Seasonal sea-surface CO_2 fugacity in the north-eastern shelf of the Gulf of Cádiz (southwest Iberian Peninsula).

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Abstract. The seasonal evolution of fugacity of CO_2 (fCO_2) and air-sea CO_2 fluxes in the north-eastern shelf of the Gulf of Cádiz was investigated by means of studying a data set from 4 cruises covering a seasonal cycle and three years of hidrological data set from a moored platform. fCO_2 was modeled as a function of sea surface temperature and day of the year. So, the seasonal cycle of fCO_2 and its air-sea fluxes were obtained using daily surface data in the area. Over the year, the north-eastern shelf of the Gulf of Cádiz ($1.4 \cdot 10^6$ m^2) acts as a net sink of CO_2 (-1.5 mmol m^{-2} day^{-1}). From September to July, the zone is a stronger sink for CO_2 (-1.8 mmol m^{-2} day^{-1}), while in August and September, it behaves as a weak CO_2 source (0.3 mmol m^{-2} day^{-1}).

Key Words: CO_2 fluxes; seasonal variations; climatology; air-water exchange; Spain; Gulf of Cádiz. 36.9 °N–36.3 °N; 6.9 °W–6.2 °W.

1. Introduction

Although the continental marginal seas occupy only a little over 8% of the ocean surface area and less than 0.5% of the ocean volume, they play a major role in the biogeochemical cycles of carbon and associated elements (Alongi 1998; Chen and Borges 2009). In order to constrain carbon fluxes in coastal systems, large scale international efforts e.g. Surface Ocean CO_2 Atlas project, are currently being undertaken. Quantification of the role of coastal ecosystems as an atmospheric sink or source of CO_2 is one of the major scientific issues to be addressed. One tool that has show great utility is the moored platforms. Long-term time series are important in order to evaluate the biogeochemical cycles in the ocean. There are some long-term ocean time series observations of seawater CO_2: (a) the Bermuda Atlantic Time series Study (BATS) and the Hydrostation S station located near Bermuda in the NW Atlantic Ocean (e.g. (Bates 2001; Bates *et al*. 1996); (b) the Hawaii Ocean Time series station (HOT), located at ALOHA near Hawaii in the North Pacific Ocean (Brix *et al*. 2004; Keeling *et al*. 2004); (c) the European Station for Time series in the Ocean (ESTOC), located off the Canary

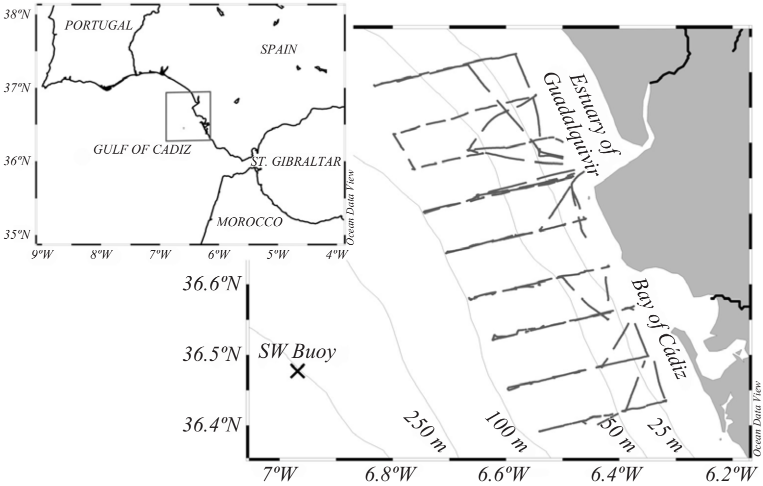

Figure 1 Map of the north-eastern shelf of the Gulf of Cádiz. Isolines represent the bathymetry. The two important coastal ecosystems are depicted: Guadalquivir Estuary and Bay of Cádiz. An exemple of the cruise track is shown by the broken gray line. The location of the buoy from which meteorological and oceanographical data were obtained is also shown.

