Short-term variability of surface carbon dioxide and sea-air CO₂ fluxes in the shelf waters of the Galician coastal upwelling system

ALBA MARINA COBO-VIVEROS 1, XOSÉ ANTONIO PADIN 1, PABLO OTERO 2, MERCEDES DE LA PAZ 1, MANUEL RUIZ-VILLARREAL 2, AIDA F. RÍOS 1 and FIZ F. PÉREZ 1

1 Instituto de Investigaciónes Mariñas (IIM-CSIC), Eduardo Cabello 6, 36208 Vigo, Spain. E-mail: almacovi@iim.csic.es
2 Instituto Español de Oceanografía (IEO), Paseo marítimo Alcalde Francisco Vázquez 10, 15001 A Coruña, Spain.

SUMMARY: Using data collected during the DYBAGA and ECO cruises, remote sensing chlorophyll-a estimations and the averaged upwelling index of the previous fortnight (Iw'), we studied the variability of the sea surface CO₂ fugacity (fCO₂) over the Galician continental shelf during three seasonal cycles. Sea surface salinity (SSS) distribution controlled fCO₂ mainly in spring, while sea surface temperature (SST) did so during periods of intense cooling in November and warming in June. The uptake of carbon by photosynthetic activity, which was more intense during spring and autumn, masked the surface increase in the dissolved inorganic carbon concentration during upwelling events, especially during spring. A significant low correlation between fCO₂ and Iw' was found during spring and summer when upwelling events were observed, whereas no relationship was observed during the downwelling period. High fCO₂ exceeding atmospheric values was only found during the summer stratification breakdown. Although sea-air CO₂ fluxes showed a marked inter-annual variability, surface waters off the Galician coast were net sinks for atmospheric CO₂ in every seasonal cycle, showing a lower CO₂ uptake (~65%) compared to previously published values. Marked inter-annual changes in the sea-air CO₂ fluxes seem to be influenced by fresh water inputs on the continental shelf under different meteorological scenarios.

Keywords: carbon dioxide, coastal upwelling, sea-air gas exchanges, carbon sinks.

RESUMEN: Variabilidad de dióxido de carbono y flujos de CO₂ océano-atmósfera, a corto plazo, en aguas de la plataforma del afloramiento costero en Galicia. – Durante tres ciclos estacionales se estudió la variabilidad superficial de la fugacidad de CO₂ (fCO₂) en la plataforma continental gallega, utilizando datos recogidos durante los proyectos DYBAGA y ECO, así como estimaciones de clorofila-a a partir de datos de satélite, y promedios quincenales del índice de afloramiento (Iw'). Los cambios de salinidad controlaron la variabilidad de fCO₂ en primavera, mientras que la temperatura lo hizo durante el máximo enfriamiento de Noviembre y máximo calentamiento de Junio. La captación de carbono por la actividad fotosintética, más intensa durante primavera y otoño, enmascaró el incremento superficial de carbono inorgánico durante los episodios de afloramiento, especialmente en primavera. Se observó una correlación significativa, aunque pequeña, entre fCO₂ e Iw' durante el período de afloramiento, mientras que no se encontró ninguna durante el hundimiento. Sólo se encontraron valores de fCO₂ superiores a los atmosféricos durante la ruptura de la estratificación estival. Aunque el intercambio de CO₂ océano-atmósfera mostró una marcada variabilidad interanual, la plataforma continental gallega fue un sumidero neto de CO₂ atmosférico. Los valores encontrados son inferiores a otros publicados anteriormente (~65% menos). Estos cambios interanuales parecen estar influidos por los aportes de agua dulce en la plataforma continental bajo distintas condiciones meteorológicas.

Palabras clave: dióxido de carbono, afloramiento costero, intercambios de gas océano-atmósfera, sumideros de carbono.

INTRODUCTION

Coastal upwelling develops on the eastern margins of subtropical gyres when predominant along-shore winds induce the rise of subsurface waters close to the coast into the photic layer (Wooster et al. 1976, Tomczak and Godfrey 2003, Arístegui et al. 2009). The entrance of cold and nutrient-rich deep water triggers the
high phytoplankton production that supports rich coastal marine ecosystems and productive fisheries (Paula and Christensen 1995). Furthermore, the exchange of large amounts of organic matter and energy with land, sediment and atmosphere (Walsh 1991, Mackenzie et al. 1998, Muller-Karger et al. 2005), makes coastal waters one of the most biogeochemically active areas of the biosphere in terms of sea-air CO2 exchange, carbon recycling and offshore exportation.

Coastal environments are important components of the global carbon cycle, even though their role as sinks or sources of CO2 has not been well defined in the past due to their strong spatial heterogeneity, temporal variability and the relative paucity of data (Borges et al. 2005). The carbon flows in these waters can shift rapidly (Gypens et al. 2005), making the estimate of the sea-air CO2 flux subject to large uncertainties (Borges 2005, Borges et al. 2005, Chen and Borges 2009). Earlier publications described continental margins as net sources of CO2 in agreement with the large CO2 emissions observed in inner estuaries (Frankignoulle et al. 1998, Mackenzie et al. 2000, Gago et al. 2003a). However, this view of the coastal oceans has changed since the proposal of a “continental shelf pump” by Tsunogai et al. (1999), who described a mechanism for the atmospheric CO2 absorption in shallow waters of continental shelves. After that, the studies reporting continental shelves as CO2 sinks outweighed those reporting them as CO2 sources. This diverging view on carbon cycling in the coastal oceans was solved by Rabouille et al. (2001), who split coastal waters into proximal continental shelves acting as a CO2 source, and distal continental shelves acting as a CO2 sink (Chen and Borges 2009).

