SEA SURFACE CARBON DIOXIDE OFF IBERIAN PENINSULA (EAST NORTH ATLANTIC OCEAN)

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Abstract

The variability of the carbon dioxide in the eastern North Atlantic Ocean was investigated by studying three seasons with different hydrographical and meteorological conditions that lead to two main different situations: upwelling and downwelling. No correlation between surface pCO₂ and chlorophyll was found in spring, although significant correlation was found in autumn when strong downwelling was the observed. The convergence developed over the slope produce different regimes of stability of the water column on the shelf creating areas of high and low pCO₂ levels. A positive correlation ($r^2=0.50$; $n=33$) between surface pCO₂ and chlorophyll points out during the upwelling season. High pCO₂ is found when the greatest concentration of chlorophyll exists. The uptake of carbon by photosynthetic activity masks the increase of dissolved inorganic carbon concentrations in surface due to the upwelling event. Without this biological effect the increase of pCO₂ during the upwelling will be even higher. Air-sea fluxes of CO₂ were calculated for the three studied seasons. The average CO₂ flux from the atmosphere to the ocean ($0.47 \text{ mmol m}^{-2} \cdot \text{d}^{-1}$) in the eastern margin of North Atlantic was slightly lower than those given in previous studies in the North Atlantic ocean because of the influence of upwelling.

1. Introduction

It is well established that the surface current regime and the upwelling-downwelling pattern in the eastern boundary off Iberian Peninsula is marked by a strong seasonality (Wooster et al., 1976; Fraga, 1981; McClain et al., 1986; Frouin et al., 1990; Pingree and Le Cann, 1990, Bakun and Nelson, 1991; Haynes et al., 1993). This has been attributed to the marked seasonal changes in wind stress along the North Africa and Iberian coasts which is related to the long term climatology of the North-eastern Atlantic. During the summer, when the Azores high is located in the Central Atlantic and the Greenland low has diminished in intensity, the pressure gradient forces the air to flow southward along the Iberian coast. This wind pattern induces coastal upwelling. In summer, the Iberian coastal transition zone results in a region of active upwelling features, such as cool filaments. Haynes et al. (1993) examined the development, persistence and variability of upwelling filaments off the Atlantic coast of the Iberian

Peninsula. Although the upwelling season encompasses the period from May until late September or early October, the major filament structures begin to form in late July or August. These filaments reach the maximum length (200-250 km) in September, and "disappear" in late October. In winter, the Azores high pressure is located off the north-western African coast and a deep low is situated off the south-eastern coast of Greenland (Blanton et al., 1984). The pressure gradient between the two pressure systems, results in an onshore wind with a component of wind stress northward off Iberian peninsula forcing coastal downwelling. The winter circulation pattern is dominated by a surface poleward flow of warm water. Satellite images demonstrate winter (October-March) inflow along the Iberian slope. Evidence of warm and salty surface current flowing poleward has been described as far south as Cape St. Vicente (37 °N) (Frouin et al. 1990, Haynes and Barton, 1990), and penetrating as north as the Armorican shelf (Pingree and Le Cann, 1990), being clearly constrained by topography. This poleward flow is a relatively low-energy phenomenon with surface currents of 0.1-0.2cm-s⁻¹.

On the other hand, the role of the oceans as a source or sinking of CO₂ is a topical issue (Takahashi, 1989). Many studies were performed in the North Atlantic, in order to know the amount of anthropogenic CO₂ sequestered in the polar and subpolar regions (Brewer, 1978; Roos and Gravenhorst, 1984; Takahashi, 1989, Murphy et al., 1991, Poisson et al. 1993; Bellerby et al., 1993; Takahashi et al., 1993; Robertson and Watson, 1995), and to examine if the tropical oceans and strong upwelling regions are source zones of CO₂ (Andri et al., 1986; Oudot et al., 1987; Anderson et al., 1990; Garon et al., 1989; Murphy et al., 1991). However, there is a limited knowledge in eastern boundary regions with seasonal changes of dynamics and circulation. The alternate regimes of upwelling-downwelling off the Iberian peninsula, together with the fall-winter warm current over the shelf-break, results in to differentiate situations with very variable net fluxes of CO₂. So, it is difficult to establish, as a first approximation, the role of this region in the air-sea CO₂ exchange.

The aims of this paper are 1) to describe the variability of pCO₂ caused by upwelling and subtropical poleward current in the eastern boundary of North Atlantic Ocean and 2) to estimate the amount of CO₂ exchange in the shelf and open sea under the main two situations: upwelling and downwelling.

