - f\text{CO}_2^{\text{atm}}_{\text{year } i \text{ month } j}) \quad (1)$$

213 Air–water CO_2 flux was computed as:

$$F = k\alpha \Delta f\text{CO}_2 \quad (2)$$

215 where ~~F denotes the air-sea CO_2 flux~~, k represents the gas transfer velocity, α is the
216 CO_2 solubility coefficient given by Weiss (1974), and $\Delta f\text{CO}_2$ is the air-sea $f\text{CO}_2$ gradient.
217 The gas transfer velocity as formulated by Nightingale et al. (2000) was estimated as a
218 function of wind speed corrected to 10 m. The 6-hourly wind speed data were provided
219 by the Spanish *Agencia Estatal de Meteorología* from the station located at Tarifa
220 (Figure 1).

222 3. Results and discussion:

223 3.1. Biogeochemical properties in the surface water.

224 Data gathered between 1997 and 2009 in the Strait are given in Table 1. Seasonal
225 $f\text{CO}_2^{\text{sw}}$ data from all years was integrated to represent a composite seasonal cycle
226 (Figure 2), referred arbitrarily to the year 2005.

227 Average in-situ surface water temperature (SST) for cruises varied between 15.6 and
228 22.8 °C. Minimum and maximum temperatures were recorded in March and September
229 respectively. This seasonal pattern of temperature was a direct consequence of
230 seasonal heating and cooling of surface waters at these temperate latitudes (Fig. 2a).
231 However, SSS did not show such a distinctive seasonal pattern, as its values ranged
232 between 36.06 and 36.55 (Fig. 2b). Data gathered on cruises close to each other in

233 time exhibited an evident scattering, which suggests that the thermohaline properties in
234 the Strait might be also subjected to short-term variability. Nevertheless, the averaged
235 values obtained for SSS in the Strait remain within the range of the haline signature
236 described by Gascard and Richez (1985) for NASW: that is, between 36.2 and 36.4.

FIGURE 2

240 The most notable feature of the seasonal $f\text{CO}_2^{\text{SW}}_{2005}$ cycle in the Strait of Gibraltar is the
241 decrease detected during spring, attributed to the withdrawal of carbon by biological
242 activity. A minimum of $320 \mu\text{atm}$ was measured in May (Fig. 2c). $f\text{CO}_2^{\text{SW}}_{2005}$ gradually
243 increased until late summer, ~~which reflected~~ an increase in respiratory processes and
244 ~~is due also to~~ surface warming. Maximum averaged monthly $f\text{CO}_2^{\text{SW}}_{2005}$ values (≈ 385
245 μatm) were observed in late summer (August). ~~However, some particular values~~
246 indicated in Table 1 deviate from this seasonal pattern, the highest averaged value
247 from the cruises being observed in October ($396 \mu\text{atm}$). It is worth noting that the
248 greatest variability for $f\text{CO}_2^{\text{SW}}_{2005}$ was also observed in October, with values ranging
249 from 339 to $396 \mu\text{atm}$. Coincidentally, October is the month when the most sampling
250 cruises took place: 9 out of the total 36 cruises considered were made during this
251 month. For that reason, temporal scales other than seasonal were examined in detail,
252 as described in the next section.

254 Temperature plays an important role in determining the pattern of surface water $f\text{CO}_2^{\text{SW}}$
255 by controlling the thermodynamic equilibrium of the inorganic carbon system. To
256 remove the temperature effect, $f\text{CO}_2^{\text{SW}}$ needs to be normalized to a common
257 temperature, using the temperature dependence of $f\text{CO}_2$ in isochemical conditions ($\delta \ln$
258 $f\text{CO}_2 / \delta \text{SST}$) which is equal to $4.23 \% \cdot ^\circ\text{C}^{-1}$ (Takahashi et al. 1993). After removing the
259 thermal effect induced by seasonal SST changes, the composite annual cycle for

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260 $f\text{CO}_2^{\text{sw}}$ ($f\text{CO}_{2@2005@T\text{mean}}$) was estimated. In essence, $f\text{CO}_{2@2005@T\text{mean}}$ represents the
261 added effects of biological processes, vertical mixing and air-water CO_2 exchange on
262 $f\text{CO}_2$. The $f\text{CO}_{2@2005@T\text{mean}}$ distribution mirrors that observed for the SST, with the
263 minimum and maximum values being observed during late summer and winter,
264 respectively (Fig. 2d).

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11 265 The net annual effect of the temperature control on $f\text{CO}_2^{\text{sw}}$ can be evaluated using the
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13 266 methods of Takahashi et al. (1993), perturbing the annual mean $f\text{CO}_2^{\text{sw}}_{2005}$ of $360 \mu\text{atm}$
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15 267 with an SST seasonal amplitude of $6.6 \text{ }^\circ\text{C}$. Accordingly, the resulting seasonal
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17 268 amplitude of $f\text{CO}_2^{\text{sw}}$ induced by the seasonal SST cycle is found to be $100 \mu\text{atm}$. Apart
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19 269 from temperature variations other effects can be quantified from the seasonal
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21 270 amplitude of the $f\text{CO}_{\text{sw}@2005@T\text{mean}}$; these additional effects amount to $61 \mu\text{atm}$. The ratio
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24 271 between the two amplitudes was 1.6, which indicated that the main mechanism for the
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26 272 observed seasonal variability of $f\text{CO}_2^{\text{sw}}$ in the Strait was temperature. Other
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28 273 mechanisms, which include tidally-induced vertical mixing, biology and air-water
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30 274 exchange, are also involved in the $f\text{CO}_2^{\text{sw}}$. The quantification of these individually is,
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33 275 however, quite complex in this region, owing to the high spatiotemporal variability on a
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35 276 short time-scale. Regarding the contribution of biology, some studies on primary
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37 277 production in the Strait indicate that productivity is significantly low compared to that
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39 278 occurring in the adjacent waters of the Alboran Sea (Macías et al., 2007a, Macías et
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41 279 al., 2009). Macias et al. (2007a) used a set of weekly composite Sea-Wifs images
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43 280 (from 1998 to 2004) and assessed the temporal and spatial variability of the surface
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45 281 chlorophyll distribution in the North-western Alboran Sea, including the study area
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47 282 considered in the present article. These authors found that the lowest mean chlorophyll
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49 283 concentrations of $0.2\text{-}0.5 \text{ mg m}^{-3}$ were present in the centre of the Strait. This finding
50
51 284 has been related to the low residence time of the water in the Strait (Macias et al.,
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53 285 2007b). The coupled physical-biological model formulated by Macias et al. (2007b)
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55 286 found that residence times within the channel are so short that phytoplankton
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58 287 communities cannot grow appreciably during their transit. Thus, water in the central
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288 channel of the Strait represented oligotrophic NASW that flowed quickly into the
289 Mediterranean basin.

