Short-term variations of the partial pressure of CO₂ in surface waters of the Galician upwelling system

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Abstract

The partial pressure of CO₂ (pCO₂) and dissolved oxygen saturation level (%O₂) were monitored continuously during a cruise in August 1998, which sampled surface waters off the Galician coast. Data are presented from two Lagrangian experiments carried out in an upwelling on the continental shelf and in the core of an offshore filament. The data show that daily variations in surface pCO₂ and oxygen (%O₂) were controlled by the diurnal cycle of primary production/respiration, temperature variations and air–sea exchange. Data obtained during various cross-shelf and cross-filament transects are also discussed and give an insight into the processes controlling large-scale variations of pCO₂ and %O₂ in the Galician upwelling system. These data suggest that upwelling filaments are an important feature of the inorganic carbon cycle of upwelling systems. However more field data in the various eastern boundary current systems worldwide are needed. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since Walsh, Rowe, Iverson and McRoy (1981) suggested that continental shelves and slopes could be significant sinks for atmospheric CO₂, several research programmes have been devoted to the study of cross-shelf exchange processes. These include, SEEP I and SEEP II in the Mid Atlantic Bight (Walsh, Biscay, & Csanady, 1988; Biscaye, Flagg, & Falkowski, 1994), ECOMARGE in the Gulf of Lions (Monaco, Biscaye, Soyer, Pocklington, & Heussner, 1990), KEEP in the East China Sea (Wong, Chao, Li, & Shiah, 2000), ECOFER and OMEX I in the Bay of Biscay (Monaco, Biscaye, & Laborde, 1999; Wollast & Chou, 2001). Wollast (1998) summarised the sediment trap results from some of these experiments and concluded that the export of sinking organic matter from the shelf to deep waters of the slope accounts for ≈ 10% of the primary production over the shelf break. Moreover, the preservation of organic matter in the slope sediments accounts for <1% of the shelf break primary production. Thus, the continental slopes studied so far have not proved to be major carbon depocenters, although the transfer of organic matter into the deep waters of the continental slope can be considered as a sink of CO₂ over a time scale of ~1000 years, i.e. the required time for the ventilation of the deep ocean (Wollast, 1993). Although marginal continental shelves are net exporters of organic carbon (see e.g. Gattuso, Frankignoulle, & Wollast, 1998), their role in the dissolved inorganic carbon cycle (in particular with respect to air–sea exchange of CO₂) is uncertain because it depends on the integration of a number of processes:

(a) Production, degradation and export of organic carbon,
(b) Production, dissolution and export of carbonates,
(c) Inputs of dissolved inorganic carbon by complex vertical mixing processes at the shelf edge, and
(d) Seawater temperature variations and water mass mixing.

An alternative to indirect budgeting calculations is the estimation of air–sea fluxes from direct measurements of the gradient of CO₂ across the air–sea interface, since these integrate all the relevant physical and biogeochemical processes. This approach has been applied in the East China Sea (Tsunogai, Watanabe, & Šato, 1999; Wang, Chen, Hong, & Chung, 2000) and the Bay of Biscay (Frankignoulle & Borges, 2001). In both these regions, the net annual integrated air–sea fluxes ranged from ~3 to ~8 mmol m⁻².d⁻¹, thus confirming that marginal continental shelves at mid-latitudes are significant sinks of atmospheric CO₂. However, estimation of large-scale spatial distribution of dissolved inorganic carbon in coastal seas is still needed before the air–sea flux of CO₂ can be integrated at a global scale. The proximal continental shelves that are directly influenced by terrestrial inputs are known to be net heterotrophic systems (Smith & Mackenzie, 1987; Smith & Hollibaugh, 1993; Gattuso et al., 1998) and are significant sources of atmospheric CO₂ based on direct measurements of the gradient of CO₂ across the air–sea interface (Kempe, 1982; Cai & Wang, 1998; Frankignoulle et al., 1998; Borges & Frankignoulle, 1999).

Investigation of the major processes that control spatio–temporal patterns of surface water pCO₂ is an important first step to develop models that can accurately describe dissolved inorganic carbon dynamics in these complex systems. Studies of short-term (daily to weekly) variations can give very useful information on physical and biological forcing of dissolved inorganic carbon dynamics as has been seen in

4. Conclusions

Acknowledgements

References
open ocean systems by Oudot and Andrie (1989); Chipman, Marra and Takahashi (1993); Robertson, Watson, Langdon, Ling and Wood (1993); Goyet and Peltzer (1997) and Bates, Takahashi, Chipman and Knap (1998). In coastal areas, dissolved inorganic carbon data from fixed stations have been successfully correlated to biological processes in areas of relatively low physical forcing, such as seagrass beds and coral reefs (Frankignoulle & Bouquegneau, 1990; Frankignoulle et al., 1996). However, in dynamic coastal areas, dissolved inorganic carbon data sets from fixed stations are difficult to interpret because of the influence of the various physical forcing processes (tidal or residual advection of different water masses, water mass mixing, etc.) on dissolved inorganic carbon dynamics are just as important as biological forcing and acts at the same time (Friederich, Brewer, Herlien, & Chavez, 1995; DeGrandpre, Hammar, Wallace, & Wirick, 1997; Bakker, de Baar, & de Wilde, 1996; DeGrandpre, Hammar, & Wirick, 1998; Borges & Frankignoulle, 1999). Lagrangian drift experiments permit focussing on biological forcing and minimise the influence of the physical forcing on dissolved inorganic carbon dynamics. Lagrangian studies of dissolved inorganic carbon have only been reported in open ocean systems: the northern North Atlantic (Robertson & Watson, 1993; Robertson et al., 1993) and the eastern Tropical Atlantic (Oudot & Andrie, 1989).