The role of different coastal ecosystems as sinks or sources of atmospheric CO2 allows opposing views on carbon cycling in the coastal ocean to be reconciled, but the integrated sea-air CO2 flux in the global coastal ocean (estuaries and continental shelves) is still not clear. Chen and Borges (2009) recently evaluated these sea-air CO2 fluxes as scaled estimates from a compilation of CO2 measurements. They showed that the integrated sea-air CO2 flux in the global coastal ocean resulted in continental shelves absorbing atmospheric CO2 between –0.33 and –0.36 Pg C yr⁻¹; and inner estuaries, salt marshes and mangroves emitting up to 0.50 Pg C yr⁻¹. Laruelle et al. (2010) reported another estimation of the sea-air CO2 flux, showing absorption by continental shelves (~0.21 Pg C yr⁻¹) close to that reported by Chen and Borges (2009), and emission from estuaries (0.27 Pg C yr⁻¹) lower than this previous estimation. The largest uncertainties of scaling approaches used to estimate the role of the continental shelf seas are the availability of CO2 data that describe the spatial variability in the region and that capture relevant temporal scales. At present, the lack of sufficient data is the major limitation in the quantification of the spatial and temporal variability of CO2 fluxes in the different coastal environments.

The Galician coast is located at the northern limit of the Canary Current Upwelling System, in the subtropical gyre of the North Atlantic Ocean (Wooster et al. 1976, Aristegui et al. 2004). The upwelling pattern on the Galician coast is marked by a strong seasonality (Wooster et al. 1976, Fraga 1981, Frouin et al. 1990, Pingree and Le Cann 1990, Bakun and Nelson 1991, Haynes et al. 1993) due to marked seasonal changes in wind stress determined by the Azores High and Icelandic Low pressure systems. Upwelling events are commonly observed during spring-summer with the predominance of northeasterly winds (Blanton et al. 1984). The offshore zonal Ekman transport of surface waters produces the rise of a cold, nutrient-rich, deep water mass called Eastern North Atlantic Central Water (ENACW) (Ríos et al. 1992). During these upwelling events, upwelling filaments of surface water extending westward also occur in the shelf waters to the south of Cape Finisterre (Álvarez-Salgado et al. 1993, Haynes et al. 1993, Barton et al. 2001, Borges and Frankignoule 2001). These filaments are major routes of primary production exportation of shelf waters from the Rías Baixas, because they provide a mechanism through which organic material produced in shelf waters is transported hundreds of kilometers offshore into the ocean (Álvarez-Salgado et al. 2001). Although these filaments seem to be oligotrophic and relatively unproductive systems, they act as a stronger net sink for atmospheric CO2 than the surrounding offshore waters (Borges and Frankignoule 2001).

Although winter upwelling is sometimes observed in this area (Álvarez et al. 2009), the usual northerly winds occurring in this season force the coastal downwelling of surface waters (Blanton et al. 1984). This season is also characterized by a poleward undercurrent of warm and salty waters of subtropical origin (Fraga et al. 1982), called the Iberian Poleward Current (IPC), that flows clearly constrained to the Iberian shelf break (Frouin et al. 1990). Moreover, run-off from local rivers contributes to the presence of river plumes over the shelf, which varies in fast response to wind event variability (Otero et al. 2008). This wind event variability, along with the development of filaments, eddies, the IPC and river plumes, turn the Galician coast into a region with variable physical processes with high rates of primary production. Furthermore, the absence of a shallow oxygen minimum zone, present in the upwelling systems of the Pacific and Indian Oceans, does not lead to an excess of dissolved inorganic carbon (Friederich et al. 2008) in subsurface waters, thus avoiding the intense release of CO2 during the upwelling events.

High absorption rates of CO2 ranging from ~0.09 (during late autumn) to ~0.51 mol C m⁻² yr⁻¹ (during spring) have been previously found for the Galician continental shelf (Pérez et al. 1999). During summer upwelling events, the continental shelf behaves as a marginal source of CO2, with emission values of 0.10 mol C m⁻² yr⁻¹ (Pérez et al. 1999). On the contrary, Borges and Frankignoule (2001) reported values rang-
ing from $-0.66$ to $-1.17$ mol C m$^{-2}$ yr$^{-1}$ for the Galician continental shelf at the end of August. During the upwelling season, Borges and Frankignoulle (2002) computed CO$_2$ sea-air fluxes over the Galician continental shelf in the range of $-0.84$ to $-1.72$ mol C m$^{-2}$ yr$^{-1}$. The oceanic zone of the Ría de Vigo also acts as a CO$_2$ sink during the upwelling period with values between $-0.27$ and $-0.48$ mol C m$^{-2}$ yr$^{-1}$, and only releases CO$_2$ in October (Gago et al. 2003a). CO$_2$ in surface waters is mainly controlled by the input of upwelling deep cold waters with high CO$_2$ content, primary production (Borges and Frankignoulle 2002), vertical advection, turbulent diffusion and net ecosystem production of organic carbon components (Gago et al. 2003b).

In order to improve the description of this particular typology of continental shelf seas, we studied the variability of CO$_2$ observed in surface waters of the Galician continental shelf during three complete seasonal cycles. This database allowed us to obtain a broader view of the temporal variability of annual net sea-air CO$_2$ fluxes on the Galician continental shelf. The main aims were to improve estimates of the spatial and temporal variability of the sea-air CO$_2$ fluxes, and understand how natural drivers in a coastal upwelling affect these processes.

**MATERIALS AND METHODS**

**The Dybaga and ECO cruises**

Underway measurements collected during the DYBAGA (Dynamics and Biogeochemical variability on the Galician continental shelf at short-scale) and ECO (Evolution of CO$_2$ increase using ships of Opportunity: Galicia and Bay of Biscay) oceanographic cruises are gathered in this article (Fig. 1). The DYBAGA cruises were carried out along an across-shore section on the Galician continental shelf. During a complete seasonal cycle, from May 2001 to May 2002, one transect was sampled weekly, giving a total of 46 transects. The ECO cruises were carried out on board ships of opportunity from the Company Flota Suardíaz (RO-RO L’Audace and RO-RO Surprise) in a regular route that linked Vigo (Spain) and St. Nazaire (France). Throughout two entire seasonal cycles, between December 2002 and December 2004, 145 tracks were sampled over the Galician continental shelf with a frequency of around 10 transects per month.