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291 In order to analyse short-term variability of $f\text{CO}_2$, the longitudinal distribution of the
292 SST, $f\text{CO}_2^{\text{sw}}$, and the $f\text{CO}_{2@2005@T_{\text{mean}}}$ along the east-west axis was plotted (Fig. 3).
293 October data were selected because this month was sampled more than any other. As
294 for the thermohaline properties, the spatial distribution of surface $f\text{CO}_2^{\text{sw}}$ values were
295 highly variable, and this resulted in a wide standard deviation ~~associated with the~~
296 $f\text{CO}_2^{\text{sw}}$ values (Table 1). The distribution pattern found on the western side of the Strait
297 was typically more homogeneous than ~~that observed~~ on the eastern side for SST,
298 $f\text{CO}_2^{\text{sw}}$, and especially in the case of $f\text{CO}_{2@2005@T_{\text{mean}}}$; which displayed the most
299 marked east-west variability. This finding is attributed to internal waves and was
300 previously described in the area by Santana-Casiano et al. (2002) and de la Paz et al.
301 (2008a).

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

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316 The detection of surface waters associated with the occurrence of internal waves is
317 difficult if based solely on salinity considerations, because no apparent changes in SSS
318 were evidenced. However, thermal differences are more apparent and the decrease of
319 SST clearly demarcates the vertical intrusion of colder water from greater depths
320 (Figure 3). The maximum temperature difference was observed in October 2000 when
321 a decrease in SST of ~3°C from west to east (Fig 3A) was recorded, accompanied by
322 steep increases in both $f\text{CO}_2^{\text{SW}}$ and $f\text{CO}_{2@2005@T_{\text{mean}}}$ equivalent to ~50 μatm and ~90
323 μatm , respectively. These increases are greater than the increase expected for $f\text{CO}_2^{\text{SW}}$
324 under isochemical conditions (Takahashi et al., 1993).

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FIGURE 3.

328 The tidal-induced variability of the inorganic carbon in the Strait of Gibraltar has been
329 addressed in a previous study (de la Paz et al., 2008a). The $f\text{CO}_2^{\text{SW}}$ database used in
330 this study included the available $f\text{CO}_2^{\text{SW}}$ data already published for the Strait, e.g.
331 Santana-Casiano et al. (2002) and de la Paz et al. (2008b). These earlier studies,
332 however, were limited, and seasonal coverage for $f\text{CO}_2^{\text{SW}}$ was not as consistent as in
333 the present study. In order to obtain more robust seasonal trends of $f\text{CO}_2^{\text{SW}}$, the
334 database was integrated into a composite seasonal cycle (Fig. 2). Climatological
335 seasonal cycles of SST, $f\text{CO}_2^{\text{SW}}$, and $f\text{CO}_{2@2005@T_{\text{mean}}}$ were obtained by fitting averaged
336 cruise values to a harmonic function in the form of:

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

337
338 where y is either SST, $f\text{CO}_2^{\text{SW}}$, and $f\text{CO}_{2@2005@T_{\text{mean}}}$, x represents the time expressed in
339 Julian days, and b_0 , b_1 , and b_2 , φ_1 and φ_2 are fitted constants. The resulting plots of the
340 fitted equations indicated in Table 2 are shown in Fig. 2. The estimated values closely
341 follow the seasonal pattern of the actual data and statistical analysis shows that this is

342 significant ($p < 0.05$) and characterized by relatively strong regression coefficients
343 ($0.6 < r < 0.86$).

345 TABLE 2

346 A study was made of deviations from the expected seasonal patterns, taken as the
347 difference between the averaged cruise value and the predicted value obtained by
348 applying equation (3) to each variable. The object of investigating these anomalies is
349 to understand the potential mechanisms responsible for the fCO₂^{sw} Observed. The only
350 statistically significant relationship between anomalies was a negative one ($r^2 = -0.5$)
351 between SST and fCO_{2@2005@Tmean} (Fig. 4). This is consistent with the hypothesis that
352 CO₂-enriched colder water is brought to the surface via upwelling processes. In
353 contrast, no relationship was observed between fCO_{2@2005@Tmean} and the SSS
354 anomalies. Positive and negative anomalies for SST and fCO_{2@2005@Tmean} were
355 distributed throughout the year with no apparent pattern, which implies that upwelling is
356 not seasonally dependent in this area. This distribution is different from that observed
357 in other oceanic regions, e.g. the southern waters of Tasmania where reported SST
358 anomalies were associated with negative fCO_{2@2005@Tmean} anomalies (Borges et al,
359 2008). The correlation observed there was attributed to a reduced input of dissolved
360 inorganic carbon during the fall-winter period, which coincided with phases of positive
361 SST anomalies related to changes in wind regimes and shifts in the mixed layer depth.

362
363 FIGURE 4.

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365 To assess the inter-annual variability, the mean rate of change for fCO₂^{sw} was
366 estimated by linear regression of the de-seasonalized monthly values. These were
367 computed as the difference between observations and averaged monthly values for all
368 cruise data. No significant inter-annual trends in SST and fCO₂^{sw}₂₀₀₅ were found.