Coastal upwelling areas may be sites of intense transfer of organic carbon across the shelf edge. Indeed, these regions support a disproportionate fraction (11% of 7.2 GtC.year\(^{-1}\)) of new primary production in the global ocean in relation to their relative surface area (<1% of 360.10\(^6\) km\(^2\), Alongi, 1997). Also, in some areas such as the Galician coast, during upwelling events there is inhibition of the slope current, which restrains shelf/shelf break/open ocean exchanges (e.g. Huthnance, 1995; Pingree, Sinha, & Griffiths, 1999). Finally, in coastal upwelling regions such as the Galician coast, filaments of upwelled water are frequently observed advecting surface water, together with its enhanced content of organic carbon (both as dissolved and suspended particulate organic carbon), offshore from the continental shelf into the adjacent oceanic waters (Álvarez-Salgado et al., 2001 and references therein).

However, air–sea exchanges of CO\(_2\) in coastal upwelling systems are particularly complex because they are the result of processes that have antagonistic effects on the surface pCO\(_2\) values. Upwelling brings to the surface of the continental shelf deep water, which is over-saturated in CO\(_2\). Conversely, the high rates of primary production fuelled by higher nutrient concentrations in the upwelled water lowers pCO\(_2\) (Watson, 1995). In addition, the warming of upwelled water increases pCO\(_2\) values by modifying the chemical equilibria of the inorganic carbon system. The complexity of these interactions may contribute to the large range of values of surface water pCO\(_2\) that have been reported in some coastal upwelling areas (Simpson & Zirino, 1980; Simpson, 1984; Copin-Montégut & Raimbault, 1994; Copin-Montégut & Avril, 1995; Körtzinger, Duinker, & Mintrop, 1997; Boehme, Sabine, & Reimers, 1998; Goyet et al., 1998; Lefèvre, Moore, Aiken, Watson, & Cooper, 1998; Rutllant, Fuenzalida, Torres, & Figuerola, 1998; Bakker, de Baar, & de Jong, 1999; Pérez, Rios, & Róson, 1999; Torres, Turner, Silva, & Rutllant, 1999; Van Green et al., 2000). For instance, Simpson and Zirino (1980) report pCO\(_2\) values ranging from 140 to 980 µatm in the Peruvian upwelling area.

In this study, we report on the dissolved inorganic carbon data collected during two Lagrangian experiments and various cross-shelf and cross-filament transects, carried out at the Galician margin as a contribution to the understanding of air–sea exchange of CO\(_2\) dynamics in the framework of the OMEX II (Ocean Margin EXchange) project.

2. Material and methods

Data presented in this paper were obtained in August 1998, on board the RRS Charles Darwin (cruise CD114, 29 July–24 August). Underway parameters (pCO\(_2\), dissolved oxygen, salinity, water temperature and fluorescence) were sampled with a frequency of 1 min from the non-toxic seawater supply of the ship
(pump inlet at a depth of 2.5 m). A non-dispersive infrared gas analyser (Li-cor®, LI-6262) was used to measure pCO₂ in wet air equilibrated with seawater. The Li-cor® was calibrated daily using two gas standards of 0µatm (nitrogen, Air Liquide Belgium) and 360.5µatm (National Oceanic and Atmospheric Administration). The equilibrator consisted of a Plexiglas cylinder (height: 80cm, diameter: 10cm) filled with glass spheres (marbles) to increase the exchange surface area. Seawater ran (3 l.min⁻¹) from the top to the bottom of the equilibrator and air was pumped upwards (3 l.min⁻¹). The temperature at the outlet of the equilibrator was monitored using a platinum resistance thermometer (Metrohm®). The pCO₂ values were corrected for the temperature difference between in situ seawater and water in the equilibrator, using the algorithm proposed by Copin-Montégut (1988). The offset in temperature varied between 0.1° and 0.5°C. More details on equilibration technique and quality control can be found in Frankignoulle, Borges and Biondo (2001). A second Li-cor® was used to measure atmospheric pCO₂ sampled at the bow of the ship at a height of approximately 10m above the sea surface. Underway dissolved oxygen was measured using a galvanic electrode (Kent®) calibrated every 12 hours from discrete samples that were measured by the Winkler method using a potentiometric end-point determination. The concentration of O₂ at saturation was calculated using the algorithm proposed by Benson and Krause (1984). Two parameters that involve the observed concentration of dissolved O₂ (O₂obs) and the concentration of O₂ at saturation (O₂sat) were computed: O₂ saturation level (%O₂) = O₂obs/O₂sat *100 and Apparent Oxygen Utilisation (AOU) = O₂sat − O₂obs (in µmol.kg⁻¹). Salinity and in situ temperature were measured using a Falmouth Scientific Instruments® thermostalinograph. Underway fluorescence was measured with a Wet Star® (WS35-246) fluorometer.