2. Methods

2.1. Observational measurements

The observations reported in this work were carried out in three MORENA cruises as part of the shelf-ocean MAST II program. The MORENA I cruise was performed on board R/V "Cornide de Saavedra" between 10 and 26 May 1993. Ninety-two stations were studied between 40°N to 43°N and the coast to 11°W along 13 latitudinal sections (Fig. 1a). A similar track was performed during the MORENA II on board of R/V "Hakon Mosby" between 16 November and 2 December 1993. Seventy

stations were surveyed between 40°N to 41.7°N and the coast to 11°W, along 8 latitudinal sections (Fig. 1b). The MORENA III cruise was also performed on board of R/V “Håkon Mosby” between 26 July and 8 August 1994. Thirty-five stations were visited between 40.8°N to 42.5°N and the coast to 11°W, in two latitudinal and one meridional sections following the filaments detected by satellite images during the cruise (Fig. 1c). Temperature and salinity in the surface underway were measured by the Seabird thermosalinograph. The wind was measured on board for mean meteorology located in the main mast about 10 m above the sea level.

At each station, temperature, salinity and pressure were measured with a Mark III Neil-Brown CTD. Samples from Niskin bottles, at standard levels in the 200 upper meters, were taken to measure salinity, alkalinity, nutrients, pH and chlorophyll.

Nutrients were determined by colorimetric methods, using a Technicon autoanalyser. Nitrate was determined after reduction to nitrite in a Cd-Cu column (Mouriño and Fraga, 1985). The standard deviation for duplication was $0.06 \mu\text{mol.Kg}^{-1}$ for nitrate, 0.5% full scale reproducibility.

A Metrohm E-654 pH-meter equipped with a Ross (Orion 81-04) combined glass electrode was used to determine pH. The temperature of the samples was measured using a platinum resistance thermometer to correct for the effect of temperature on pH (Pérez and Fraga, 1987a). All the pH values were corrected to a standard temperature of 15°C (pH_{15}). The method has a shipboard precision of $\pm 0.002 \text{ pH}_{15}$ based on 184 replicate analysis corresponding to two different oceanographic bottles fired at the same depth at each station (Ríos and Rosón, 1996). The accuracy of $\pm 0.004 \text{ pH}_{15}$ has been estimated using samples of Certified Reference Material (CRMs) provided by Dr. Dickson of University of California (Ríos and Pérez, submitted; Ríos and Rellán, in press).

Alkalinity was determined by automatic potentiometric titration with HCl at a final pH of 4.44 (Pérez and Fraga, 1987b). The electrodes were standardised using an NBS buffer of pH 7.413 at 25°C and checked using an NBS buffer of 4.008. This method of determining alkalinity has a precision of 0.1% (Pérez and Fraga, 1987b), and the accuracy of $1.4 \mu\text{mol.kg}^{-1}$ was estimated from cross-calculation with measured CRMs (Ríos and Pérez, submitted; Ríos and Rellán, in press). The partial pressure of CO_2 (pCO_2) was estimated from pH_{15} and alkalinity using the thermodynamic equations of the carbonate system (Dickson, 1981) and the constants determined by Mehrbach et al. (1973) and Weiss (1974) with an accuracy of 5 μatm (Millero, 1995, Lee et al., 1997). We have preferred to use the Mehrbach' constants than those recently determined because the temperature effect on pCO_2 obtained through the Merhbach' constants are more consistent with the experimental values than the modern ones (Millero et al, 1994, Lee et al., 1997). In order to verify this procedure, a comparative experiments was performed between 3 January and 27 March 1994 in the South Atlantic where pCO_2 was determined directly and calculated from pH_{15} and alkalinity using the above procedure

(Chipman, 1996; Ríos and Rosón, 1996). The results were very similar with an average and standard deviation of $1 \pm 7 \mu\text{atm}$ (Ríos et al., in press).

Chlorophyll was measured by fluorescence using a Turner Design 1000 R fluorometer (Falkowski and Kiefer, 1985). For calibration, 100 ml of water was filtered through Whatman GF/F filters and chlorophyll extracted with 90% acetone.

2.2. Algorithm for air-sea Exchange of CO_2

The exchange of carbon between the atmosphere and ocean, F ($\text{mmol m}^{-2} \text{d}^{-1}$), can be calculated using the following equation:

$$F = 0.24kS(p\text{CO}_{2\text{ sea}} - p\text{CO}_{2\text{ air}}) \quad (1)$$

where k (cm h^{-1}) is the exchange coefficient or "piston velocity", S ($\text{mol l}^{-1} \text{atm}^{-1}$) is the solubility of CO_2 in seawater, $p\text{CO}_{2\text{ sea}}$ is $p\text{CO}_2$ in the sea surface, and $p\text{CO}_{2\text{ air}}$ is the partial pressure of CO_2 in air (both in μatm). The factor 0.24 converts between units. The seasonal and inter-annual variations in the atmospheric $p\text{CO}_2$ are small when compared to $p\text{CO}_2$ variations in the surface ocean (Andrié et al., 1986). We therefore assumed for each cruise a constant atmospheric CO_2 partial pressure (354, 355 and 356 ppm for MORENA I, II and III respectively) according to Keeling et al. (1995).