369 Taking into account that $f\text{CO}_2^{\text{SW}}_{2005}$ compilation (see Section 2.2: eq .1) assumes that
370 surface water tracks the atmospheric CO_2 increase ($\sim 1.5 \mu\text{atm yr}^{-1}$), the resulting long-
371 term rate of $f\text{CO}_2^{\text{SW}}$ would match the atmospheric rate. The high $f\text{CO}_2^{\text{SW}}$ variability
372 observed in this system on the seasonal ($\sim 70 \mu\text{atm}$) and tidal ($\sim 50 \mu\text{atm}$) time-scales
373 obstruct the observation of any other inter-annual CO_2 trend that may be statistically
374 significant and distinct from the atmospheric trend. This finding is in agreement with the
375 results obtained at the ESTOC site and in other subtropical regions (Bates, 2007;
376 Santana-Casiano et al., 2007).

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379 3.2. Seasonal cycle of the air-water CO_2 exchange in the Strait

380

381 The calculation and interpretation of instantaneous CO_2 fluxes from short-term cruise
382 data can provide a process-level understanding of hourly trends and patterns, but this
383 assessment reveals little about the overall status of the Strait as a CO_2 source-sink.
384 Atmospheric conditions (wind, atmospheric pressure) change rapidly, whereas oceanic
385 conditions (SST, salinity, $f\text{CO}_2^{\text{SW}}$) generally vary much more slowly (Else et al., 2008).
386 In our analysis, conditions of slow oceanic change were considered to ~~compute the~~
387 ~~most representative~~ estimate of the integrated annual flux of CO_2 along the Strait of
388 Gibraltar.

389 The air-water CO_2 fluxes were calculated using equation 2, where the air-water $f\text{CO}_2$
390 gradient was estimated from the difference between the monthly atmospheric $f\text{CO}_2$
391 value in 2005, and the monthly $f\text{CO}_2^{\text{SW}}$ in surface waters. The last term was computed
392 from the $f\text{CO}_{2@2005@T_{\text{mean}}}$ obtained by applying equation (3), which was subsequently
393 corrected to the SST in 2005 (equation 3) and the expression proposed by Takahashi
394 et al. (1993). The gas transfer velocity (k) was computed using the monthly
395 climatological wind speed.

396 In the assessment of the air-water CO₂ fluxes, the greatest uncertainty is often
397 associated with the parameterization of k and, hence, ~~some discrepancies~~ frequently
398 ~~arise about~~ the expression ~~that~~ should be selected to calculate it. In the present study,
399 we applied the wind-driven, air-sea exchange parameterization proposed by
400 Nightingale et al. (2000) to derive k; ~~however, in order to compare results,~~ fluxes were
401 also computed using the k value calculated using the method of Wanninkhof (1992).
402 ~~This~~ has previously been applied widely in all oceanic environments, and was
403 previously used to estimate the air-sea CO₂ exchange in the Strait of Gibraltar
404 (Santana-Casiano et al., 2002; de la Paz et al., 2008b). Data obtained using the
405 Wanninkhof coefficient are hereafter shown in parentheses and ~~indicated with~~ the
406 acronym W92.

407 FIGURE 5

408
409 Results show that surface waters of the Strait of Gibraltar behave as a CO₂ source
410 during summer and autumn whereas, during winter and spring, they ~~shift and~~ act as a
411 CO₂ sink. The maximum absorption of atmospheric CO₂ occurs in late spring, with
412 ~~values~~ of -1.60 mmol m⁻²d⁻¹ (W92: -1.56). The most under-saturated ~~CO₂ values of~~
413 ΔfCO₂ (~21 μatm) ~~were~~ observed at the same time. After this minimum, ΔfCO₂
414 progressively increases throughout the summer months and ~~results in the air-sea CO₂~~
415 ~~exchange status~~ changing ~~from sink to~~ source. The magnitude of this source reaches
416 its maximum in August, with estimated CO₂ fluxes from surface waters of 1.68 mmol m⁻²
417 d⁻¹ (W92: 2.2) and a ΔfCO₂ of ~ 25 μatm.

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

424 ~~wind speed is a relevant pumping mechanism driving CO₂ exchange,~~ the strength of
425 the Strait as a CO₂ sink/source is determined by the seasonal carbon dynamics.

426 When considered on an annual basis, the Strait of Gibraltar is nearly in equilibrium with
427 the atmospheric CO₂; ~~however,~~ the CO₂ sink in spring/autumn months ~~has a~~ slightly
428 ~~predominance over~~ the source. Consequently, the calculated air-sea CO₂ flux for 2005
429 was $-0.06 \pm 0.12 \text{ mol m}^{-2} \text{ yr}^{-1}$ (W92: -0.02 ± 0.13) $\text{mol m}^{-2} \text{ yr}^{-1}$.

430 The formulation of k is ~~wind dependent with~~ a non-linear fit. Hence, the effect of short-
431 term wind speed variability on an annual scale was evaluated by calculating k from the
432 climatological daily wind speed data. The CO₂ flux values derived using this approach
433 are identical to those derived using mean monthly wind speeds i.e. $-0.06 \pm 0.18 \text{ mol m}^{-2}$
434 yr^{-1} (W92: $-0.02 \pm 0.19 \text{ mol m}^{-2} \text{ yr}^{-1}$). These data indicate that short-term variability of the
435 wind speed is not a significant uncertainty on annual times scales for air-sea CO₂
436 exchange in the Strait. In order to test the effect of wind speed variability on calculated
437 annual CO₂ fluxes, a constant value of k (9.9 cm h^{-1}), which represents the annual
438 mean, was applied. This resulted in a ~50% decrease ($-0.03 \pm 0.15 \text{ mol m}^{-2} \text{ yr}^{-1}$) in CO₂
439 fluxes compared to the values derived using either daily or monthly integrated wind
440 speeds. Daily and monthly wind speeds are considered more representative of
441 seasonal wind speeds, which are higher in the summer months (Figure 5), when the
442 Strait typically behaves as a CO₂ source. Therefore, although the Strait acts as a sink of
443 CO₂ for a longer period than it does as a CO₂ source ~~during the year~~ (Figure 5), this is
444 counterbalanced by relatively high emissions of CO₂ in summer because of higher
445 observed wind speeds. ~~As a consequence,~~ on an annual basis the Strait remains close
446 to equilibrium with atmospheric CO₂. Furthermore, the discrepancies derived from the
447 use of k computations given by Nightingale et al (2000) or Wanninkhof (1992) are
448 minimum and not relevant for the status as a source or sink that can be attributed to
449 the Strait of Gibraltar. Thus, although wind speeds ~~and k computations~~ play an