Underway measurements of the seawater CO$_2$ molar fraction (xCO$_2^{sw}$), sea surface salinity (SSS) and temperature (SST) were collected using an autonomous homemade device called GASPAR (see detailed description in Padin et al. 2010). The device worked by pumping a water volume from 3 m below the waterline into the ship’s hull; this volume was bifurcated so it passed through a sea-air equilibrator system. A thermostalimograph (SBE-45-MicroTSG) was connected to the same uncontaminated seawater supply, in parallel with the CO$_2$ measuring system, and recorded underway SST and SSS during the cruises with accuracies of ±0.002°C and ±0.003 respectively. Measurements of the CO$_2$ molar fraction were made with a non-dispersive infrared gas analyzer (Licor, LI-6262), which was calibrated at the beginning and end of each transit (which usually took 24 h) using two CO$_2$ gas standards: a synthetic free-CO$_2$ air and a high CO$_2$ standard of ~375 ppmv in synthetic air. The Instituto Meteorológico Nacional (Izaña, Canary Islands), belonging to the NOAA/ESRL Global Monitoring Division, certified the CO$_2$ concentration in both standards. Data reduction, the seawater CO$_2$ fugacity (fCO$_2$) calculation from raw data (with the exception of just using two gas standards) referenced to saturated water vapor pressure using in situ atmospheric pressure readings, was carried out following the recommendations of Dickson et al. (2007). The fCO$_2$ values were then corrected for the seawater temperature increase that occurs while the sample travels from the hull’s inlet into the equilibration chamber. This temperature shift was usually <1°C. The temperature was tracked with platinum resistance thermometers and then the empirical equation proposed by Takahashi et al. (1993) was applied.

**Fig. 1. – Map of the Galician continental shelf, showing DYBAGA (grey points) and ECO (black points) cruise tracks. The Rías of Vigo, Pontevedra and Arousa are shown, as well as the Miño River. Schematic circulation in the area during typical upwelling (spring and summer; light grey) and typical downwelling (autumn–winter; black) seasons is indicated. Note that a typical season is a simplification and the system is subject to event variability that can dominate the response of the system (Ruiz-Villareal et al. 2006). The black arrow heading northwards during autumn-winter represents the Iberian Poleward Current (IPC). The light grey arrows heading southwards during spring-summer represent the equatorward shelf-slope currents.**
The underway measurements during these projects were initially logged with different frequencies, but were later averaged every 5 min cycle in order to homogenize the dataset. Surface observations measured between the 60 and 200 m isobaths were selected. The ETOPO2v2 bathymetry (U.S. Department of Commerce et al. 2006) was used for merging depth records using two-dimensional linear interpolation functions of every layer. After applying all of these selection criteria, a final DYBAGA and ECO dataset comprising 348 and 1608 observations respectively, was obtained. Finally each cruise was averaged in order to obtain a mean value of each track crossing the continental shelf.

Remotely sensed chlorophyll-α (chl α) was included in the DYBAGA and ECO dataset as a proxy of the photosynthetic activity. Weekly fields of chl α, with a spatial resolution of 1/24° at the equator (4.63 km) and a frequency of 8 days (which were continuous starting from the first day of each calendar year), were retrieved from the GlobColour global level-3 binned products (www.globcolour.info). The chl α selected product was generated from the GSM (Garver-Siegel-Maritorena) model, a merging technique based on Maritorena and Siegel (2005). The GSM model provided the best fit to in situ chl α and had the added advantage of providing other products (Sea-viewing Wide Field-of-view Sensor (SeaWiFS), Moderate Resolution Imaging Spectrometer (MODIS) and Medium Resolution Imaging Spectrometer Instrument (MERIS)) that, compared to each of the original data sources, showed enhanced global daily coverage and lower uncertainties in the retrieved variables. The GSM model can also calculate pixel-by-pixel error bars. Selection criteria for the choice of pixels in considering only chl α measurements taken within ±4 days (orbital over-passing) of the ship measurement date, and within ±3.3 km off the cruise track. The number of collocated observations of chl α achieved 85% of the 5-minute averages of chl α measurements.

The upwelling index (Iw′), calculated following Wooster et al. (1976) as the estimation of the upwelled water flow per kilometer of coast, was added as an ancillary variable:

\[
I_w = \frac{\rho_{air} C_p V_s W S}{\rho_{sw} f} \quad (1)
\]

where \(\rho_{air}\) is the air density (1.22 kg m\(^{-3}\) at 15°C), \(C_p\) is an empirical dimensionless drag coefficient (1.4 10\(^{-3}\); according to Hidy 1972), WS is wind speed, \(\rho_{sw}\) is the seawater density (1025 kg m\(^{-3}\)), \(f\) is the Coriolis parameter; and \(V_s\) is the wind speed component parallel to the coast, that is, the meridional component of wind speed due to coast orientation. Positive (negative) values of \(I_w\) correspond to upwelling (downwelling) in the Iberian Upwelling System. Wind speed data were obtained from the National Center for Environmental Prediction (NCEP) Reanalysis project maintained by the NOAA/OAR/ESRL/PSD at Boulder, Colorado, USA (http://www.cdc.noaa.gov/). These data have been widely used for forcing coastal ocean models because of their availability, the long and consistent time-series and full spatial coverage. We selected the NCEP/NCAR Reanalysis 1 project (Kalnay et al. 1996), which uses a state-of-the-art analysis/forecast system to perform data assimilation using data from 1948 to the present, in order to obtain wind speed in the location of 43°N 11°W as a reference point of the upwelling events on the Galician continental shelf (Pérez et al. 2010). Instead of the corresponding \(I_w\) attending to date, an averaged \(I_w\) during the previous fortnight (\(I_w'\)) was preferred due to the more significant influence on the fCO₂ measurements, as was also found with the net production of the community (Álvarez-Salgado et al. 2002).