The impact of wind speed on the exchange coefficient, k , was taken into account using the equations given by Woolf and Thorpe (1991):

$$k = 0.17U_{10}(600/Sc)^{2/3} \quad U_{10} < U_1: \text{smooth water regime} \quad (2)$$

$$k = (2.85U_{10} - 9.65)(600/Sc)^{1/2} \quad U_{10} > U_1: \text{rough water regime} \quad (3)$$

$$U_1 = 9.65 [2.85 - 0.17(600/Sc)^{1/6}]^{-1} \quad (4)$$

where Sc is Schmidt number, and U_{10} is the wind speed 10 m above the ocean surface (m s^{-1}). We obtain $U_1 = 3.6 \text{ m s}^{-1}$ for our temperature range (14° to 20°C). Ríos et al (1995) have derived the following equation:

$$\text{Ln}(600/Sc) = -1.0687 + 0.05127 \cdot t \text{ (}^\circ\text{C)} \quad r^2 = 0.995 \quad (5)$$

which relate Schmidt number to temperature, using data tabulated by Andrié et al. (1986: table 1).

3. Results

3.1. Wind regime and thermohaline field

The wind regime in the three MORENA cruises was very different. During MORENA I cruise, the dominant wind was south-westerly reaching velocities higher than 15 m.s^{-1} (Fig. 2a) with an average of 6.3 m.s^{-1} . The strongest winds were southerly, while the weak winds were mainly westerly or south-westerly. The average south and westerly components were 1.6 and 2.7 m.s^{-1} respectively. The wind regime was certainly

anomalous taking account that generally the prevailing wind is northerly from April to September.

During the second cruise (November 1993), the wind regime was similar to the first one (Fig. 2b). The recorded maximum velocity of wind was 15 m.s^{-1} , and the average 7.0 m.s^{-1} . The dominant component was southerly except for two short periods with strong northerly winds. In MORENA II, the average south component was 0.34 m.s^{-1} while the east component was null. Also, there seems to exist an irregular alternation of northeasterlies with southwesterlies, which reach the maximum strength at the end of November.

During the MORENA III cruise, the meteorological conditions were the expected for the summer period (Fig. 2c). The northerly wind component was dominant with an average of 1.6 m.s^{-1} , while the average of the westerly component was 1.4 m.s^{-1} . The recorded maximum wind (17 m.s^{-1}) occurred on 28 July during periods of strong northerly winds. Another maximum wind, recorded the 5 August, shows an upwelling alternation of 7 or 8 days. This period is shorter than the two weeks of upwelling oscillation reported by several authors in this area (Fiúza, 1984, Alvarez-Salgado et al., 1993).

The sea surface temperature (SST) recorded in MORENA I and II cruises (Fig. 3a,b) shows a similar pattern in the offshore region. Whereas in MORENA III cruise (Fig. 3c), the cold waters of the coastal upwelling were evident. In the two first cruises the minimum temperature was located in the north-west corner of the study area, implying the advection of northern water. During MORENA I the highest SST was found near the coast spreading off the shelf along 42°N , and suggesting a later spreading to the north along 10°W . The southern part of the area shows very small changes in SST. The poleward current is not very evident here from the SST distribution. Conversely, in the MORENA II cruise there is another SST minimum close to the coast produced by atmospheric cooling and vertical mixing. The highest SST seems to correspond to warm poleward current which usually arises in fall and early winter (Pingree and Le Cann, 1990, Frouin et al. 1990). The typical summer pattern of SST recorded during MORENA III cruise (FIG. 3c), shows a coastal upwelling with SST lower than 15°C close to coast and higher than 19°C in open ocean. Although there is a north-south thermal gradient in the open sea, it is possible to observe two minimum of SST which spreads along 41.8°N and along 41°N , associated to cold filaments of upwelled water (Budgell and Johannessen, 1995). These filaments were also observed from thermal satellite images (Fig. 3c). The skin temperature given by satellite is clearly higher than the observed SST.

The sea surface salinity (SSS) measured in the two first cruises also shows several resemblance (Fig. 4). However, the last cruise shows values of SSS slightly lower. In MORENA I and MORENA II cruises there was a minimum of salinity in the north-west corner of the sampled area. This is a clear signal of the advection of cold and less saline water outcropped in the north (Harvey, 1982, Ríos et al. 1992). The coastal water seems to be confined by the saline poleward current along 10°W in both cruises.

Especially, in the MORENA I (Fig. 4a) the maximum of salinity is higher in the south-west corner and also at 41.3°N 11°W. This saline water seems to extend to the north generating a divergence front at the 43°N 11°W with the cold and less saline water coming from the north. The accumulation of coastal water with low salinity is higher in MORENA II than MORENA I, generating a strong zonal gradient with the saline water which reached the highest values of the three cruises. The zonal maximum of salinity shows clearly the poleward which produces two fronts (42°N 10.5°W and 40°N, 11°N) with the low saline water coming from to the north. During MORENA III (Fig. 4c) the coastal zone shows low SST and SSS suggesting the strong mixing of runoff with upwelled ENACW (Eastern North Atlantic Central Water). In the open ocean the high SSS values were recorded in the south being around 0.2 lower than those measured in the other two cruises at the same latitude.