Vertical profile data were obtained from samples collected by a 24 bottle rosette coupled to a SeaBird CTD. Total Alkalinity (TAlk) was determined using the classical Gran electro-titration method, on 100ml unfiltered samples. Total Alkalinity calculation was made with corrections for fluoride and sulphate according to Hansson and Jagner (1973). The reproducibility of TAlk measurements performed on board was 2µeq.kg⁻¹ (standard deviation from the difference of a set of 30 duplicate measurements during the cruise). Dissolved inorganic carbon (DIC) was computed from the measurements of underway pCO₂ and TAlk with the dissociation constants of carbonic acid from Roy et al. (1993), the borate molality obtained from the Culkin (1965) ratio to salinity and the dissociation constant of boric acid from Dickson (1990).

3. Results and discussion

3.1. Experimental setting

Fig. 1 shows the position of CTD stations and ship track during the two Lagrangian experiments carried out off the Galician coast in August 1998. A drifting buoy for in situ primary production incubations was used as a water mass marker. During the second Lagrangian experiment the behaviour of this drifting buoy was compared with mixed layer Argos drifters drogued at 15m depth. This showed that the drifting buoy from PML was an efficient water mass marker (Joint et al., 2001a; Barton, Inall, Sherwin, & Torres, 2001). The first Lagrangian experiment started over the continental shelf on 3 August (42.62°N, 9.40°W) and the drifter moved southwards until 7 August (42.07°N, 9.44°W) when the experiment ended. The second Lagrangian experiment started in the core of a recently developed upwelling filament (i.e. offshore extension of upwelled water) on 14 August (41.95°N, 9.83°W) and the drifter moved south-westwards until 18 August (41.80°N, 10.13°W) and then slowly turned inshore and crossed the southern boundary of the upwelling filament. The experiment ended on 19 August (41.76°N, 10.10°W). Details on the hydrodynamics during the two Lagrangian experiments and SST satellite images that describe the development and behaviour of the upwelling filament can be found respectively in Barton et al. (2001) and Smyth, Miller, Groom and Lavender (2001).
3.2. Cross-shelf transect

Fig. 2 shows the distribution of underway parameters along a cross-shelf transect carried out on 2 August 1998 along parallel 42.61°N (see Fig. 1, line A). Close to the coast (9.1°W), the distribution of temperature shows that pCO$_2$ and dissolved oxygen concentration (O$_2$) were at saturation as a result of the upwelling. From the coast to 9.3°W, significant CO$_2$ undersaturation was observed, probably as a result of biological activity since it was accompanied by an increase in the %O$_2$. Further confirmation comes from in situ fluorescence, which is an indicator of chlorophyll concentration. Unfortunately, signal drift of the fluorometer and the low frequency of chlorophyll sampling did not allow accurate calibration of the fluorometer. However, as shown in Fig. 2, fluorescence is a useful parameter in the interpretation of pCO$_2$ distribution, so the raw data are shown here, and in other figures, as relative fluorescence (no units). From 9.3°W to 9.6°W (shelf break), the pCO$_2$ was below the atmospheric value and relatively stable. The variations in salinity suggest that between the coast and 9.3°W, where significant variations of pCO$_2$ were observed,
Fig. 2. Distribution of underway parameters (seawater pCO$_2$ (µatm), atmospheric pCO$_2$ (µatm), dissolved oxygen saturation level (%), temperature (°C), salinity and relative fluorescence (no units)) along a cross-shelf transect, along parallel 42.61°N, carried out on 2 August. The dotted line indicates the position of deployment of the drifter for the first Lagrangian experiment in the upwelling. The position of transect A is shown in Fig. 1.

was being influenced by outflows from the Ría of Muros. Indeed, the outwelling from the Rías (i.e. outflow onto the shelf of water that has upwelled within the Rías and then has been mixed to a small extent with fresh water) has been described as an important influence in the chemistry and biology of the inner shelf of the Galician coast (e.g. Álvarez-Salgado, Doval, & Pérez, 1999, and references therein). In Fig. 2, the vertical dotted line indicates the deployment site of the drifter at the start of the first Lagrangian experiment.

3.3. First Lagrangian experiment in an upwelling over the continental shelf

Fig. 3 shows the evolution of underway parameters during the first Lagrangian experiment (see Fig. 1, line 1). The evolution of pCO$_2$ during the last two days shows high frequency variations that followed temperature changes. These variations result from the effect of temperature on equilibrium constants of dissolved inorganic carbon and, in particular, on the solubility coefficient of CO$_2$ (an increase in pCO$_2$ of ~4% for every °C increase in temperature). The high frequency temperature variations (up to 1.3°C in one minute) resulted from either vertical or horizontal gradients. During the last two days of the experiment, the wind speed decreased. As a result intense stratification developed in the upper layer, which contrasted with the vertical structure during the first two days, when temperature had been homogeneous throughout the mixed layer. The temperature gradient between ~1m and 10m depth was 0°C for the first CTD cast and 1.5°C for last CTD cast of the experiment (see also Fig. 7 of Joint et al., 2001a). The high frequency of the temperature and pCO$_2$ variations can be explained by the seawater supply inlet (at 2.5m depth) oscillating through a vertical gradient. During the first two days of the experiment, seawater temperature evolved in a periodic way that followed the signal of solar radiation and was a result of the daily cycle of heat exchange. In the open ocean, this phenomenon is the primary source of daily scale variations in pCO$_2$, through the effect of temperature on the CO$_2$ solubility coefficient; examples include Goyet and Peltzer (1997) in the equatorial Pacific Ocean and Bates et al. (1998) in the Sargasso Sea. To filter out