Estimation of sea-air CO₂ exchange

The CO₂ exchange between the ocean and atmosphere (FCO₂, in mol m\(^{-2}\) yr\(^{-1}\)) was calculated using the following equation:

\[
FCO_2 = kS \Delta CO_2 \quad (2)
\]

where \(k\) is the monthly mean CO₂ transfer velocity (cm h\(^{-1}\)); calculated using Wanninkhof’s parameterization (Wanninkhof 1992) and 6-hourly estimations of the zonal and meridional components of winds from the NCEP/NCAR Reanalysis project (NOAA-CIRES Climate Diagnostics Center, http://www.cdc.noaa.gov/); \(S\) is the CO₂ solubility in seawater (mol kg\(^{-1}\) atm\(^{-1}\)), calculated from Weiss (1974); and \(\Delta CO_2\) is the CO₂ disequilibrium between sea and air. The atmospheric CO₂ fugacity (fCO₂ atm) was estimated from the monthly values of the atmospheric CO₂ molar fraction (xCO₂ atm) recorded in the meteorological stations of the NOAA/ESRL Global Monitoring Division stations. The xCO₂ atm measurements were linearly interpolated versus latitude from observations at Azores (38.77°N) and Mace Head (53.55°N). The final xCO₂ atm dataset was then converted to atmospheric CO₂ partial pressure (pCO₂ atm), considering atmospheric pressure (P atm) and water vapor partial pressure (pH₂O, in atm), which was calculated from in situ SST readings (\(T_s\), Eq. 3 and 4) according to Weiss and Price (1980) and following Pierrot et al. (2009). The pCO₂ atm values were then converted to fCO₂ atm assuming a decrease of 0.3% from the pCO₂ atm value (Weiss 1974) due to the non-ideal behavior of carbon dioxide (Gago et al. 2003a).

\[
pCO_2 = xCO_2 atm(P_{atm} - pH_2O) \quad (3)
\]

\[
pH_2O = 0.981 \exp \left[ 14.32602 - \left( \frac{5306.83}{273.15 + T_s} \right) \right] \quad (4)
\]

The measured xCO₂ atm data were converted to fCO₂ referenced to saturated water vapor pressure using in situ atmospheric pressure readings.
Biogeochemical variability and control of fCO₂

The processes controlling fCO₂ variability on the Galician shelf are due to several factors: thermodynamic control, biological production and respiration, alkalinity change, water mixing, and stratification of the water column. The influence of thermal and non-thermal processes on the fCO₂ variability was evaluated with the approach described by Takahashi et al. (2002). Using the well-known temperature control on fCO₂ of 4.23% °C⁻¹ (Takahashi et al. 1993), the impact of thermal (fCO₂) and non-thermal (non-fCO₂) processes forcing the fCO₂ seasonal cycle was estimated as:

\[ \text{non-fCO}_2 = \text{fCO}_2 \exp(0.0423(SST_{mean} - SST)) \]  
\[ \text{fCO}_2 = \text{fCO}_{2\text{mean}} \exp(0.0423(SST - SST_{mean})) \] (5) (6)

where non-fCO₂ denotes the seawater fCO₂ normalized to the annual mean SST (SST_{mean}) and fCO₂ represents the effect of the SST distribution on the annual mean seawater fCO₂ (fCO₂mean). In other words, non-fCO₂ represents changes in the total CO₂ concentration, which include effects of the net CO₂ utilization, a small amount of net alkalinity change due to carbonate production and nitrate utilization, sea-air exchange of CO₂, and an addition of CO₂ and alkalinity by the vertical mixing of subsurface waters (Takahashi et al. 2002).

The analysis of the biogeochemical control of fCO₂ variability was extended by performing multiple linear regressions taking into account all the measured variables. However, the statistical analysis was performed on the ΔCO₂ distribution because it also takes into account small changes in the fCO₂ atm. The correlations between ΔCO₂ and the ancillary parameters in the shelf waters were assessed for the four seasons: winter (December-February), spring (March-May), summer (June-August) and autumn (September-November).

An empirical algorithm was computed fitting ΔCO₂ values with second-order multiple polynomials using SST and chl a observations (Stephens et al. 1995, Ono et al. 2004, Padin et al. 2009), and linear relationships with SSS, WS, Iw', geographical position and depth as independent variables according to Equation 7:

\[ fCO₂ = \text{fCO}_2 + A\text{lat} + B\text{Depth} + \]  
\[ \sum_{i=1}^{2} (SST - \mu_{SST}) + C(\text{SSS} - \mu_{\text{SSS}}) + \]  
\[ + \sum_{i=1}^{2} \beta_i(\text{chl a}) + DWS + EI_w \] (7)

The multiple linear regression coefficients were obtained using a forward stepwise method in which only significant parameters that accounted for at least 1% of the ΔfCO₂ variability were included in the algorithm. The µ parameter stands for the average SST or SSS value for the corresponding period.

RESULTS

Biogeochemical variability

The temporal variability of sea surface properties on the continental shelf of the Galician coast was analyzed from average values of each DYBAGA and ECO cruise that described three complete seasonal cycles from May 2001 to December 2004. Furthermore, Iw' was also included in Figure 2 in order to identify the upwelling and downwelling favorable wind events.