The T-S distribution of all sea surface samples allow us to distinguish clearly the different clusters of the three cruises (Fig. 5). In May, the T-S points (small dots) are included in a triangle formed by the segment of ENACW (Fiúza, 1984; Ríos et al. 1992) and the point (16.5°C and 35.3). In summer (black points), the sea surface thermohaline properties were quite different to the ENACW, mainly due to the summer heating and runoff. In fall, the T-S points (open circles) were located around 15°C, between the salinity maximum of ENACW with temperatures close to 16°C and the coastal waters with low salinity and temperature slightly lower than 15°C.

Summarising, the meteorological and thermohaline conditions in MORENA I and II cruises were similar, although in fall the poleward current seems to be stronger than spring (Fig. 4). The coastal waters were limited by a front over the shelf because of the downwelling, distinguishing in the open sea, a divergence front between the poleward current and the cold and less saline water coming from the north. The MORENA III cruise shows a clear condition of coastal upwelling driven by northerly winds with the presence two filaments (Fig. 3) which favour the shelf-ocean exchange. This upwelling did not record any ENACW in surface.

3.2. Chemical field

The surface nitrate concentrations were very low in the whole area (Fig. 6). Other nutrients (phosphate, ammonium and silicate) were also determined, but not shown here because their surface concentrations display similar distributions. Only some regions of divergence fronts or coastal upwelling are able to maintain significant concentrations of nitrate in surface. During the spring (MORENA I), only at the western side of the sampling area, nitrate concentrations higher than $0.5 \mu\text{mol.kg}^{-1}$ were measured which are associated to the spreading waters of northern origin. At the southern side, during small events of northerly winds (20 and 21st May), significant nitrate concentrations higher than $0.5 \mu\text{mol.kg}^{-1}$ were recorded. The coastal waters does not show significant levels of nitrate although the salinity decrease traces the influence of continental waters (Fig. 6a).

In autumn (MORENA II), the pattern of nitrate concentrations in surface is rather similar to the recorded in May, excluding the coastal domain where the low saline waters contribute to increase the nitrate levels by vertical mixing with regenerated subsurface water and by runoff (Fig. 6b). A minimum of nitrate can be observed along the slope associated to the salinity maximum which traces the poleward current. The salinity minimum at 41.2° were matched with a low levels of nitrate while the maximum of nitrate about 5 $\mu\text{mol}\cdot\text{kg}^{-1}$ were recorded in coastal water with rather similar low salinity at 40°N. The significant levels of nitrate recorded in the oceanic surface waters in the northern part are associated to the northerly low saline waters as was already described in the MORENA I cruise. In summer cruise (Fig. 6c), the oceanic nitrate levels were practically depleted ($<0.2 \mu\text{mol}\cdot\text{kg}^{-1}$) including the filament of coastal water. Only in the innermost part of the shelf were very significant concentrations of nitrate (about 5 $\mu\text{mol}\cdot\text{kg}^{-1}$) recorded due to the cold and low saline water generated by the mixing of upwelled ENACW and runoff.

The pattern of surface chlorophyll (Fig. 7) resembles the thermohaline distributions. In May several surface maximum in open-sea were linked to the thermohaline front described in the north-western side where the surface nitrate maximum were recorded (Fig. 7a). The rest of the oceanic water dominated by warm and saline water contains very low chlorophyll concentrations. Also, the coastal water confined to the coast by this saline current have low chlorophyll levels. The southern maximum of chlorophyll seems to be associated to the nitrate maximum. During late autumn (Fig. 7b) in the coastal zone, the chlorophyll maximum was located close to the minimum of nitrate and vice versa, as expected. In the open sea the low levels of chlorophyll were the general pattern although it is possible to draw the line of chlorophyll minimum following the saline maximum which traces the poleward current. The relative maximum of chlorophyll in oceanic waters is coincident with the relative maximum of nitrate which is associated with the cold and low saline water. During the upwelling season (Fig. 7c) the surface chlorophyll maximum was located in the coastal zone where the nitrate maximum was also recorded. The correlation between surface nitrate and chlorophyll is high and positive ($r^2=0.76$; $n=33$; $p<0.00000$). In surface oceanic waters the chlorophyll levels were very low.

The surface distribution of pCO_2 shows different patterns according to the different water bodies and photosynthetic activity in each period (Fig. 8). In spring, the maximum values of pCO_2 ($\approx 350 \mu\text{atm}$) were located at the northeast in open ocean and in the shelf break (41.6°N to 42°N), respectively. Two minimum values of pCO_2 can be observed, one located in the southern part of the shelf at 40.3°N and the other one in the northwest side associated to the northerly cold waters (Fig. 8a). Both oceanic and coastal minima (about 320 μatm) are associated to the maximum values of chlorophyll, as expected. The pCO_2 average was 335 μatm which is 19 μatm lower than the atmospheric

one, indicating that in spring the study area behaves as a sink of CO₂. The correlation between pCO₂ and chlorophyll was very low ($p < 0.23$).