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450 important role in regulating CO₂ fluxes, the CO₂ source/sink status of the Strait of
451 Gibraltar is mainly dependent on seasonal carbon dynamics.

452
453 Previous estimates of air-sea CO₂ fluxes in the Strait of Gibraltar have also reported
454 that the area behaves as an atmospheric sink of CO₂ on an annual basis. Santana-
455 Casiano et al. (2002) described the Strait as a source of CO₂ in summer and a sink
456 during the winter, and provided a net annual flux estimation by averaging the CO₂
457 fluxes obtained during September and February (1997/1998). A net CO₂ flux of -2.5
458 mol m⁻² yr⁻¹ based on Wanninkhof (1992) was estimated, ~5 times the CO₂ sink value
459 reported here. This was possibly the consequence of high winds (8 to 15 m s⁻¹) during
460 a relatively short time period. These data demonstrate how seasonal bias in sampling
461 strategies may result in CO₂ flux overestimations. Other previous studies had more
462 comprehensive seasonal coverage. de la Paz et al. (2008b) considered averaged
463 seasonal CO₂ fluxes for March, May, September and December (2005/2006) for
464 calculating an annual CO₂ flux. Essentially, these results showed the same trends as
465 those presented here, with the Strait acting as a CO₂ sink one order of magnitude
466 larger (-0.28 mol m⁻² yr⁻¹) than the value calculated in this study. This discrepancy
467 demonstrates the need for high resolution CO₂ data, in both time and space, to produce
468 accurate annual flux estimates in any area.

469 Based on an estimated area of 1500 km² defined by the Strait's western and eastern
470 limits at Cape Spartel and Point Almina respectively (Fig. 1), the total amount of CO₂
471 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
472 is instructive to quantify this in the context of the amount of carbon that is exchanged
473 between the Atlantic Ocean and the Mediterranean Sea through the Strait of Gibraltar
474 (Dafner et al., 2001; Ait-Ameur and Goyet, 2006; de la Paz et al., 2008a; Huertas et
475 al., 2009). The most recent estimation by Huertas et al. (2009) reported a net carbon
476 export from the Mediterranean to the Atlantic equivalent to 2.11 TmolC yr⁻¹. Thus
477 carbon transport through the water column is more than one order of magnitude higher

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478 than the net annual CO₂ transfer across the air-water interface. Nonetheless, it is still
479 relevant to elucidate what role is played by the air-sea CO₂ exchange in the overall
480 ~~picture of the~~ carbon cycle in the Strait of Gibraltar. Therefore, the results presented in
481 this study, based on a comprehensive analysis of a ~~database compiled with 12 years of~~
482 ~~data~~, contribute to completing the carbon budget in this key oceanic region.

483 The relevance of coastal areas in the global carbon cycle has recently been highlighted
484 by Chen and Borges (2009), who performed the scaling of the air-water CO₂ fluxes
485 using the ~~present~~ database ~~available~~ for the coastal ocean. These authors estimated
486 that the world's continental shelves are responsible for the absorption of atmospheric
487 CO₂ in the range of 0.33 to 0.36 PgC yr⁻¹, which corresponds to an additional sink of
488 27% to 30% of the CO₂ taken up by the open ocean based on the recent fCO₂
489 climatology ~~given by~~ Takahashi et al. (2009). The net annual CO₂ flux obtained in the
490 Strait of Gibraltar falls ~~then~~ within the values reported ~~by these two compilations, being~~
491 ~~close to the -0.8 mol C m⁻² yr⁻¹ provided~~ by Chen and Borges (2009) for the NE Atlantic
492 continental shelf, and to the -0.6 mol C m⁻² yr⁻¹ computed by Takahashi et al. (2009) for
493 the Eastern North Atlantic Ocean.

494

495 4. Summary and Conclusions:

496 This study reports the variability of fCO₂ in the Strait of Gibraltar on the seasonal scale
497 and ~~analyses~~ the mechanisms regulating this variability. The assessment is based on
498 data gathered in 36 cruises undertaken in the area from 1997 to 2009, ~~and a~~
499 climatological seasonal cycle ~~has been~~ reconstructed, ~~arbitrarily~~, for the ~~year~~ 2005.

500 This climatological seasonal cycle for the air-water CO₂ exchange varies throughout
501 the year: the Strait behaves as a CO₂ source during summer and autumn, and as a
502 CO₂ sink during winter and spring. ~~However~~, on an annual basis, the CO₂ efflux
503 recorded during the months of emission are counterbalanced by the CO₂ influx ~~found~~
504 during the months of absorption, resulting in a neutral status (-0.06 ± 0.12 mol C m⁻² yr⁻¹).
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506 This study also demonstrates that processes on a shorter-term time scale, such as the
507 enrichment of $f\text{CO}_2$ in surface waters brought about by the vertical mixing induced by
508 the tidal regime, are difficult to assess in this particular area. These short-term
509 processes hinder an accurate assessment of the carbon budget on longer time scales
510 (e.g. inter-annual and decadal). An accurate assessment of the short-term $f\text{CO}_2^{\text{sw}}$
511 variability in the Strait, and the mechanisms involved, would require other observational
512 strategies, such as in-situ continuous monitoring of the $f\text{CO}_2$ and ancillary
513 measurements in surface waters. Such observations would be particularly difficult to
514 perform in this region, not least because of the continuous heavy maritime traffic, and
515 socio-political factors associated with its geographical position.