Fig. 3. Evolution of underway parameters (seawater pCO₂ (μatm) at in situ temperature, temperature (°C), seawater pCO₂ normalised to 17°C (μatm), dissolved oxygen saturation level (%), solar radiation (watts m⁻²), atmospheric pCO₂ (μatm), easterly wind speed component (m.s⁻¹)) during the first Lagrangian experiment (3 August, 0330 UT – 7 August, 1310 UT).

these effects of temperature, so that we could focus on the potential biological factors affecting pCO₂, we have computed pCO₂ values at an average temperature of 17°C. This approach has been widely used in the interpretation of pCO₂ data at daily scale (e.g. Oudot & André, 1989; Robertson et al., 1993; Yamashita, Fujiwara, Liu, & Ohtaki, 1993). The variation of pCO₂ (17°C) was smoother than the variation of pCO₂ at in situ temperature and throughout the experiment there was a general trend for pCO₂ to decrease. This decrease of pCO₂ (17°C) was correlated with an increase in the %O₂, suggesting a relationship with the net ecosystem production within the mixed layer. It is also apparent that both pCO₂ (17°C) and %O₂ showed a diel periodicity for the first two days and tended to stabilise during the last two days. The periodicity of the signal of pCO₂ (17°C) and %O₂ could be attributed to the daily cycle of photosynthesis/respiration since the maximum pCO₂ (17°C) was observed at dawn, and the minimum at
dusk. There was a time lag between the daily maximum of solar radiation and the daily maximum of %O₂; this could be attributed to net autotrophy lasting until dusk whereas community respiration dominated the signal at night. The absence of a periodical signal in pCO₂ (17°C) and %O₂ variations during the last two days of the experiment may have had two causes. Firstly, the decline in the nutrient concentrations in the upper water column and the shift of the maximum phytoplankton biomass from the surface to 30m (Joint et al., 2001a; Joint, Rees, & Woodward, 2001b). Secondly, as the upper water column became intensely stratified, the daily oscillation between net community primary production and respiration could still occurred but at the maximum of phytoplankton biomass, where it would not have affected pCO₂ and O₂ values in the upper water column.

On the basis of daily variations of pCO₂ during a Lagrangian experiment in the northern North Atlantic Ocean, Chipman et al. (1993) computed primary production rates that were consistent with ¹⁴C incorporation estimates. The requirement for such computations is that the mixed layer is relatively well defined and that it remains relatively constant throughout the experiment (see also Robertson et al., 1993). During the first Lagrangian experiment off the Galician coast, the mixed layer was only clearly defined during the first two days, although it shifted from about 20m to 45m in 24h. During the last three days of the experiment, the mixed layer was very shallow (<10m) as a result of intense surface stratification (see Fig. 7 of Joint et al., 2001a). Under such conditions, it is difficult to compare in a meaningful way, the temporal evolution of dissolved inorganic carbon with estimates of biological activity. However, such a comparison was possible for the second Lagrangian experiment.

Significant variations in atmospheric pCO₂ were observed (349–375 µatm) that closely followed the wind direction, showing that different air masses (offshore and continental origin) were sampled during the experiment. Higher atmospheric pCO₂ values were associated with winds with a strong easterly component (i.e. blowing from the continent) and lower values to winds with a strong westerly component. Various authors have shown that air masses with a continental origin consistently have a CO₂ content that is higher by ~30µatm, than that of offshore air masses (Friederich et al., 1995; Bakker et al., 1996; Körtzinger et al., 1996). These variations in atmospheric pCO₂ are larger than those reported between air masses from open oceanic regions (<10µatm, Oudot & Andrée, 1989; Bates et al., 1998).

What was the effect of air–sea exchange on the observed pCO₂ and O₂ variations? The CO₂ air–sea flux (F) can be computed from the air–sea gradient (∆pCO₂) and the gas exchange coefficient (K) using the equation F = α.K.∆pCO₂, where α is the solubility coefficient of CO₂. The value of the gas exchange coefficient is a function of various processes, such as wind speed, turbulence at the interface, air bubbles, surface films, etc. However, wind speed is recognised as the main forcing factor on the K value and several algorithms to derive K from wind speed have been proposed. In our calculations, we have applied the two most commonly used algorithms proposed by Liss and Merlivat (1986) and by Wanninkhof (1992). Air–sea flux of CO₂ directly affects DIC, and to compute this effect on pCO₂ we have used the homogeneous buffer factor β, defined by (∆pCO₂/pCO₂)*/(DIC/∆DIC), that relates a variation of DIC to a variation of pCO₂ and vice versa. The value of β is a function of the inorganic carbon species, which induce the DIC change and is about 10 for dissolved CO₂ (air–sea exchange).