In autumn, the range of pCO₂ was wider than during spring (Fig. 8b). The maximum of pCO₂ (380 µatm) was located in the southern part of the shelf where the chlorophyll was low and the nitrate was high. The minimum of pCO₂ (320 µatm) was found over the shelf at 41.6°N just where the surface chlorophyll was high (Fig. 8b). In open sea the pCO₂ values were close to the atmospheric one (354 µatm). The correlation between chlorophyll and pCO₂ was negative, as expected,

$$pCO_2 (\pm 9) = 355(\pm 2) - 11(\pm 2) Chla \quad r^2 = 0.24 \text{ (n=67; } p < 0.00002)$$

The y-intercept is just the atmospheric pCO₂ assigned according to Keeling et al (1995). The strong wind recorded during the cruise and the low photosynthetic activity due to the low light available (typical conditions in this season), favoured the pCO₂ equilibrium between the mixed layer of the ocean and the atmosphere.

During the upwelling season (Fig. 8c), very high levels of pCO₂ were recorded on the shelf where the cold and nutrient-rich water was evident. However, in open sea the pCO₂ values were close to the atmospheric one. The gradient along 41.8°N was very sharply founding a secondary maximum at 10°W probably due to the spreading of the shelf waters to the open sea. Maximum values of chlorophyll were also measured on the shelf and a significant positive correlation with pCO₂ was found,

$$pCO_2 (\pm 17) = 346(\pm 4) + 25(\pm 4) Chla \quad r^2 = 0.50 \text{ (n=33; } p < 0.000004)$$

Both variables are significantly correlated with surface nitrate concentrations.

The three MORENA cruises gathered a variety of hydrographical patterns with different biogeochemical consequences. The coastal upwelling associated to northerly winds and the convergence created by the saline poleward currents show relations between pCO₂ and chlorophyll very different to the observed in open sea (Watson et al., 1991). To understand better the mechanisms that drive to these differences, we have selected two sections which allow to describe the thermohaline and biochemical subsurface properties. Fig. 9 shows the vertical distribution of temperature, salinity, pCO₂ and chlorophyll along 41.25°N during MORENA II cruise which cross the saline poleward current. Between 11.2°W and the slope, a mixed layer of about 60 to 100 meters thick has been developed due to the strong winds (Fig. 2b). This mixed layer has low chlorophyll concentration and homogenous pCO₂ close to the atmospheric one (354 µatm) or even slightly lower. Just on the slope (station 22), the poleward current traced by the maximum of salinity and temperature, blocks the spreading of fresh and light shelf water, forming a convergence or downwelling on the shelf-break. On the shelf, the vertical haline stratification due to the runoff increases slightly the nitrate concentration

(about $1.5 \mu\text{mol.kg}^{-1}$ at 35.5 of salinity). This low saline layer of 25-30 meters contains high levels of chlorophyll which decrease pCO_2 below atmospheric, generating a region for uptake of CO_2 . It is interesting to note that similar hydrographic conditions showed lower chlorophyll and higher pCO_2 at 40°N than at 41.25°N (Figs. 8 and 9). Less significant runoff at 40°N reduces the stability of the water column (Fig. 4) and also the accumulation of phytoplankton.

The other selected section, along 41.8°N surveyed in MORENA III cruise (Fig. 10), shows the typical pattern of coastal upwelling when northerly winds blow. However, the ENACW does not reach the surface (see Fig. 5). Only in the innermost part of the shelf, temperatures of about 15°C were measured at the surface. Several factors like wind and runoff mask the advection of ENACW to the surface. In any case, we can observe the steady elevation of isotherms over 13.5°C and the salinity maximum (upper layer of ENACW) from 11°W to the coast. The advected ENACW seems to be diluted on the shelf by the runoff and the mixing produced by wind. The pCO_2 distribution is very similar to that of the nutrients (not shown), exhibiting concentrations higher than expected by the advected ENACW. The additional contribution to these high nutrient and CO_2 concentrations is due to mineralization processes (Fraga, 1981, Alvarez-Salgado et al., 1993, Alvarez-Salgado et al., 1997). The high levels of chlorophyll recorded close to the coast seem to spread and deepen generating a subsurface maximum of chlorophyll in open sea. These high concentrations of chlorophyll near the coast seems to be in contradiction with the high values of nutrients and pCO_2 that should decrease as phytoplankton is growing, as occurs in station 31 where a pCO_2 minimum coincides with a chlorophyll maximum. But the important input of nutrients and pCO_2 from the upwelling event and mineralization processes make imperceptible the decrease of these variables. The runoff contributes to give stability to the surface layer, accumulating the biomass of phytoplankton which grows at the expense of the nutrients advected by the upwelling. The surface chlorophyll concentration decreases towards the open sea. In the water column the chlorophyll content is rather constant or increases slightly as far as the shelf-break because the photic layer deepens.