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517

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1 **Figure captions:**

2 Figure 1. Map of the Strait of Gibraltar and ~~the tracks of the~~ cruises made to obtain
3 data for the analysis of $f\text{CO}_2$ temporal variability.

4 Figure 2. Climatological seasonal cycles for SST, SSS, $f\text{CO}_2^{2005}$ and $f\text{CO}_{2@2005@mean}$.
5 The black dotted line in the third graph represents the seasonal variability of the
6 atmospheric $f\text{CO}_2$. The filled black circles are values obtained from continuous $p\text{CO}_2$
7 measurements by equilibration/IR absorption. The unfilled circles are values calculated
8 from A_T and pH_T . The grey line denotes the sinusoidal fit of each variable, whose
9 parameters are indicated in Table 2.

10 Figure 3. Longitudinal variability of the SST, $f\text{CO}_2$ and $f\text{CO}_2$ normalised to a
11 temperature of $18.5\text{ }^\circ\text{C}$ for data collected during cruises made in the month of October
12 in several years.

13 Figure 4. Monthly anomalies of the $f\text{CO}_2$ normalised to a temperature $18.5\text{ }^\circ\text{C}$, plotted
14 against monthly anomalies of sea surface temperature (SST). Monthly anomalies have
15 been calculated as the difference between monthly averaged values from observed
16 values and those obtained from the sinusoidal fit indicated in Table 2.

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

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Table 1

Scientific Program	Ship	date	SST (°C)	SSS	fCO ₂ ^{sw} (µatm)	fCO ₂ ²⁰⁰⁵ _{@18.5} (µatm)	pCO ₂ method
CANIGO	R/V Thalassa	6-Sep-97	19.02 ± 1.58	36.38±0.17	357±11	366±23	pCO ₂ underway
AZORES 1	R/V Hespérides	26-Aug-98	20.98 ± 0.63	36.46±0.20	371±4	347±7	pCO ₂ underway
FICARAM	R/V Hespérides	26-Oct-00	18.45 ± 1.58	36.9	364±7	378±40	pCO ₂ underway
FICARAM	R/V Hespérides	15-Apr-01	16.46 ± 0.23	36.06±0.23	335±9	373±12	pCO ₂ underway
FICARAM	R/V Hespérides	28-Oct-01	19.05 ± 0.51	36.22±0.10	354±4	355±6	pCO ₂ underway
FICARAM	R/V Hespérides	29-Oct-02	18.11 ± 0.62	36.37±0.11	349±6	363±7	pCO ₂ underway
FICARAM	R/V Hespérides	22-Apr-03	16.14 ± 0.39	36.37±0.15	330±11	368±13	pCO ₂ underway
FICARAM	R/V Hespérides	22-Oct-04	20.80 ± 0.79	36.15±0.10	357±4	328±12	pCO ₂ 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	pCO ₂ underway
FICARAM	R/V Hespérides	19-Oct-05	18.61 ± 0.79	36.43±0.11	372±3	371±14	pCO ₂ 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	pCO ₂ 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	pCO ₂ underway
FICARAM	R/V Las Palmas	26-Sep-06	21.47 ± 0.62	36.43±0.05	362±7	318±4	pCO ₂ 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	pCO ₂ 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	pCO ₂ 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	pCO ₂ underway
ICCABA	MSC Benedetta	25-Nov-07	18.13 ± 0.60	36.50±0.04	347±3	354±11	pCO ₂ underway
ICCABA	MSC Benedetta	26-Feb-08	16.74 ± 0.17	36.41±0.03	365±4	388±6	pCO ₂ 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	pCO ₂ 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	pCO ₂ 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	pCO ₂ underway
ICCABA	MSC-Marta	29-Dec-08	16.16 ± 0.27	36.30±0.00	365±5	398±8	pCO ₂ underway
ICCABA	MSC-Marta	9-Jan-09	16.19 ± 0.38	36.42±0.08	364±6	393±9	pCO ₂ underway

Table 1: Cruises / research program, ships, dates (dd-mmm-yy) and averaged values for SST, SSS, fCO₂^{sw} (µatm), fCO₂²⁰⁰⁵_{@18.5} (µatm) and the technique used for the fCO₂^{sw} measurements. *** mark the two cruises where both analytical techniques were employed (See section 2).

Table 2

	b₀	b₁	φ₁	b₂	φ₂	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 parameters of the wave function used for the climatological seasonal cycles of SST, fCO_{sw}, and fCO_{sw@2005@Tmean}.