The temporal evolution of thermohaline properties showed a marked seasonality throughout the sampled period, even though significant differences were also found among the three seasonal cycles (Fig. 2, Table 1). The warmest waters were found at the beginning of October 2003 (19.6°C) and the coldest waters in January 2004 (12.0°C), setting a temperature range of 7.6°C throughout the entire sampling period. The lowest temperature range (5.1°C) and mean cold waters (15.3±1.4°C) were found during the first seasonal cycle measured in the DYBAGA cruises. The following seasonal cycles sampled during the ECO cruises showed warmer temperatures than the ones found during the first seasonal cycle, with the highest mean SST found in 2003 (15.8±1.9°C). The temperature ranges of the ECO cruises were 6.8°C and 7.4°C.

Fig. 2 – Biogeochemical variability observed during DYBAGA (May 2001 - May 2002) and ECO (December 2002 - December 2004) cruises; a) Average upwelling index during the previous fortnight (Iw'), which delimits upwelling and downwelling favorable wind events; b) Sea surface temperature (SST; light grey circles); c) Sea surface salinity (SSS, white circles); d) Chlorophyll-a concentration (chl a, dark grey circles); e) Seawater CO₂ fugacity (fCO₂, black circles) and atmospheric CO₂ fugacity (fCO₂ atm, continuous line).
The SSS distribution was nearly uniform for the three years (35.15±0.65) with some recurrent events of low SSS values during winter and spring (Table 1). A SSS minimum of 32.48 was measured in February 2004. Although high SSS values were also observed during summer (Fig. 2), the most saline waters were found in January 2002, with a value of 35.98.

Remote sensed measurements of chl \(a\) did not show a clear seasonal distribution (Fig. 2). High values of chl \(a\) reached an outstanding concentration in May 2004 (7.72 mg m\(^{-3}\), Fig. 2); similar values were mainly recorded across two pulses in spring and autumn, usually exceeding 2 mg m\(^{-3}\). Minimum values of chl \(a\) were observed in winter.

Several general features were shared by every seasonal \(\text{CO}_2\) cycle (Fig. 2). Surface waters of the continental shelf showed a general \(\text{CO}_2\) undersaturation in relation to the atmosphere. The minimum value was found in winter in 2003/2004 (~58±29 µatm), while \(\text{CO}_2\) supersaturation in relation to the atmosphere was found only occasionally in autumn and winter. Minimum values were observed during spring blooms, followed by a constant increase until autumn. The \(\text{CO}_2\) trend closely followed the warming of surface waters, even extending beyond the warmer months. The lowest \(\text{CO}_2\) value (200 µatm) was found in February 2004, and the highest value was reached at the end of November 2004, when it exceeded the atmospheric value by around 17 µatm (Fig. 2).

In spite of these similarities, some differences were found in the \(\text{CO}_2\) distribution in the seasonal cycles. During the seasonal cycle described by the DYBAGA cruises, \(\text{CO}_2\) increased by around 67 µatm, from 311 µatm in August 2001, to 377 µatm in February 2002 (Fig. 3). During this period, the seasonal cooling caused a decrease in the \(\text{CO}_2\) from 357 µatm in October 2001, to 299 µatm in March 2002. The thermal control, with a seasonal range of 58 µatm, was similar in magnitude to the non-thermal effect on \(\text{CO}_2\). However, they were approximately 6 months out of phase, which makes them partially cancel each other out. The effect of biological processes vs. thermal control in Galician shelf waters was estimated as the ratio between the seasonal range of \(\text{CO}_2\) and non-thermal \(\text{CO}_2\). A value of 0.87 indicates that over this period, the non-thermal effect exceeded the thermal effect in 16%. During the second seasonal cycle, biological utilization of \(\text{CO}_2\) and other non-thermal processes, shifted \(\text{CO}_2\) values by about 55 µatm from 351 µatm in January-March 2002 to 296 µatm in August 2003. On the other hand, the effect of winter-to-summer warming on \(\text{CO}_2\) is seen in the \(\text{CO}_2\) distribution as an increase of around 83 µatm, from 293 µatm in February 2003 to 381 µatm in August 2003. The comparison of the two processes showed a thermal/non-thermal ratio of 1.59, highlighting that the temperature control has a significant impact. During the last seasonal cycle sampled in ECO cruises, non-thermal \(\text{CO}_2\) values showed a decrease of about 67 µatm, ranging from 363 µatm in January 2004 to 296 µatm in June 2004. The temperature variability in the year 2004 took the \(\text{CO}_2\) distribution from about 292 µatm in January to 366 µatm in June, exceeding the non-thermal \(\text{CO}_2\) range by 12%. Taking into account the complete database, thermal processes throughout the three seasonal cycles were 16% stronger than non-thermal processes in the \(\text{CO}_2\) dynamics in shelf waters.
Sea-air CO₂ exchange