We computed by iteration (1 minute time-step) for a range of wind speeds, the variation over one day of pCO₂ in the mixed layer caused by air–sea exchange. We used the following initial conditions: mixed layer 22m deep, salinity =35.7, temperature =15.5°C, dissolved pCO₂ =326 µatm, atmospheric pCO₂ =358µatm, β =10, DIC =2056 µmol.kg⁻¹ (calculated from a measured TAlk of 2342 µeq.kg⁻¹). We estimated using the Liss and Merlivat (1986) gas exchange coefficient, that there were increases in pCO₂ of 0.1, 0.3 and 0.7µatm per day for wind speeds of 5, 10 and 15m.s⁻¹ respectively. Using the Wanninkhof (1992) gas exchange coefficient, the estimated increases in pCO₂ were 0.1, 0.5 and 1.2µatm per day for wind speeds of 5, 10 and 15 m.s⁻¹ respectively. As expected, the effect on air–sea exchange is relatively small compared to the observed variations (~30µatm). O₂ air–sea flux was also calculated with the gas exchange coefficient from Liss and Merlivat (1986) by iteration using a 1 minute time step, for the two
extreme observed values: 252.6 and 263.8 µmol.kg\(^{-1}\) (respectively 103.5 and 112.3% of saturation at 15.5° and 17.7°C). Considering a mixed layer 22m deep and an initial \(\text{O}_2\) concentration of 252.6µmol.kg\(^{-1}\), we compute a decrease of 0.4, 1.4 and 2.7µmol.kg\(^{-1}\) (0.2, 0.6 and 1.1% of saturation) per day, for wind speeds of 5, 10 and 15 m s\(^{-1}\) respectively. For an initial \(\text{O}_2\) concentration of 263.8µmol.kg\(^{-1}\), the decrease of \(\text{O}_2\) concentration is 1.3, 5.1 and 9.5 µmol.kg\(^{-1}\) (0.6, 2.2 and 4.1% of saturation) per day for wind speeds of 5, 10 and 15 m.s\(^{-1}\). The decrease of %\(\text{O}_2\) related to air-sea exchange during the first Lagrangian experiment is estimated to be \(\sim 1\%\) of saturation per day since the highest wind speeds (5–15m.s\(^{-1}\)) coincided with the lower gradients of \(\text{O}_2\), whereas the lower wind speeds (~5 m.s\(^{-1}\)) coincided with the higher gradients of \(\text{O}_2\). These variations are relatively important compared to the observed variation of %\(\text{O}_2\) (~8%) but do not change our interpretation of the data, since the observed signal integrates both air–sea exchange and biological activity.

3.4. Second Lagrangian experiment in a upwelling filament

Fig. 4 shows the evolution of underway parameters during the second Lagrangian experiment in an offshore filament (Fig. 1, line 2). The stability of pCO\(_2\) (17°C) and \%\(\text{O}_2\) values throughout this experiment suggested biological activity was low in the surface layer. The surface layer was depleted in nutrients and phytoplanktonic biomass was about 4 times lower and primary production was 3 times lower than observed during the first Lagrangian experiment (Joint et al., 2001a,b). The phytoplankton biomass was throughout concentrated at the nutricline, which coincided with the thermocline (Álvarez-Salgado et al., 2001; Joint et al., 2001a,b). Heterotrophic activity was also lower during the second Lagrangian experiment; Barbosa et al. (2001) found bacterial production and growth rates were lower, although the bacterial biomass was similar. In addition, Fileman and Burkill (2001) found that both the biomass and the herbivory of heterotrophic microzooplankton were lower in the filament than during the upwelling experiment.

During the second Lagrangian experiment, the variations in atmospheric pCO\(_2\) were much smaller (349–357µatm) than in the first experiment, and the relationship with wind direction was not so clear; i.e. the effect of the continental air mass was smaller. This is to be expected since the second experiment was carried out further offshore.

3.4.1. Simulated evolution of pCO\(_2\) and \(\text{O}_2\)

To confirm that the evolution of pCO\(_2\) and \%\(\text{O}_2\) in surface waters was largely unrelated to biological activity, we computed by iteration (1 minute time step) the evolution of surface \%\(\text{O}_2\) and pCO\(_2\), taking into account only air–sea exchange and the evolution of temperature and mixed layer depth. The calculation was made from the start of the experiment until the evening station on 16 August (Julian day 231.6). The last station was excluded from the analysis because it exhibited characteristics of offshore water (warm, \(\text{O}_2\) and pCO\(_2\) closer to saturation) after the drifter had crossed the southern boundary of the upwelling filament. Initial values were 244.7µmol.kg\(^{-1}\) for \(\text{O}_2\), 333µatm for pCO\(_2\), at 16.96°C and a salinity of 35.73. Figure 5 shows the interpolated evolution of the mixed layer depth, wind speed and temperature. Computed \(\text{O}_2\), %\(\text{O}_2\) and pCO\(_2\) values show excellent agreement with the first 6 observed values (from Julian day 227.1 to 229.6). This suggests that, for this time span, the effect of biological activity on pCO\(_2\) and %\(\text{O}_2\) was insignificant. The variation of %\(\text{O}_2\) depended on temperature change and air–sea exchange. That the variation of pCO\(_2\) was mainly controlled by temperature is shown by the small difference between the calculated evolution of pCO\(_2\) taking into account air–sea exchange, and the calculated evolution based only on temperature change. The last four observations deviate from the calculated values and the trend suggests the influence of primary production (increase of %\(\text{O}_2\) and decrease of pCO\(_2\)).