3.3. CO_2 air-sea exchange.

Table 1 shows the average of CO_2 exchange between air and sea and the surface chlorophyll in the three cruises. The CO_2 exchange was determined using the algorithm described before. During the spring cruise, the net exchange of CO_2 was negative (from the atmosphere to the sea) in all the studied area, with an average rate of $-1.0 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. On the shelf south 40.9°N an area point out with a high CO_2 flux to the sea due to the pCO_2 minimum (Fig. 8). During the late autumn 1993, the average CO_2 flux from the atmosphere to the sea was slightly lower than the former ($-0.60 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$). In the open ocean the average CO_2 flux was also similar in both MORENA I and MORENA II cruises. However, during the fall cruise, there were two different exchange regimes on

the shelf. North 40.9°N, the low pCO₂ values produce a mean rate -1.2 mmol·m⁻²·d⁻¹ while south 40.9°N, the high pCO₂ values yield an average CO₂ exchange of +0.32 mmol·m⁻²·d⁻¹. During the upwelling observed in July, the whole studied area behaved as a slightly source with more variability over the shelf with regard to the open ocean. The most striking feature is the strong CO₂ fluxes from the sea in four coastal stations (1.5±1.3 mmol·m⁻²·d⁻¹) due to the presence of high pCO₂ waters. These stations showed moderate chlorophyll (2.0±1.2 µg.l⁻¹). These fluxes can change due to increase of atmosphere pCO₂ owing to the influence of the terrestrial and upwelling inputs. In open ocean, recently measurements in winter 1997 for atmospheric pCO₂ (359±1.5µatm) showed a close agreement with the expected pCO₂ (Keeling et al. 1993). However, spring and summer measurements made in 1997 showed an increase of atmospheric pCO₂ of 5±9µatm close to the Galician coast. The extrapolation of this bias to the coastal stations means a decrease of 15% in the rate of exchange to the atmosphere in our gross estimations.

4. Discussion

Examination of the meteorological conditions together with the thermohaline distributions shows three different situations in spring (MORENA I), summer (MORENA III) and autumn (MORENA II). During spring and autumn, the south-westerly winds were dominant (Fig. 2) which help to drive a poleward current that typically appears in late fall (Pingree and Le Cann, 1990 and Frouin et al, 1990). In both cruises MORENA I and II, the highest values of salinity trace the poleward current. The poleward made a stronger and clear salinity signal in fall cruise with regard to the spring (Fig. 4). The T-S distributions of the surface water (Fig. 5) in spring and autumn were rather similar. However, it could be remarked the low temperature range and the high salinity range in the fall cruise. The highest and lowest salinity signal is due the poleward and runoff, respectively. The poleward event generated a strong downwelling on the slope constraining the low saline coastal waters. During summer, the northerly winds favoured the conditions for a typical coastal upwelling characterised by cold waters in surface (Fraga, 1981, Blanton et al, 1984) with the presence of two filaments (Fig. 4). In summer (MORENA III) the heating and the mixing with runoff of the ENACW produce a T-S distribution quite different with regard to the former cruises. The pure ENACW did not reach the surface but the T-S slope of the ENACW relationship seems to translate to the surface suggesting that the surface water is produced mainly by subsurface ENACW heating (Fig. 5) .

The very low chlorophyll and nutrient concentrations in surface, the development of subsurface chlorophyll maximum and the advanced epoch of the spring (McClain, et al, 1990) reveal a situation of post-bloom during MORENA I cruise. The low levels of pCO₂ generated by the spring blooms stay some time in water column while the chlorophyll disappear by grazing and sinking. Thus the decrease of CO₂ generated by the bloom

remain for weeks (Taylor et al., 1992) while the chlorophyll was degraded. Any correlation between $p\text{CO}_2$ and chlorophyll has been found at that time. Also during a spring postbloom, Ríos et al. (1995), analysing all data of five latitudinal sections in the Eastern North Atlantic, have not found any correlation between $p\text{CO}_2$ and chlorophyll. Although in a small temporal-scale, Watson et al (1991) found significant correlations between $p\text{CO}_2$ and chlorophyll. The average flux in spring (MORENA I) showed the highest rate of CO_2 sinking coinciding with the lowest average chlorophyll, suggesting that the uptake of CO_2 by the sea is favoured in May before the summer heating.

A significant correlation ($r^2=0.24$, $n=67$, $p<0.00002$) between $p\text{CO}_2$ and chlorophyll was found during MORENA II in autumn. Similar correlation with slopes very close to the obtained here, have been obtained by Watson et al. (1991) in a region further to the north ($47^\circ\text{-}60^\circ\text{N}$, 20°W). This spatial correlation is supported in the concurrence of three different conditions generated by the physical forcing. In open ocean, the cooling and strong winds produce important vertical mixing (Fig. 9) and create a 60 m homogenous layer with moderate chlorophyll levels and $p\text{CO}_2$ slightly lower than the atmospheric $p\text{CO}_2$. These conditions favoured the uptake of CO_2 by the ocean ($-0.71 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$). The dynamic effect of the poleward blocking the shelf-ocean exchange (Castro et al., 1997) created different patterns in the CO_2 exchange depending on the stability of the water column which is controlled by runoff and wind mixing. In the north part of the shelf, the strong river Douro runoff at 41.2°N created enough stability to accumulate chlorophyll ($1.95 \mu\text{g}\cdot\text{l}^{-1}$) and to decrease the $p\text{CO}_2$ (Figs. 7 and 8) in surface. This situation get an average CO_2 uptake of $-1.2 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. In the south part of the shelf, the decrease of salinity did not preclude the mixing of the water column by the wind, generating high $p\text{CO}_2$ and low chlorophyll levels in surface. In this circumstance there is a slight source of CO_2 to the atmosphere ($+0.32 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$).