The measurements of CO₂ fluxes indicate that the shelf waters of the Galician coast were significant net sinks for atmospheric CO₂ in every seasonal cycle (Table 1, Fig. 4). The DYBAGA cruises showed minor annual absorption of $-0.78 \pm 0.62 \text{ mol C m}^{-2} \text{ yr}^{-1}$, estimated from a WS value of $4.9 \pm 1.7 \text{ m s}^{-1}$. The years 2003 and 2004 showed analogous annual CO₂ absorptions of $-1.38 \pm 1.14$ and $-1.44 \pm 1.22 \text{ mol C m}^{-2} \text{ yr}^{-1}$ respectively, from annual $\Delta f$CO₂ averages of $-45 \pm 27$ and $-47 \pm 23 \mu\text{atm}$ respectively, and similar wind speed (WS) values of $5.8 \pm 2.0 \text{ m s}^{-1}$. The highest seasonal absorption was estimated in winter 2003/2004 ($-3.48 \pm 2.31 \text{ mol C m}^{-2} \text{ yr}^{-1}$) in which a cruise on the continental shelf showed a maximum mean uptake of $-9.81 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Fig. 4), estimated from $\Delta f$CO₂ and WS values of $-60 \mu\text{atm}$ and $13.4 \text{ m s}^{-1}$ respectively. Coinciding with this observation, mean CO₂ absorption in winter was higher than in any other season ($-1.82 \pm 1.53 \text{ mol C m}^{-2} \text{ yr}^{-1}$). However, the DYBAGA cruises and the 2003 ECO seasonal cycle achieved the highest CO₂ uptakes during spring, namely $-1.20 \pm 0.81$ and $-2.47 \pm 1.50 \text{ mol C m}^{-2} \text{ yr}^{-1}$. Only during some autumn events did the Galician shelf behave as a marginal source of CO₂, showing a maximum CO₂ emission of $1.58 \text{ mol C m}^{-2} \text{ yr}^{-1}$ in September 2001 (Fig. 4). In any case, the smallest uptake capacity was found during autumn, reaching a mean value of $-0.56 \pm 0.68 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Table 1).

Biogeochemical control of $f$CO₂

A statistical analysis of the $\Delta f$CO₂ distribution during the DYBAGA and ECO cruises was carried out in order to identify the environmental forcing factors that drive the sea-air CO₂ disequilibrium, fitting the $\Delta f$CO₂ values according to Equation 7. The regression coefficients and the percentage of normalized $\Delta f$CO₂ variability explained by each parameter in the different seasons are given in Table 2.

In general terms, seasonal empirical algorithms fitted the observed $\Delta f$CO₂ variability during each sea-
son correctly. The ΔfCO2 winter measurements were weakly reproduced showing a standard error of 16.5 μatm and an explained ΔfCO2 variability of 64%. The main driver in this season was SST in its quadratic form, explaining 39% of the ΔfCO2 changes with a coefficient of −4.2±0.9 μatm °C⁻². The algorithm was completed with the contribution of quadratic chl a, depth and WS, explaining 19%, 3% and 3%, respectively.

The highest regression coefficient was found in spring (0.68), mainly due to the significant control of SSS changes (27%), which exceeded the contribution of quadratic chl a in this season by 12%. During this season, depth was also a significant factor: it was inversely proportional to ΔfCO2 values with a rate of −0.3±0.1 μatm m⁻¹, controlling 5% of the spring ΔfCO2 distribution, as well as Iw'.

The empirical algorithm fitting the summer ΔfCO2 observations reported a root mean square error of 8.3 μatm, the minimum of the four seasons. During this season, SST was again the main forcing factor, controlling 46% of the ΔfCO2 changes with its two forms, showing positive and negative coefficients of 18.2±4.4 μatm °C⁻¹ and −2.2±1.1 μatm °C⁻². Latitude and Iw' also played a significant role, explaining 9% and 4% of the ΔfCO2 variability; their coefficients showed a northward ΔfCO2 decrease and extended the inverse relationship between ΔfCO2 and upwelling events to the summer.

Even though the autumn season only explained 16% of the total ΔfCO2 variability, a low ΔfCO2 error of 15.3 μatm was also found. The only contribution of chl a and SST, which showed an inverse control, closely reproduced the ΔfCO2 measurements, explaining 17% and 4% of the total ΔfCO2 variability respectively.

DISCUSSION

After the examination of the underway measurements of SST, SSS, fCO2 and other ancillary variables (average upwelling index of the previous fortnight, Iw'), and remotely retrieved chl a, the Galician continental shelf could be described as a complex, heterogeneous and highly biogeochemical active region from May 2001 to December 2004. The high variability observed, both at short and seasonal scales, was related to meteorological conditions, the presence of different water bodies and changes in chl a estimations. Winter and summer showed the expected downwelling and upwelling conditions respectively, with seasonal Iw' values of −269 and 327 m³ km⁻¹ s⁻¹ respectively. On the contrary, every autumn season had wind conditions that showed noticeable seasonal changes (Fraga 1981, Blanton et al. 1984). Northerly winds were extended beyond the summer, so upwelling favorable conditions, with an average value of 67 m³ km⁻¹ s⁻¹, prevailed over the characteristic downwelling scenario of every autumn.

The winter dominance of southwesterly winds favored the coastal downwelling and the presence of subtropical waters transported by the IPC. The IPC was clearly sampled during winter 2001/2002, attending to the warm and saline water between November 2001 and February 2002. Very low levels of chl a and moderate undersaturation of CO2 were also found during this period of time, coinciding with more intense downwelling conditions (~770 m³ km⁻¹ s⁻¹; Fig. 2, Table 1). These offshore waters of subtropical origin made winter 2001/2002 the warmest and saltiest with Iw' 9°C2 and other ancillary variables (estimation made following Otero et al. 2010). Average discharge values estimated for winters 2002/2003 and 2003/2004 (1251.7±670.8 and 612.4±89.9 m³ s⁻¹ respectively) were notably higher than the value re-
ported for winter 2001/2002 (147.2±4.5 m³ s⁻¹; Fig. 3). In spite of showing the highest river discharge, the strong downwelling conditions found for winter 2002/2003 seemed to have retained freshwater in the near coast, preventing lower SSS values in the studied zone. This is because downwelling events, as well as the IPC, block the spreading of fresh shelf water and form a convergence front at the shelf-break (Pérez et al. 1999) between coastal and ocean waters (Castro et al. 1997, Borges and Frankignoulle 2002). Therefore, under less intense downwelling conditions, the lower river discharge of winter 2003/2004 was able to spread offshore, so that the SSS variability measured on the platform showed minimum values.