However, we must determine if the increase of primary production was real or whether it resulted from a poor tracking of the water mass, for example if the drifter had progressively moved into another, more productive, water mass. As mentioned above, the drifter crossed the filament boundary and the steady
decrease of the mixed layer depth from Julian day 230.1 shows that the drifter had moved into the boundary of the filament. Indeed, Barton et al. (2001) show the deepening of the isotherms at the filament boundaries. The cross-filament transects discussed in Section 3.5 also show lower pCO₂ values and higher %O₂ values at the filament boundaries. We can assume that the deviation of calculated pCO₂ and %O₂ from observed values in the last two days of the second Lagrangian experiment were related to the progressive drift into a different water mass rather than a change of primary production rate within the water mass.

3.4.2. Coupling of the evolution of pCO₂ and biological activity

For the CTD stations where primary production and heterotrophic respiration were measured, the daily variation of pCO₂ from each biological process has been computed. Table 1 shows the rates obtained within
Fig. 5. Calculated seawater pCO₂ (µatm), dissolved oxygen concentration (µmol.kg⁻¹) and dissolved oxygen saturation (%) incorporating air–sea exchange, the evolution of the mixed layer depth (m) and temperature (°C) in the second Lagrangian experiment. Solid lines correspond to interpolated data in the case of mixed layer depth, temperature and wind speed (m.s⁻¹) and to calculated values in the case of seawater pCO₂, dissolved oxygen concentration and dissolved oxygen saturation level. Open and filled circles correspond to observations. CO₂ air–sea fluxes were calculated according Liss and Merlivat (1986), (labelled L&M) and Wanninkhof (1992), (labelled W). Evolution of seawater pCO₂ calculated from temperature alone is noted ‘temp’. Oxygen air–sea fluxes were calculated according to Liss and Merlivat (1986).

The input of DIC across the thermocline was computed using the vertical eddy diffusivity of 0.01cm².s⁻¹ reported for the core of the upwelling filament by Barton et al. (2001), the thickness the thermocline defined between 15° and 17°C (Barton et al., 2001), and a DIC value at 15°C of 2085 µmol.kg⁻¹ (based on vertical profile data, not shown).

Table 1 shows that, during the first three days of the second Lagrangian experiment, primary production induced, daily variations of pCO₂ in the mixed layer ranging between −1.4 and −0.8µatm.d⁻¹. If the data of Joint et al. (2001b) are considered to be representative of net primary production (gross primary pro-
Table 1
Biological rates (mmolC.m\(^{-2}\).d\(^{-1}\)) determined on water samples taken within the mixed layer at dawn in the offshore filament and daily variation of pCO\(_2\) (µatm.d\(^{-1}\)) in the mixed layer resulting from biological and physical processes (see text for details of computations)

<table>
<thead>
<tr>
<th>Julian day</th>
<th>Daily biological rates (mmolC.m(^{-2}).d(^{-1}))</th>
<th>Daily change of surface water pCO(_2) (µatm.d(^{-1}))</th>
<th>Air-sea exchange</th>
<th>Vertical eddy diffusion</th>
<th>Net</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Daily production</td>
<td>Bacterial respiration</td>
<td>Microplankton respiration</td>
<td>Macroplankton respiration</td>
<td>Primary production</td>
</tr>
<tr>
<td>227.1</td>
<td>26.2</td>
<td>6.2</td>
<td>8.1</td>
<td>0.6</td>
<td>−1.40</td>
</tr>
<tr>
<td>228.1</td>
<td>11.7</td>
<td>3.9</td>
<td>7.8</td>
<td>0.1</td>
<td>−0.96</td>
</tr>
<tr>
<td>229.1</td>
<td>17.9</td>
<td>7.1</td>
<td>9.2</td>
<td>0.5</td>
<td>−0.83</td>
</tr>
<tr>
<td>230.1</td>
<td>21.8</td>
<td>6.2</td>
<td>13.2</td>
<td>0.3</td>
<td>−1.14</td>
</tr>
</tbody>
</table>

\(^{a}\) Joint et al. (2001b).
\(^{b}\) Barbosa et al. (2001).
\(^{c}\) Fileman & Burkill (2001).
\(^{d}\) Halvorsen et al. (2001).
duction minus autotrophic respiration), then to obtain the net biological effect on the daily variation of pCO$_2$, we must account for total heterotrophic respiration. The largest contribution of heterotrophic respiration to the daily variation of pCO$_2$ within the mixed layer was from micro-zooplankton (range +0.6 to +0.4 µatm$\cdot$d$^{-1}$), followed by bacteria (+0.3 µatm$\cdot$d$^{-1}$), while the contribution from macro-zooplankton was one order of magnitude lower. Among the physical processes, only the input from air–sea exchange is significant in comparison with heterotrophic respiration. The net effect of both biological and physical processes on the daily variation of pCO$_2$ within the mixed layer varied from +0.1 to −0.4 µatm$\cdot$d$^{-1}$. These variations are one to two orders of magnitude lower than those from the effect of temperature on pCO$_2$ (10 µatm), that we computed in Section 3.4.1 (see Fig. 5), confirming our first interpretation that biological processes were not significantly affecting daily variations of pCO$_2$ during the second Lagrangian experiment.