Figure 1
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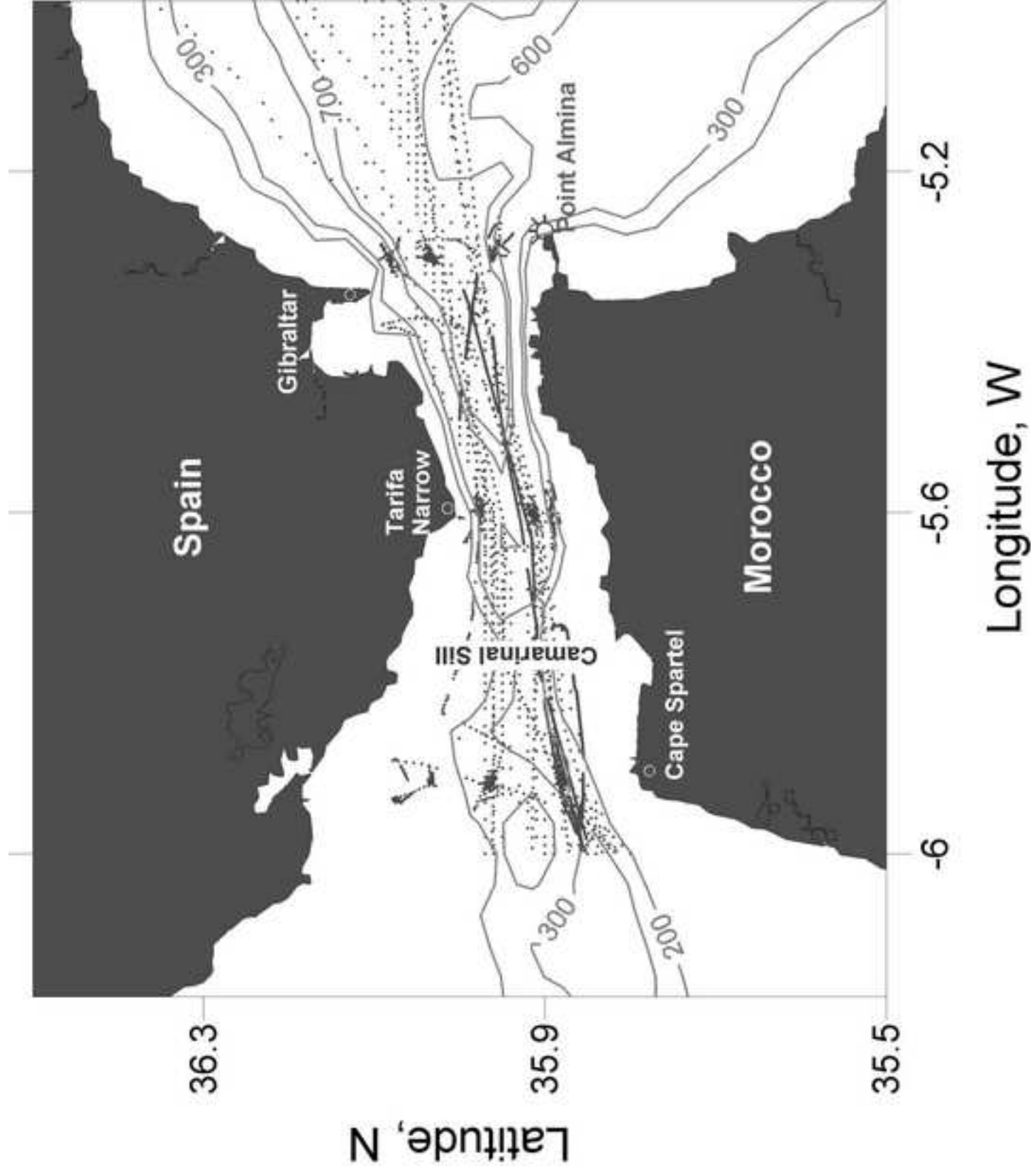