Islands in the NE Atlantic Ocean (González-Dávila *et al.* 2010; Santana-Casiano *et al.* 2007). However, there are not in nearby continental shelf and they will be a powerful tool for investigating any changes in ocean biogeochemistry in coastal area. In addition, there are some moored platforms which are used for hydrographic and meteorological monitoring. They could be an ideal platform, where install biogeochemical sensors at reasonable cost.

Only a few studies have been carried out in the Gulf of Cádiz to evaluate the variability of the sea-surface fCO_2 (Aït-Ameur and Goyet, 2006; González-Dávila *et al.* 2003; Huertas *et al.* 2006; Ribas-Ribas *et al.* 2011) which clearly hampers our ability to estimate the air-sea CO_2 flux of the north-eastern shelf of the Gulf of Cádiz.

A better understanding of the Gulf of Cádiz flux is fundamental before it can be placed in a global context. In this study, we looked at four direct fCO_2 measurement surveys in the north-eastern shelf of the Gulf of Cádiz and three years of hidrological data from a moored platform. This data set provides us fCO_2 with enough resolution to examine the intra-annuality of the air-sea CO_2 flux of the north-eastern shelf of the Gulf of Cádiz. This region, covering a 0.6° x 0.6° area, represents ~ 10 % of the northern shelf of the Gulf of Cádiz surface area (Figure 1), and is a highly dynamic zone both in terms of physical and biogeochemical processes.

This region is of special interest, being immediately adjacent to the Strait of Gibraltar (Figure 1). It has already been emphasized that the Gulf of Cádiz plays an important role in the carbon cycle of the eastern North Atlantic (Parrilla 1998) and the Mediterranean Sea (Dafner *et al*. 2001). In the Gulf of Cádiz several water masses mix together to form the "Atlantic inflow", which is responsible for supplying water to the Mediterranean Sea from the west (Minas *et al*. 1991). Moreover, this area is on the pathway of the "Mediterranean outflow" which thereafter enters the open ocean and influences water circulation in the entire North Atlantic, and the climate in general (Rahmstorf 1998). The basin receives significant fluvial inputs associated with the discharge of large rivers such as the Guadiana, the Guadalquivir, the Guadalete and the Tinto-Odiel (Figure 1).

The main objective of the present paper is to find a correlation between the seawater fCO_2, sea surface temperature (SST) and day of the year in order to propose an initial climatological approach to the modeling of this phenomenon.

2. Material and Methods

2.1. Field sampling and analysis

The seawatch buoy station (Figure 1, (36.47N; 6.96W)), provided by the Spanish national government (*Organismo Público Puertos del Estado*) recorded sea surface temperature, salinity, wind speed and direction and atmospheric pressure every hour. We used the data from June 2005 to May 2007.

Four cruises have been undertaken: 17-28 June 2006, 19-30 November 2006, 31 January- 9 February 2007 on board the R/V Mytilus; and 21-24 May 2007 on board the R/V Ucádiz. The study area is located between 36.39 and 36.93 °N and between 6.83 and 6.32 °W. As the location of the buoy is more oceanic than our study area (Figure 1), we have used only fCO_2 data for the shelf zone with SSS above 36. By doing this, we remove riverine and coastal influence.

Sea surface salinity (SSS), SST and fCO_2 were sampled with a frequency of 30 seconds from the surface seawater supply of the ship (pump inlet at a depth of 3 m). SSS and SST were measured, using a SeaBird thermosalinograph (Micro-SeaBird 45), before water entry into the gas equilibrator. SST and SSS are estimated to be accurate to ±0.004 °C and ±0.005, respectively, according to the SeaBird calibration data.