We also computed the increase of primary production rate that would be needed to account for the difference of 3.4 µatm between simulated and observed pCO$_2$ values on Julian day 230.1 (see Fig. 5). This corresponds to a difference in DIC of 22 µmol.kg$^{-1}$ that can theoretically be accounted for by an increase of net primary production of about 72 mmolC.m$^{-2}$.$d^{-1}$ in a mixed layer of 32 m, assuming that total heterotrophic respiration remains constant. Table 1 shows that the observed increase of daily net primary production between Julian days 229.1 and 230.1 was one order of magnitude lower (about 4 mmolC.m$^{-2}$.$d^{-1}$), and that total heterotrophic respiration remained relatively constant. This confirms our first interpretation in Section 3.4.1 that the shift between observed and computed pCO$_2$ values was not related to major changes in biological activity but the result of the buoy’s drift into a water mass with a different pCO$_2$ signature (i.e. through the filament boundary).

Fig. 6 shows the plot of DIC normalised to a salinity of 35 (DIC$_{35}$) versus the Apparent Oxygen Utilisation (AOU) for the two Lagrangian experiments. Data from the first Lagrangian experiment are relatively well correlated considering the small range of variation; the slope of the regression line (0.78±0.18 SE), is in good agreement with the Redfield ratio of 0.77 (i.e. 138O$_2$:106CO$_2$). However, considering the extent

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Fig. 6. Plot of Dissolved Inorganic Carbon normalised to salinity 35 (DIC$_{35}$ – µmol.kg$^{-1}$) versus Apparent Oxygen Utilisation (AOU – µmol.kg$^{-1}$) for data obtained during the two Lagrangian experiments at the CTD stations where Total Alkalinity was sampled in subsurface water (−5 to −10 m depth). The straight line corresponds to the regression line of DIC$_{35}$ versus AOU for the first Lagrangian experiment: DIC$_{35} = 2031 (±4SE)+0.78 (±0.18SE)\times$AOU ($r^2=0.695, n=10$).
to which surface O₂ values were affected by air sea exchange we will not discuss the significance of this ratio. For the second Lagrangian experiment, data are not well correlated and the AOU values were closer to saturation for the lower range of DIC₃₅ than for the first experiment. This suggests that during the history of the water mass, air–sea exchange increased AOU values but had less influence on DIC₃₅. Also, the relatively low pCO₂ and DIC₃₅ values observed during the second Lagrangian experiment were a consequence of the history of the water mass and not of the relatively low primary production within the filament at the time of sampling.

This apparent paradox of low primary production associated with relatively important under-saturation of CO₂ is because air–sea exchange is a slow process compared to biological activity. Indeed, using the initial conditions of the second Lagrangian experiment, it would take about 26 and 41 months for mixed layer to come to atmospheric equilibrium using, respectively, the Wanninkhof (1992) and the Liss and Merlivat (1986) exchange coefficients. Biological activity can generate pCO₂ gradients on much shorter time scales.

3.5. Cross-filament transects

Fig. 7 shows the distribution of underway parameters along two sections across the upwelling filament (lines B and C in Fig. 1) and one section across another upwelling filament that developed further north at the end of the cruise (line D in Fig. 1). Salinity and temperature data show that transect B crossed the southern boundary of the filament. The saltier and warmer offshore water had pCO₂ and O₂ values closer to saturation than the cooler and less salty water of the filament. Close to the southern boundary (41.80°N), pCO₂ values decreased, probably as a result of biological activity, as shown by the increase of %O₂, this is confirmed by the changes in relative fluorescence. Transect C crossed both the southern and northern boundaries of the filament, and increases of %O₂ and fluorescence and a decrease of pCO₂, were observed close to the northern boundary of the filament (41.95° to 42.00°N). In the second upwelling filament
sampled along transect D, the patterns in pCO₂ and %O₂ distribution are similar to the filament described above. The offshore warmer and saltier waters showed pCO₂ and O₂ values closer to saturation, and there was a contrast in pCO₂ and %O₂ distributions between the filament’s boundary and its core.

Barton et al. (2001) show intensification of the flow at the filament boundaries (10 to 30cm.s⁻¹) as opposed to the weak flow (<5cm.s⁻¹) observed at the core of the filament. This suggests that the differences in pCO₂ and %O₂ distributions between the filament core and boundary were related to the age of the water mass. The boundary flow was bringing water that had been upwelled more recently and was thus biologically more active than the older water in the slow moving filament core. Barton et al. (2001) also show there was an increase in the turbulence and a deepening of the isotherms at the filament boundaries. This was probably advecting nutrients to the filament boundary which was stimulating primary production and contributing to the lowering of pCO₂ values.

3.6. Air–sea exchange of CO₂

Fig. 8 shows computed air–sea fluxes of CO₂ for the two Lagrangian experiments and the four transects. The magnitude of the air–sea fluxes are quite different depending on the gas exchange coefficient used, and the differences increased with wind speed. For instance, for transect B, sampled at a time of low wind speed, the largest difference between the flux calculated according to Liss and Merlivat (1986) and Wanninkhof (1992) is ~0.1mmol.m⁻².d⁻¹; for transect D (high wind speeds), the difference is ~10mmol.m⁻².d⁻¹ — an increase of ~100%. The sign of air–sea flux is imposed by the air–sea gradient of pCO₂, but the amplitude largely depends on wind speed. This is clear if we compare transects B and C that show air–sea gradients of pCO₂ of the same other of magnitude; however, for transect C the computed flux is 760% higher because wind speeds were ~5 times higher. When the air–sea gradient of pCO₂ is relatively stable and wind speed highly variable, the variations in fluxes mainly follow the wind speed variations as in the case of these two Lagrangian experiments. Only when almost constant wind speeds are observed, for instance during transects A, C and D, does the flux follow the air–sea gradient of pCO₂. For the first Lagrangian experiment, we recomputed the air–sea flux with an average atmospheric pCO₂ (358 μatm) and leaving all other parameters unchanged, and then compared it with data computed with the observed variation in atmospheric pCO₂. The largest difference between the two computations is ~1 mmol m⁻¹ day⁻¹ using the Liss and Merlivat (1986) algorithm and ~2 mmol m⁻¹ day⁻¹ using the Wanninkhof (1992) algorithm. These differences are relatively important compared to the range of variation of the computed flux and emphasise the need to measure both seawater and atmospheric pCO₂ in coastal areas.