Figure 2

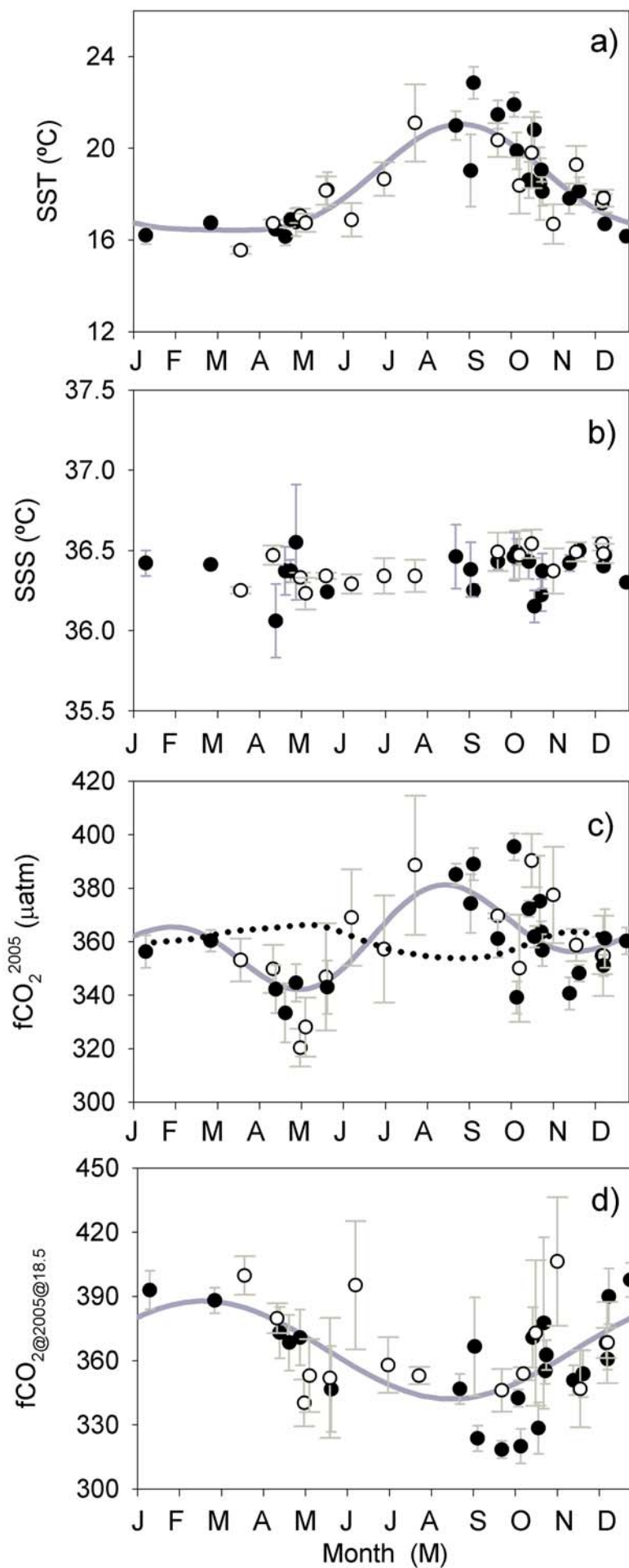


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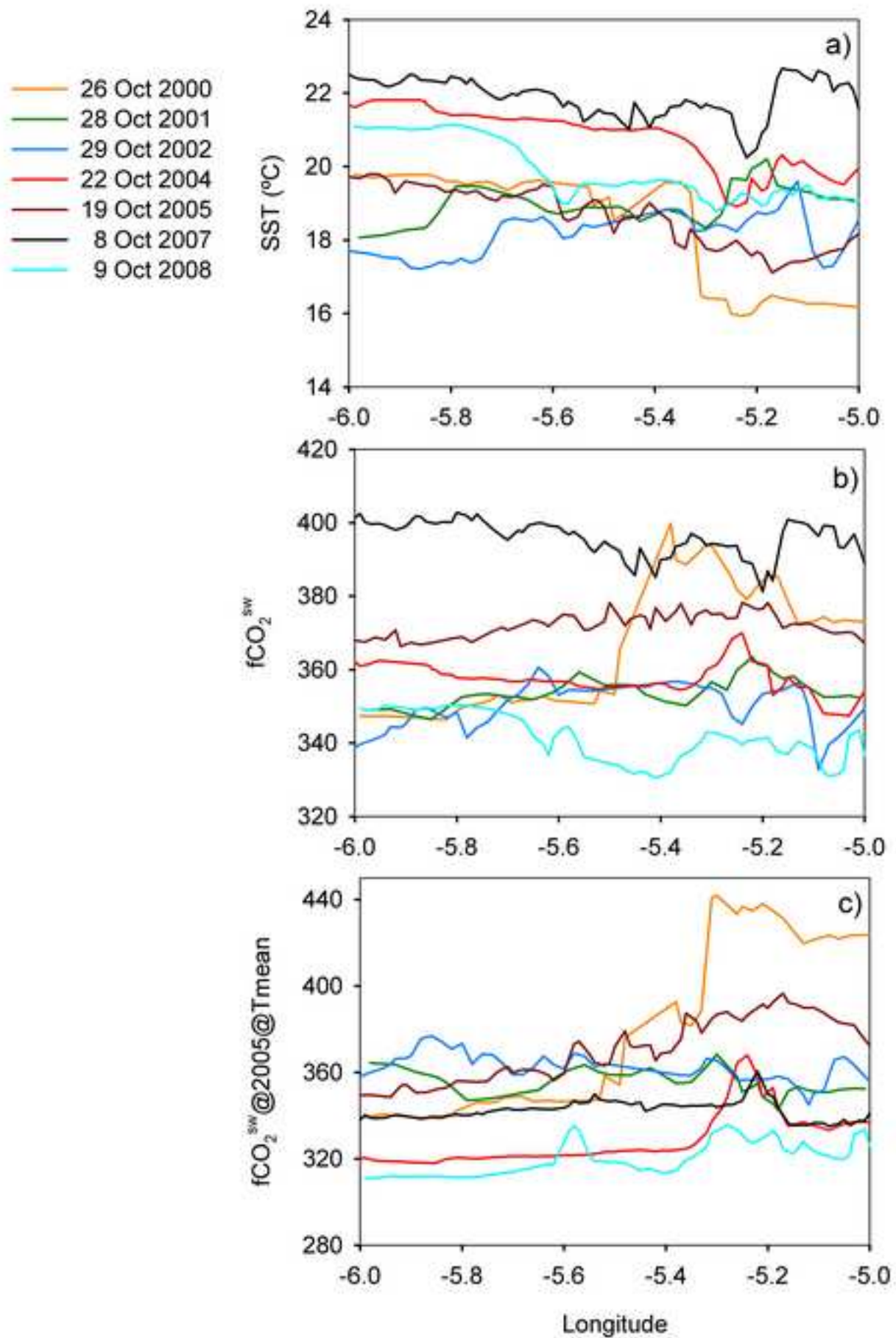