The surface water CO_2 molar fraction (xCO_2) was measured with a non-dispersive infrared gas analyzer (Licor®, LI-6262). At the beginning and the end of each day, the equipment was calibrated with two standards: CO_2 free-air and a high CO_2 standard gas with a concentration of 530 ppm (with pre-deployment laboratory calibration against Air-Liquide France standard). The temperature inside the equilibrator was measured continuously by means of a platinum resistance thermometer (PT100 probe). The temperature difference between the ship's sea inlet and the equilibration system was less than 0.8°C during all the cruises. A pressure transducer (Setra Systems, accurate to 0.05%) was used to measure the pressure inside the equilibrator. The accuracy (precision) of seawater fCO_2 measurements was ±3 (±0.5) μatm.

The water-saturated fCO_2 in the equilibrator was calculated from the xCO_2 in dry air; the atmospheric pressure data was provided by the Spanish national government (*Organismo Público Puertos del Estado*); and equilibrium water vapor was calculated according to the protocol described in Dickson *et al.* (2007). The formulation proposed by Takahashi *et al.* (1993) was employed for the partial pressure corrections to in situ water temperature.

2.2. Flux calculations

Average net air-sea CO_2 flux (FCO_2) was estimated based on the formula $FCO_2 = \alpha k \Delta fCO_2$ [1], where α is the solubility coefficient of CO_2 (Weiss 1974), k is the gas transfer velocity of CO_2 and ΔfCO_2 is the mean difference between the water and air fCO_2 .The atmospheric fCO_2 data were obtained from the monthly data at Tercerira Island station (Azores, Portugal), taken from National Oceanic and Atmospheric Administration (NOAA/CMDL/CCGG air sampling network) data available online at http://www.esrl.noaa.gov/gmd/dv/ftpdata.html. A negative value indicates air-to-sea flux and a positive flux value represents the net CO_2 exchange from the water body to the atmosphere.

The gas transfer velocity, k, was calculated using the equation $k\ (cm\ h^{-1}) = 0.31\ u^2\ (Sc/660)^{-0.5}$ [2] given by Wanninkhof (1992). Sc is the Schmidt number of CO_2 in seawater; 660 is the Sc value in seawater at 20 °C. The wind speed data, u ($m\ s^{-1}$), was recorded at the Seawatch buoy station and normalized to 10 m height using the relationship of Garratt (1977). Daily averaged wind speeds were used for the calculation of gas transfer velocities. Wind is a crucial climate factor influencing marine hydrodynamic conditions on the Cádiz coast, given its frequent strength.

2.3 Study site

The study was carried out over the north-eastern shelf of the Gulf of Cádiz, which is located on the southwestern coast of the Iberian Peninsula (Figure 1). The circulation in the north-eastern shelf of the Gulf of Cádiz is controlled mainly by the North Atlantic Surface Water (NASW), which flows towards the east and southeast to the Strait of Gibraltar, as well as by an intermittent counter-current system, which seems to be strongly linked to the wind regime (Lobo *et al.* 2004). In particular, coastal waters near the mouth of the Guadalquivir River and the Bay of Cádiz present the highest primary production within the Gulf of Cádiz (Navarro and Ruiz 2006). The coastal fringe of the Gulf of Cádiz is also characterized by the presence of waters warmer and colder than those detected in the rest of the basin during June and February, respectively (Navarro and Ruiz 2006; Vargas *et al.* 2003) and by considerable meteorological forcing caused by quasi-permanent episodes of winds. For example, the predominance of western winds is always linked to the generation of upwelling events and therefore to an increase in primary production; on the other hand easterlies lead to a decrease in phytoplankton (García-Lafuente and Ruiz 2007). Furthermore, the alternation of mixing and stratification periods in the region affects the position of the nutricline and thus also regulates the primary production (Navarro *et al.* 2006).