From the above considerations, it is clear that the air–sea fluxes computed from immediate wind speed measurements are not representative of net CO₂ air–sea exchange within upwelling filaments during the upwelling season. Indeed, the wind speed field is highly variable on the time scale of a week while the pCO₂ field can remain fairly stable. This is illustrated by the second Lagrangian experiment, when relatively small variations of pCO₂ were related to the presence of different water masses rather than to variations of biological activity. We have also computed air–sea fluxes of CO₂ for the entire inorganic carbon data set obtained in the area over a 3 year period during OMEX II. The full results will be published later. But to summarise briefly, air–sea fluxes were calculated from 3 hourly wind speed averages observed during the duration of each cruise (~10 days). This integrative approach depends on a series of assumptions, but most probably gives more representative CO₂ air–sea exchange values than those computed from immediate wind speed measurements. Upwelling filaments were also sampled during two other cruises in June/July 1998 and September 1999. The integrated pCO₂ air–sea gradient within the various observed upwelling filaments varied between −15 and −28μatm. The integrated CO₂ air–sea fluxes within upwelling filaments for each of the three cruises were always negative ranging between −0.4 and −4.5mmol.m⁻².d⁻¹ using the Liss and Merlivat (1986) exchange coefficient, and between −0.8 and −9.0 mmol.m⁻².d⁻¹ using the Wanninkhof (1992) exchange coefficient. The CO₂ air–sea fluxes within the filaments in comparison with
Fig. 8. Calculated CO₂ air–sea fluxes (mmol.m⁻².d⁻¹) according to Liss and Merlivat (1986) and Wanninkhof (1992), labelled L& M and W, wind speed (m.s⁻¹) and air–sea gradient of pCO₂ (µatm) for the two Lagrangian experiments and the four cross-shelf and cross-filament transects.

Offshore waters were systematically stronger, between 38 and 66% depending on the cruise and for both exchange coefficients. For the data obtained over the continental shelf at the end of the August 1998 cruise (data not shown), we computed the region was acting as a net sink for atmospheric CO₂ (−1.8 and −3.2mmol.m⁻².d⁻¹ respectively for the Liss and Merlivat (1986) and the Wanninkhof (1992) formulations of the CO₂ exchange coefficient). This was also the case during the other OMEX II cruises carried out in the area (July 1997, July 1998 and September 1999—Borges and Frankignoulle, 2001) and thus contradicts the belief that all coastal upwelling areas act as sources of atmospheric CO₂ by analogy to equatorial upwelling areas.

4. Conclusions

For the period and area sampled, daily variations of surface pCO₂ and %O₂ in these Lagrangian experiments, were smaller than the larger scale variations in the cross-shelf and cross-filament transects. The large-scale variations were related to differences in water masses (offshore/coastal), physical processes (upwelling and outwelling from the Rías) and net primary production. The daily variations of surface pCO₂ and %O₂ depended on the daily cycle of primary production and respiration in recently upwelled water where the maximum of phytoplankton biomass was located in the upper water layer. During periods of intense stratification, the pCO₂ signal was strongly modulated by temperature variations; it was not possible to relate pCO₂ and %O₂ variations to primary production because the upper surface waters were isolated by stratification from the maximum of phytoplankton biomass. In aged water masses (i.e. a nutrient depleted mixed layer), the relatively small daily variations of surface %O₂ were exclusively related to temperature variations and air–sea exchange, while surface pCO₂ was mainly controlled by temperature alone. Our data also suggest that the observed CO₂ undersaturation in the core of the upwelling filament was a historical water mass signal and was not related to the contemporary net primary production in the filament itself. The water at the filament boundaries, however, seemed to be more biologically active than the water in the filament core. Undersaturation of CO₂, associated with large CO₂ invasion, was observed in both the filaments sampled. Integrated air–sea CO₂ fluxes in upwelling filaments off the Galician coast based on the present cruise and other two cruises, ranged between −0.4 and −9.0mmol.m⁻².d⁻¹ depending on the cruise and the exchange coefficient used in the computations. Thus, in spite of the fact that upwelling filaments off the Galician coast seem to be oligotrophic and relatively unproductive systems, they act as a net sink for atmospheric CO₂ that is stronger than in the surrounding offshore waters. We feel that these data cannot be extrapolated to filaments worldwide because of the high variability of pCO₂ values reported in the literature for various upwelling systems. However, in all eastern boundary current regions worldwide, filaments persist for long periods and extend over very large areas (several hundreds of kilometres by tens of kilometres wide). More dissolved inorganic carbon field data are needed to estimate the potential importance of these structures in the carbon cycle of upwelling systems.

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