The influence of coastal waters under different downwelling situations also led to differences in the CO₂ uptake capacity, so that the sea-air CO₂ exchange responded to the continental influence. During winter 2001/2002, chl a values were lowest under the oligotrophic conditions prevailing in the subtropical IPC, in which shelf waters showed a ΔCO₂ of –24 µatm. On the contrary, low saline waters observed in winters 2002/2003 and 2003/2004 increased the stability of the water column on the continental shelf, triggering phytoplankton activity (Pérez et al. 1999) and causing a strong CO₂ undersaturation of –54 and –58 µatm respectively. In spite of not being the highest disequilibrium of the seasonal cycle, both winters showed an outstanding CO₂ uptake that reached the highest CO₂ absorption in winter 2003/2004, with a mean FCO₂ value of –3.48 mol C m⁻² yr⁻¹.

Reinforcing the importance of the biological CO₂ uptake in winter, chl a² explained 19% of the ΔCO₂ variability with a coefficient of –13 µatm (mg⁻¹ m⁻³)⁻² (Table 2). However, the statistical analysis did not show any relationship between low saline waters and CO₂ undersaturation in winter despite the process described above. Temperature control represented by SST² was the dominant factor explaining 39% of the winter ΔCO₂ variability with a negative coefficient of –4.2 µatm °C⁻². This correlation coincides with the one determined by Gago et al. (2003a), who found that only temperature accounts for a large percentage of the ΔCO₂ variability during the winter period.

For every seasonal cycle, ΔCO₂ reached the lowest values during the spring phytoplankton bloom (Pérez et al. 1999, Gago et al. 2003a). The lowest mean ΔCO₂ value of –76 µatm during spring 2003 coincided with moderate average chl a values (0.97 mg m⁻³) and strong downwelling favorable conditions (–464 m³ km⁻¹ s⁻¹). The maximum mean values of chl a (1.42 mg m⁻³) were observed during spring bloom 2004 under upwelling favorable conditions (218 m³ km⁻¹ s⁻¹). During this season, a high chl a observation of 7.72 mg m⁻³ was found across the continental shelf coinciding roughly with the lowest FCO₂ measurement of 245 µatm (Fig. 2; Table 1). Biological CO₂ uptake remained for some weeks (Taylor et al. 1992) after the disappearance of chl a, so that the FCO₂ increase related to upwelling events (Lampitt et al. 1995) was notably reduced.

SSS explained 27% of the spring ΔCO₂ variability (with a direct coefficient of 19 µatm), highlighting the balance between the intense CO₂ undersaturation resulting from freshwater inputs and the influence of upwelled waters. SST changes represented 20% of the ΔCO₂ variability, based on linear and quadratic coefficients that directly explained 9% and 11% respectively. The biological control represented by chl a² explained 15% of the ΔCO₂ variability with a coefficient of –1.7 µatm (mg⁻¹ m⁻³)⁻². fCO₂ showed a significant inverse correlation of –0.006 µatm m⁻³ km⁻¹ s⁻¹ with a minimum influence of 3% on the ΔCO₂ distribution. The entrance of CO₂-rich water from the subsurface seems to be represented by the direct control of SST² and SSS in the empirical algorithm. Colder and saltier waters represent the expected CO₂ supersaturation observed during upwelling events. Spring 2002 and 2004, with flux values of –1.20 and –1.90 mol C m⁻² yr⁻¹ respectively, showed the expected response to the upwelling favorable conditions during this season. The supersaturation of these waters led to lower uptake capacities, while maximum CO₂ uptakes of –2.47 mol C m⁻² yr⁻¹ were reached in spring 2003 under downwelling conditions.

According to the SST and SSS distributions, no upwelling filaments or recently upwelled waters off the Galician coast were sampled on the continental shelf. Consequently, ΔCO₂ summer values remained around –36 µatm. This season behaved as a moderate CO₂ sink of –0.82 mol C m⁻² yr⁻¹ (Table 1), coinciding with the results of Borges and Frankignoulle (2001). Values of chl a decreased after spring blooms, returning to the values observed in winter. However, unlike in winter, chl a did not show any role in the control of summer ΔCO₂, which was mainly explained by the SSS (46%). The estimated linear SST²/fCO₂ coefficient of 18.2 µatm °C⁻¹ slightly exceeded the theoretical temperature effect on ΔCO₂, which would be around 14 µatm °C⁻¹ for an average fCO₂ of around 330 µatm, based on the coefficient of 4.23 °C⁻¹ described by Takahashi et al. (1993). Latitude was also significant showing a growing CO₂ undersaturation northward with a rate of –98 µatm per latitudinal degree. According to the cruise tracks, latitude could represent the increasing distance from the coast, that is, the landward CO₂ saturation of surface waters observed in the proximal continental shelf during upwelling seasons.

Strong winds during late summer and early autumn broke the summer stratification and activated phytoplankton growth in September. In autumn, the upward input of nutrients through water mixing triggered chl a values, closely reaching those seen in spring but exceeding the percentage of variation explained (17% of the ΔCO₂ changes). A negative correlation coefficient between chl a and ΔCO₂ was also found (–8 µatm (mg m⁻³)⁻¹), coinciding with the results found by Pérez et al. (1999) for a region further south (40°41.7°N, and from coast to 11°W). SSS and SST values were also a
result of vertical mixing, and high SSS values, repeating those found in summer, were related to intense evaporation. These mixing processes seemed to weakly drive $\Delta f$CO$_2$ according to an inverse SST-$\Delta f$CO$_2$ correlation coefficient of $-3 \mu$atm °C$^{-1}$. Even though these features responded to normal autumn conditions, no features of the IPC were observed in distributions of SST, SSS or chl a; this signal was only found in winter 2001/2002 under the downwelling scenario. Unlike other seasons, atmospheric fCO$_2$ values were slightly exceeded in certain events during autumn, leading to the highest seasonal fCO$_2$ value of 344 µatm. This is probably due to degradation of organic matter, as stated by Gago et al. (2003a). In any case, these waters behaved as a CO$_2$ sink as well, with an average uptake of $-0.56$ mol C m$^{-2}$ yr$^{-1}$.