3. Results and discussion

3.1 Climatological for the shelf data

In order to establish the seasonal FCO_2 and as an initial approach to modeling this based on climatological data in the area, we use SST and wind data for three years obtained from the *Puertos del estado* buoy. The climatological approach has been applied successfully by Ríos *et al.* (2005), who modeled monthly CO_2 fugacity as a function of SST and month for 1998 in the Azores area, with the aim

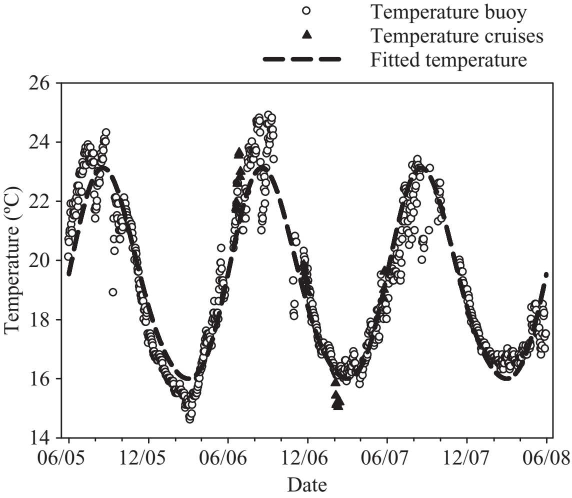

Figure 2 Three-year climatological seasonal cycles of sea surface temperature in the north-eastern shelf of the Gulf of Cádiz. Open circles are data from the seawatch buoy (Figure 1), black triangles are data from cruises in the continental shelf area and broken line is temperature fitted by the sigmoidal equation.

of establishing the CO_2 seasonal cycle. Lüger *et al.* (2004) estimated the effects on the annual cycle of pCO_2 and related this property to parameters such as temperature in the mid-latitude North Atlantic Ocean, with the same approach. González-Dávila *et al.* (2009) used the same wave function to determine the seasonal cycles of SST and fCO_2 in the Angola-Benguela region. However, spare studies have been found that have applied this approach in coastal areas (Kuss *et al.* 2006; Nemoto *et al.* 2009).

Following Zeng *et al.* (2002), the seasonality of SST was analyzed with a sine and cosine function (Figure 2) which can be expressed by a harmonic equation:

$x(t)=c_0+c_1\cdot\sin(2\pi t)+c_2\cdot\cos(2\pi t)+c_3\cdot\sin(4\pi t)+c_4\cdot\cos(4\pi t)$ [3]

From the SST, considering SSS to be constant and equal to the average (SSS=36.2), we assume a linear relationship between sea water fCO_2 and SST in the outer area not affected by the river discharge (i.e. no data off Guadalquivir Estuary and the Bay of Cádiz):

$fCO_2=293.55+3.80\cdot SST$ [4] ($r^2=0.84$).

It is important to point out that, in order to remove all the riverine and coastal influence, we only used fCO_2 data from the shelf zone with $S>36$. We also did this in order to fit our fCO_2 data base as closely as possible to hydrodynamic data from the buoy (Figure 1). In a first approach, the linear relationship between fCO_2 and temperature is valid because it has been demonstrated that in this area thermodynamic played the mayor role in the control of fCO_2 (Ribas-Ribas *et al.* 2011). These authors reported a straight fCO_2-temperature plot for the shelf data. Moreover, it could seem that fCO_2 could be better predicted when it is related to chlorophyll-a and nutrients, but this statement should be cautiously used because

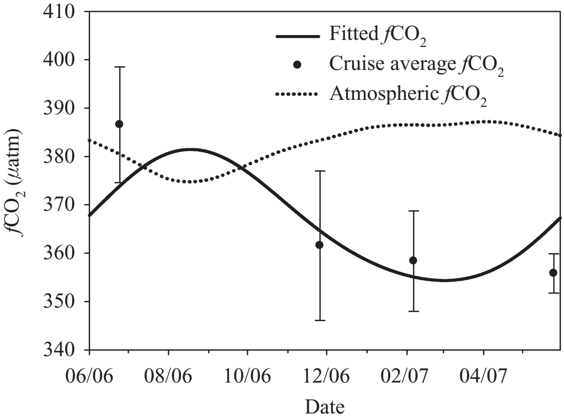

Figure 3 Seasonal cycles of the fitted surface seawater fugacity of CO_2 (fCO_2), atmospheric fCO_2 and cruise average (with standard deviation) fCO_2 in the shelf area.

in many cases, it is not true (Watson *et al.* 1994).