In both MORENA I and II cruises, the dynamic behaviour of the coastal water and the convergence developed over the slope by the saline front, generated two typical patterns in function of the stratification of the water column also dependent on the runoff. If the salinity is low enough, the biomass of phytoplankton has a steady development, generating a decrease of $p\text{CO}_2$ and so, a sinking of CO_2 occurs. This was observed in the southern part of MORENA I and in the northern part of MORENA II. On the contrary, if the stability is weak, the mixing and the advection of subsurface water rich in nutrients and CO_2 (Alvarez-Salgado et al. 1997) result in an increase of $p\text{CO}_2$ and a source of CO_2 is developed in the coastal water. Although the runoff also changes the TIC and TA and therefore the $p\text{CO}_2$, calculations based in the dilution of oceanic water ($S=35.91$) with freshwater to produce the salinity minimum found ($S=34.69$), yield a $p\text{CO}_2$ decrease about 4% which is about 30% of the decreasing $p\text{CO}_2$ observed. Conversely, the low correlation between $p\text{CO}_2$ and salinity ($r^2= 0.02$, $n=16$, $p<0.59$) against the significant correlation between $p\text{CO}_2$ and chlorophyll ($r^2= 0.36$, $n=14$, $p<0.023$) on the shelf, show that the dilution effect of the runoff over the $p\text{CO}_2$ is not very important.

In summer the positive correlation ($r^2=0.50$, $n=32$, $p<0.000004$) between $p\text{CO}_2$ and chlorophyll seems to be in contradiction to the expected by photosynthetic activity. The upwelled water with high concentrations of total inorganic carbon (TIC) contributes to produce this fact. Upwelled water from 50m depth at 13°C and $440\ \mu\text{atm}$ of $p\text{CO}_2$, when reaches the surface increases in 2°C its temperature (Fig. 10). An increase of two degrees causes a $p\text{CO}_2$ increase of $38\ \mu\text{atm}$. We ignore any changes in alkalinity due to nutrient utilisation and calcification because the observed alkalinity variability correlates strongly with salinity ($r^2=0.96$, $n=33$, $p<0.00000$), and the effect of both variables over $p\text{CO}_2$ is lower than 1%. The average ratio carbon/chlorophyll ($\mu\text{mol.kg}^{-1}:\mu\text{g.l}^{-1}$) measured in the upwelled water is about 4 (Pérez et al., 1995). The chlorophyll concentration in the upwelling zone in surface is about $4\ \mu\text{g.l}^{-1}$. Therefore, the decrease in the total inorganic carbon through photosynthesis is $16\ \mu\text{mol.kg}^{-1}$ at 15°C , which represents a decrease in $p\text{CO}_2$ of $42\ \mu\text{atm}$. This value is very close with the increase in $p\text{CO}_2$ due to the increase temperature of the upwelled water. Consequently, the effect of the photosynthetic production on the $p\text{CO}_2$ is masked by the increase in carbon brought with the upwelled water. This increase of $p\text{CO}_2$ will be even higher without the biological effect. These mechanisms explain that high $p\text{CO}_2$ coincides with high chlorophyll concentrations. On the other hand, the surface $p\text{CO}_2$ and chlorophyll decrease as the upwelled water is advected to the open ocean by dilution with water with low chlorophyll and $p\text{CO}_2$ in balance with the atmospheric one. Hence, it generates the positive correlation between $p\text{CO}_2$ and chlorophyll in the upwelling zone. This effect also explains the vertical shape of $p\text{CO}_2$ isolines not appreciable in the distribution of temperature (Fig. 10). In the Peruvian upwelling close to the coast, Copin-Montégut and Raimbault (1994) observed also the same pattern with $p\text{CO}_2$ reaching the surface higher than $800\ \mu\text{atm}$ with the maximum chlorophyll levels about 1mg.m^{-3} .