The ECO cruises analyzed for the area near the Bay of Biscay showed seawater fCO$_2$ ranges of 72 µatm estimated during 2003 and 2004 (Padin et al. 2009). The same ECO cruises analyzed in the present work showed annual seawater fCO$_2$ ranges of 126 and 185 µatm on the Galician shelf, reflecting the stronger impact of the changing drivers on seawater fCO$_2$ variability on the continental platform (SST, SSS, chl a, latitude, WS and I$_w$). The impact of these drivers should be taken into account at different scales, including those that respond to climate variability, especially in relation to warming, weakening of the upwelling (Pérez et al. 2010), river discharges and photosynthetic activity on the continental shelf.

The steady CO$_2$ undersaturation makes the Galician continental shelf a significant CO$_2$ sink in spite of the variability at different temporal scales. The largest variability in CO$_2$ uptake at a seasonal scale was measured during winter and spring, in which CO$_2$ uptake was determined by the downwelling/upwelling conditions, the strength of water runoff to the continental shelf and the development of a phytoplankton community. Annual CO$_2$ absorption values estimated from the years 2002 to 2004 ranged from $-0.78$ to $-1.44$ mol C m$^{-2}$ yr$^{-1}$, showing a lower uptake capacity than the $-2.2$ mol C m$^{-2}$ yr$^{-1}$ reported by Borges et al. (2005) for the same region. In the most recent estimations of sea-air CO$_2$ exchange in the global coastal ocean (Tsunogai et al. 1999, Chen and Borges 2009, Laruelle et al. 2010), this estimation of annual FCO$_2$ on the continental shelf of the Galician coast was averaged with other scarce observations, globally extrapolating them as a reference uptake of a temperate upwelling in the North Atlantic region. The success of such scaling approaches depends on how representative the FCO$_2$ estimations are for a given coastal environment. In this particular case, the annual FCO$_2$ measurements show large seasonal variability that could lead to estimates of the CO$_2$ uptake of the Galician continental shelf that are 65% lower than previous studies, which would affect the regional estimations. Long time-series of pCO$_2$ measurements evenly distributed on continental shelves would allow a more robust evaluation of CO$_2$ fluxes in continental shelf seas.

CONCLUSIONS

The Galician continental shelf showed a marked seasonality throughout the sampling period, with winters showing the lowest values of SST, SSS and chl a. However, strong inter-annual variability was found between the sampled winters, especially during winter 2001/2002, when the dominance of southwesterly winds favored coastal downwelling and the presence of subtropical waters conveyed northward on the continental shelf in the Iberian Poleward Current. The main variable explaining $\Delta f$CO$_2$ variability in winter was SST. In spring, chl a values were found to be a significant driver of the changes in $\Delta f$CO$_2$. Intense decreases in fCO$_2$ coincided with moderate average chl a values, showing an effective biological CO$_2$ uptake. Upwelling pulses of CO$_2$-rich waters minimized the effect of the spring bloom on fCO$_2$ distribution by shortening the time span of biological CO$_2$ uptake, even though no CO$_2$ oversaturation of surface waters was observed. Low SSS, fCO$_2$ and high chl a values were found for this season. In summer, northerly component winds prevailed, and so did upwelling favorable conditions. The main factor explaining fCO$_2$ variability in summer was SST. In autumn the strong winds caused the summer stratification to break down, activating the autumn phytoplankton bloom and increasing fCO$_2$ values until fCO$_2$ atm was exceeded in some events. In general, the Galician continental shelf behaved as a steady and significant CO$_2$ sink, in spite of the variability noted at different temporal scales. The largest variability was measured during winter and spring due to important changes in fresh water inputs reaching the region at an inter-annual scale. fCO$_2$ annual measurements showed lower values than those previously reported, showing an outstanding variability that could lead to the CO$_2$ uptake of the Galician continental shelf being underestimated by 65% at an annual scale. Long time-series of fCO$_2$ measurements would reduce the FCO$_2$ uncertainties and improve the use of scaling methods for studying the sea-air CO$_2$ exchange in the global coastal ocean.

ACKNOWLEDGEMENTS

We would like to especially thank the captains and crew of the BIO Mytilus, the RO-RO L'Audace and the RO-RO Surprise for their hospitality and essential help. We would also like to thank Dr. S. Piedracoba from the University of Vigo for her help and comments that helped us improve the first version of this paper. The authors also wish to thank the distributors of the chlorophyll-a concentration images (www.globecolour.info) and the NOAA-CIRES Climate Diagnostics Center, Boulder, Colorado (USA), from their web site at http://www.cdc.noaa.gov/ for providing us with the wind data. We would also like to thank the NOAA/ESRL Global Monitoring Division for providing the atmospheric CO$_2$ flask data. This study was sup-
ported through the EU FP7 project CARBOCHANGE “Changes in carbon uptake and emissions by oceans in a changing climate”, which received funding from the European Community’s Seventh Framework Programme under grant agreement n. 264879. The experimental work was funded by the Spanish research project DYBAGA (CICYT. MAR1999-1039) and the ECO project (MCyT REN2002-00503/MAR). Alba Marina Cobo-Viveros is a PhD student financed by the Spanish National Research Council (CSIC) through the JAE-Predoc grants from the program “Junta de Ampliación de Estudios”, and cofinanced by the FSE. We would like to thank the JAE-Predoc grants from the program “Junta de Andalucía” and the FSE. We would also co-finance by the FSE. We would like to thank the two anonymous reviewers for their helpful comments, which greatly improved the final version of this paper”.

REFERENCES


Received November 21, 2011. Accepted June 19, 2012. Published online January 7, 2013.