The annual increase of sea water fCO_2 we take is 1.8 μatm yr^{-1}, which is the value proposed by Lefèvre *et al.* (2004).

Combining [3] and [4] and adding the annual fCO_2 increment, we obtain: $fCO_2 = 366.7 + 1.8 \cdot (yr - 2006.5) - 10.34 \cdot \sin(2\pi t) - 8.63 \cdot \cos(2\pi t) + 1.33 \cdot \sin(4\pi t) + 0.46 \cdot \cos(4\pi t)$ [5].

Measured and calculated fCO_2 are plotted in Figure 3. Although high daily variability in fCO_2 measurements, it is show that the calculated function could predict the fCO_2 behavior.

3.2 Validation

We had already said that there are only a few data in this area. However, we have tried to validate the sigmoidal function obtained with this study with data in February 1998 reported by González-Dávila *et al.* (2003). They found a mean fCO_2 concentration in seawater of 330 ± 5.6 μatm. With the climatological formula proposed in this work, a value of 338 μatm can be obtained for the days when the later study was carried out. This is in a good agreement and can be regarded as validating the proposed formula.

This formula is not only helpful for forecasting future values but also for interpolating fCO_2 values for the entire year studied, to enable the integrated air-sea CO_2 flux for the year to be calculated. For example, the cruise in June 2006 was taken as representative of the summer season, but it can be seen that, between July and September, the temperature and fCO_2 were higher than in June, and therefore the flux would also be higher. Taking into account the monthly mean of fCO_2^{atm} from the NOAA (Figure 3), and the daily mean wind speed from the buoy, corrected to a height of 10 m, we obtain an annual flux of -1.5 mmol m^{-2} day^{-1} (-0.5 mol m^{-2} yr^{-1}). The area act as a net sink from September to July as a rate of -1.8 mmol m^{-2} day^{-1}, while in August and September, it behaves as a weak CO_2 source (0.3 mmol m^{-2} day^{-1}) (Figure 4). The maxim FCO_2 was found in March, corresponding with the minimum in observed temperature (Figure 2). This fact indicated that fCO_2 distribution is mainly controlled by thermodynamic, as it was reported by Ribas-Ribas *et al.* (2011). This pattern could justify the use of a simple relationship between fCO_2 and temperature. The minimum FCO_2 fluxes in October coincide with low wind speed and low fCO_2 gradient (Figure 3).

We have also made estimates of FCO_2 using the Liss and Merlivat (1986) and the Ho *et al.* (2006) exchange coefficients. The average CO_2 influxes were -1.07 and -1.35 mmol m^{-2} day^{-1} respectively, which is 27% and 8% lower, respectively, than the mean FCO_2 value obtained with the Wanninkhof (1992) formulation.

This estimation of FCO_2 using different formulations is useful in order to compare our results with those from other authors. Similar value was obtained by

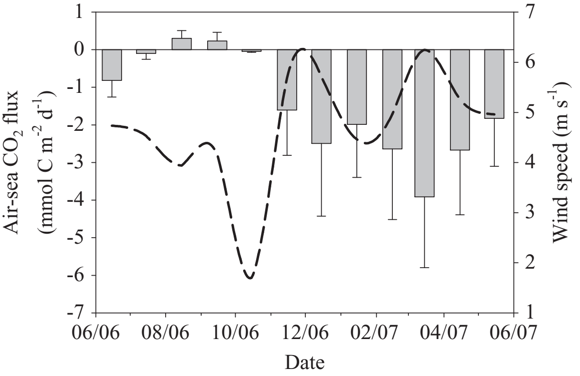

Figure 4 Seasonal variability in calculated air-sea CO_2 fluxes during the studied period in the Seawatch buoy shown in Figure 1. Monthly-average wind speed data is also shown.