With regard to the CO_2 exchanges, the four stations situated just in the upwelling show the highest rates of CO_2 release to the atmosphere ($1.5\ \text{mmol C m}^{-2}\ \text{d}^{-1}$) and chlorophyll concentrations ($2\ \mu\text{g.l}^{-1}$). The rest of the area behaves as slight source of CO_2 . In the coastal embayment affected by wind-driven upwelling, strong fluxes to the atmosphere were also observed with an average rate of $2.0\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ (Rosón et al., submitted). In the equatorial Atlantic Ocean between 2.5°N and 2.5°S (Andrié et al., 1986) a global average source of $1.23\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ during five cruises were reported. For the equatorial Pacific Ocean, between 2.5°N and 2.5°S , a strong source of CO_2 for the atmosphere with an average flux of $4.88\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ was estimated (Lefèvre and Dandonneau, 1992), which is even greater than the range $1.5\text{--}3.1\ \text{mg C m}^{-2}\ \text{d}^{-1}$ between 0° and 3°S reported by Ishii and Inoue (1995).

The average CO_2 exchange obtained for the three MORENA cruises was $-0.47\ \text{mmol.m}^{-2}\text{d}^{-1}$. This uptake value is slightly lower, due to the influence of the upwelling, than 0.68 and $0.65\ \text{mmol.m}^{-2}\text{d}^{-1}$ recorded in the North Atlantic by Merlivat et al (1991) and Ríos et al (1995) respectively. These results suggest that MORENA area behaves as a

sinking as expected by previous investigations carried out in the North Atlantic ocean (Brewer et al., 1989, Takahashi, 1989). Although the three studied cruises enable us to describe the spatial pattern in $p\text{CO}_2$ distribution, they are few cruises to establish a fair yearly rate of CO_2 exchange and further frequent samplings along the annual cycle are needed.

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Table 1

Summary and average of air-sea CO₂ exchange (mmol.m⁻².d⁻¹) and surface chlorophyll (µg.l⁻¹) in the MORENA area.

Cruise	Shelf			Ocean	Average
	>40.9°N	<40.9°N	all		
CO ₂ flux					
MORENA I May 1993	-0.43 ±0.30 (19)	-2.6 ±0.7 (14)	-1.4 ±0.5 (33)	-0.78 ±0.25 (49)	-1.0 ±0.26 (82)
MORENA II Nov 1993	-1.2 ±0.6 (6)	+0.32 ±1.5 (10)	-0.26 ±1.0 (16)	-0.71 ±0.24 (54)	-0.60 ±0.31 (70)
MORENA III Jul 1994			+0.27 ±1.2 (8)	+0.14 ±0.23 (24)	+0.18 ±0.34 (32)
"Annual Average"					-0.47
Chlorophyll					
MORENA I May 1993	0.27±0.04 (19)	0.35±0.09 (14)	0.30±0.06 (33)	0.32±0.08 (49)	0.31±0.05 (82)
MORENA II Nov 1993	2.0 ±1.3 (5)	0.97±0.14 (9)	1.32±0.41 (14)	0.74±0.07 (53)	0.86±0.12 (67)
MORENA III Jul 1994			1.48±0.70 (8)	0.51±0.08 (25)	0.75±0.24 (33)
"Annual Average"					0.64

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Captions of figures

Fig. 1 a, b, c. Map of the study area indicating the location of sampled stations for MORENA I, II and III cruises, respectively. Figs 10 and 11 are depicted as continuous lines. Dotted line represents the isobath of 1000 m.

Fig. 2 a, b, c. Distribution of wind speed, Northerly and Easterly components during MORENA I, II and III cruises, respectively.

Fig. 3 a, b, c. Distribution of sea surface temperature ($^{\circ}\text{C}$) in MORENA I, II and III cruises, respectively. The lines of 19° and 20°C Satellite STT (NOAA-11 94/08/05 17:07 TU) are drawn.

Fig. 4 a, b, c. Distribution of sea surface salinity (PSS) in MORENA I, II and III cruises, respectively.

Fig. 5. T-S relationship of surface water throughout the three MORENA cruises. Line for ENACW according to Fiúza (1984).

Fig. 6. a, b, c. Distribution of sea surface nitrate ($\mu\text{mol.kg}^{-1}$) in MORENA I, II and III cruises, respectively.

Fig. 7. a, b, c. Distribution of sea surface chlorophyll ($\mu\text{g.l}^{-1}$) in MORENA I, II and III cruises, respectively.

Fig. 8. a, b, c. Distribution of sea surface pCO_2 (μatm) in MORENA I, II and III cruises, respectively.

Fig. 9. Vertical distribution of temperature ($^{\circ}\text{C}$), salinity (PSS), pCO_2 (μatm) and chlorophyll ($\mu\text{g.l}^{-1}$) along 41.25°N during MORENA II cruise.

Fig. 10. Vertical distribution of temperature ($^{\circ}\text{C}$), salinity (PSS), pCO_2 (μatm) and chlorophyll ($\mu\text{g.l}^{-1}$) along 41.8°N during MORENA III cruise.

TEMPERATURE I May'93

TEMPERATURE II Nov'93

TEMPERATURE III- Jul'94

SALINITY I May'93

SALINITY II Nov'93

SALINITY III Jul'94

Sea Surface T-S

CHLOROPHYLL I May'93

CHLOROPHYLL II Nov'93

CHLOROPHYLL III Jul'94

pCO₂ I May'93 pCO₂ II Nov'93 pCO₂ III Jul'94