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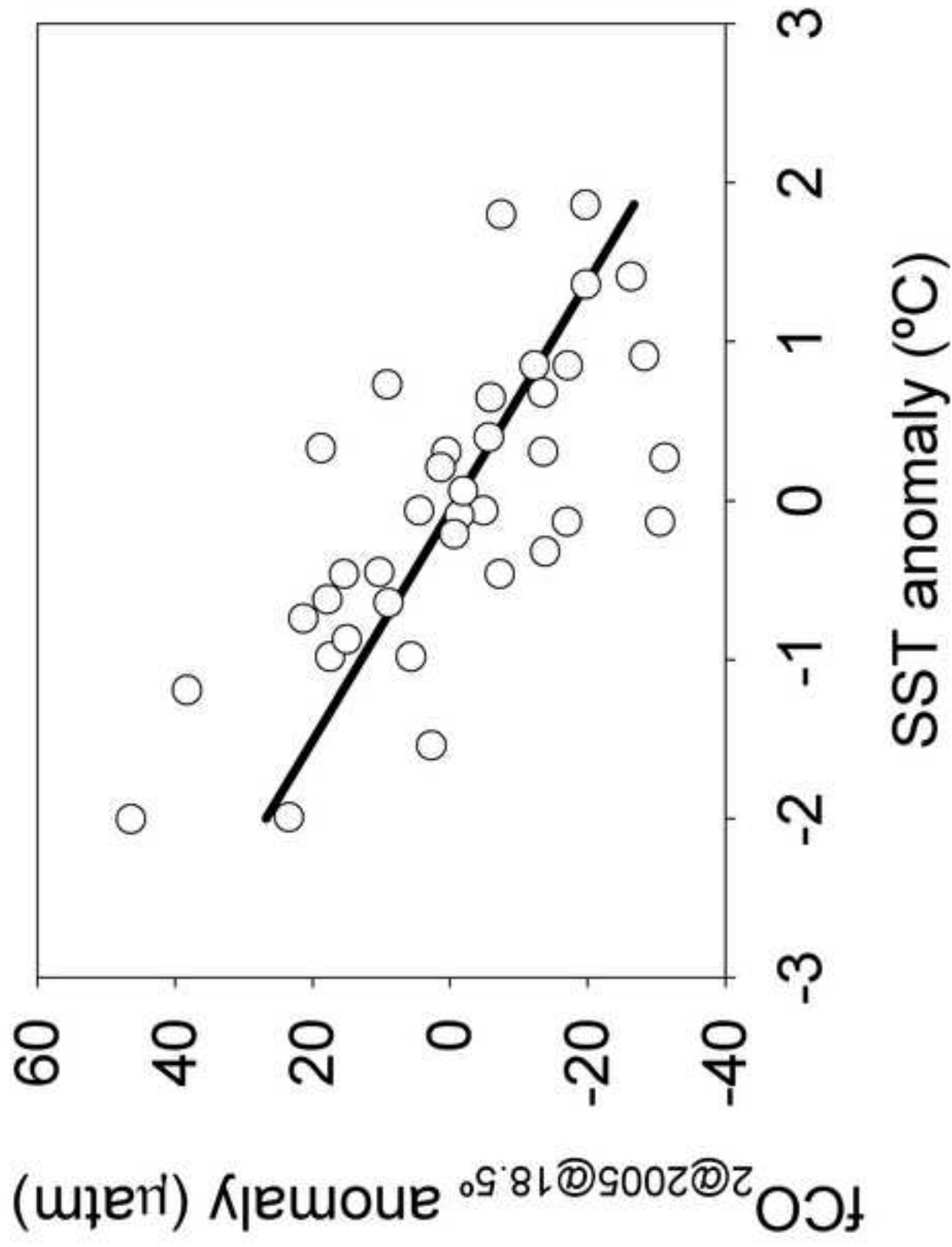
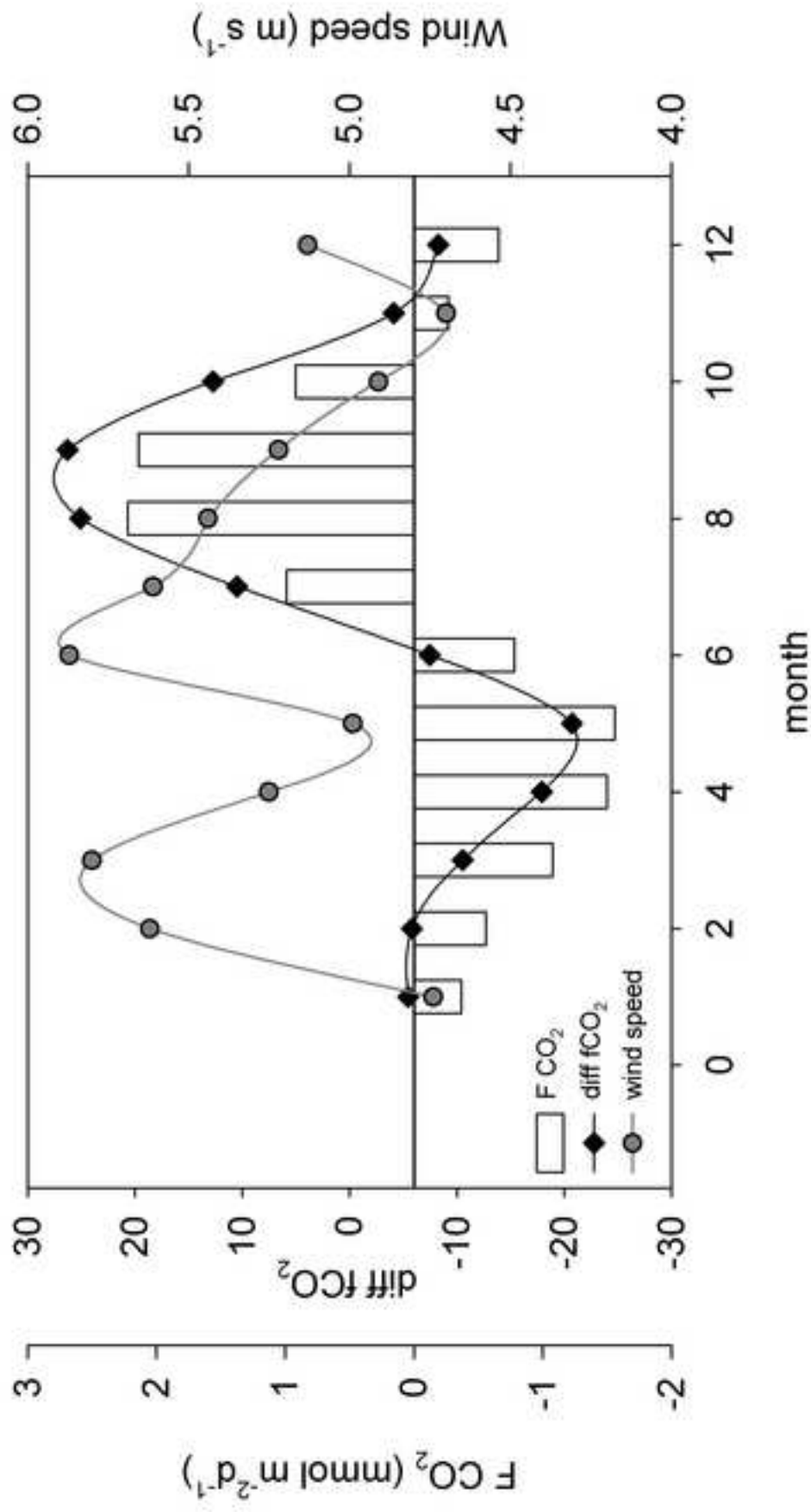


Figure 5

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*Research Highlights

- We study the seasonal variability of air-water CO₂ fluxes in the Strait of Gibraltar
- >The water temperature was is the main controlling mechanism of fCO₂ seasonality
- On annual basis, the Strait was almost in equilibrium with the atmosphere