Ríos *et al.* (2005) in the area of Azores. Aït-Ameur and Goyet (2006) reported that the surface water of the Gulf of Cádiz acted as a slight source of CO_2 for the atmosphere during July, coinciding with the trend observed in this work. A previous study carried out along an oceanic transect in the Gulf of Cádiz in February 1998 computed a greater flux of -19.5 ± 3.5 mmol m^{-2} day^{-1} although the analysis was performed under storm conditions with a high wind regime (15 ± 3 m s^{-1}) that could have had a substantial impact on the gas transference (González-Dávila *et al.* 2003).

The average value is three times higher than that calculated with direct observed data (Ribas-Ribas *et al.* 2011). This is due to the increased effect of acting as a sink in winter, and also because the position of the buoy is further out in the ocean than our study area. The air-sea CO_2 fluxes obtained demonstrate that the north-eastern shelf of the Gulf of Cádiz acts as a weak sink of CO_2 with an uptake of 7.97 Gg C yr^{-1}. This sink correspond to $0.5 \cdot 10^{-3}\%$ of the most recent estimate of the contemporary open ocean sink for atmospheric CO_2 of 1.4 PgC yr^{-1} (Takahashi *et al.* 2009). It is a small amount but still important taking into account the small surface study in comparation to the whole ocean.

3.3 Caveats

This first approach is subject to several inherent errors. The first is the assumption of a linear relationship between fCO_2 and temperature, as also assumed by several other authors (Lüger *et al.* 2004). However, it should be taken into account that, when phytoplankton blooms are present, the relationship is complex. For this reason, this simple model and relationship should be taken only as an early-stage estimation and as a first step towards modeling the climatology for this area. More direct measurements are needed to confirm the relationship and to evaluate the different factors affecting fCO_2. The second source of error is that the fCO_2 data were not obtained on the same buoy as the SST time-series, so there is a difference in temperature between the area studied and the buoy (Figure 2). A correction has been made in the final expression by subtraction 0.9 °C, the mean difference observed. There is a third possible error. The annual increase of sea water fCO_2 obtained from the adjusted climatological temperature is 0.74 μatm yr^{-1}; this value for the increase seems to be an underestimate due to the short time series used (3 years); therefore we take a value of 1.8 μatm yr^{-1}, which is the value proposed by Lefèvre *et al.* (2004) and used in a nearby area, the Gibraltar Strait by de la Paz *et al.* (2009).

4. Conclusions

We conclude the following from our study:

- An initial climatological approach to modeling has been made: $fCO_2 = 366.7 + 1.8 \cdot (yr - 2006.5) - 10.34 \cdot \sin(2\pi t) - 8.63 \cdot \cos(2\pi t) + 1.33 \cdot \sin(4\pi t) + 0.46 \cdot \cos(4\pi t)$.
- A reasonable agreement has been obtained but a larger data base will be required for better validation and future work.
- If a biochemical sensor could be installed on already moored buoys, this would make them a powerful tool for understanding the dynamics of the carbon cycle. This has been illustrated by Nemoto *et al.* (2009) for a buoy mooring location in the East China Sea and by Kuss *et al.* (2006) in the central Arkona Sea (Baltic Sea); automated pCO_2 instruments on moorings offer a complementary view to systems currently in use, by providing high-resolution temporal records of surface-ocean interactions.
- Long- term mooring-based measurements of oxygen and carbon dioxide are feasible but require inspection and intercomparison measurements to check for bio-fouling and sensor drift.

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