

Partitioning of physical and biogeochemical contributions to short-term variability of pCO₂ in a coastal upwelling system: a quantitative approach

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ABSTRACT: A considerable body of literature has addressed the role that coastal upwelling systems may play in global processes, especially in the ocean carbon cycle. It is often difficult to separate the effects of physical and biogeochemical processes on the partial pressure of carbon dioxide (pCO₂) in coastal upwelling systems due to the tight coupling between these processes. In this work we propose a novel approach to quantify physical (advection and diffusion of inorganic carbon species, *in situ* warming) and biogeochemical (production and consumption of inorganic carbon species) effects on surface pCO₂ using an inverse method. It is applied to the Ría de Vigo, a large coastal indentation in the NW Iberian shelf. Physical and biogeochemical processes affecting surface pCO₂ variability are quantified during spring, summer, autumn and winter. Our results show the dominance of vertical advection, turbulent diffusion and net ecosystem production of organic carbon (ΔC_{org}) components over other processes (calcification and surface warming) on a short timescale (2 to 4 d). The study reveals that physical transport of inorganic carbon species explains ~50 % of the observed pCO₂ variability and ΔC_{org} accounts for most of the remaining 50 %.

KEY WORDS: pCO₂ · Carbon cycle · Inversebox–methods · Coastal upwelling · Galician rías · NW Spain

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INTRODUCTION

Increased atmospheric levels of carbon dioxide (CO₂) account for about 60 % of the CO₂ emitted by fossil fuel burning and cement making. The oceans and terrestrial systems absorb the remainder of these emissions (Houghton et al. 1996). Net CO₂ uptake by the oceans ranges from 17 to 39 % of the fossil fuel emissions (e.g. Siegenthaler & Sarmiento 1993, Schimel et al. 1996). The direction of the air-sea CO₂ exchange is determined ultimately by the difference of CO₂ pressure (pCO₂) between the atmosphere and surface seawater. Atmospheric pCO₂ is relatively constant and is calculated from data measured at stations around the world (Komhyr et al. 1985). On the other hand, seawater pCO₂ varies significantly, both temporally and spatially, as a result of a superposition of physical and biogeochemical factors (e.g. Takahashi et al. 1993). Organic carbon production (photosynthetic

CO₂ fixation) and consumption (respiratory release of CO₂) influence the oceanic CO₂ system by respectively decreasing or increasing seawater pCO₂. Calcification produces a net increase of pCO₂, whereas CaCO₃ dissolution provokes a decrease. Temperature and freshwater cycles also influence seawater pCO₂ values. Temperature affects the acid constants of the CO₂ system and its solubility in seawater: an increase of 1°C provokes an increase of 4.23 % in pCO₂ (Takahashi et al. 1993). The effect of the freshwater cycle on surface pCO₂ also involves the acid constants and the solubility of CO₂ in seawater, apart from the highly variable inorganic carbon content of rivers.

Continental shelves and slopes usually have high primary production rates and enhanced water flows that results in intensified gradients of biogeochemical parameters (Walsh 1991, Wollast 1993). These processes affect seawater pCO₂ in several ways and, therefore, the air-sea exchange of CO₂. Coastal areas

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affected by wind-driven upwelling are relevant for the global carbon cycle because of their enhanced physical and biological activity compared with other environments. Equatorial and coastal upwelling systems account for 5 to 15% of the new production of the world's oceans (Knauer 1993).

A question has been recurrently addressed about the role of upwelling systems in the global carbon cycle: Do they act as a net sinks or sources of CO_2 to the atmosphere? (e.g. Watson 1995). We try to clarify this question by separating the physical and biogeochemical components of seawater pCO_2 with a quantitative approach based on the combination of relevant carbon rates and water fluxes derived with an inverse method and a first-order removal mechanism for salinity, temperature, total inorganic carbon content (C_T) and total alkalinity (A_T).

Despite the fact that inorganic carbon dynamics in coastal upwelling areas have previously been reported—e.g. by Copin-Montegut & Raimbault (1994) in Perú, Torres et al. (1999) in Chile, Borges & Frankignoulle (2002) and Gago et al. (2003) in NW Iberia—this study is one of the first attempts to quantify the relative contribution of physical (advection and diffusion of inorganic carbon species, *in situ*

warming) and biogeochemical (production and consumption of inorganic carbon species) processes to the variability of surface pCO_2 on a time scale of 2 to 4 d. Previous studies have established that this is the most suitable sampling frequency to study the coupling between meteorological forcing and hydrography in the NW Iberian margin (Álvarez-Salgado et al. 1993).

MATERIALS AND METHODS

Sampling. The study site is the coastal upwelling system of the Ría de Vigo, one of the 4 large, flooded tectonic valleys located in NW Spain (Fig. 1). Wind-driven upwelling occurs there from April–May to September–October (upwelling season) and provokes an enhanced positive circulation pattern (Wooster et al. 1976). The rest of the year (downwelling season) is characterized by southerly winds that frequently produce a reversal of positive circulation (Álvarez-Salgado et al. 2000), with the ría circulation similar to that of a negative estuary. The Ría de Vigo is a large embayment (2.76 km^3) with a unique open-boundary, whereby the typical 3-dimensional water transport over open shelves is reduced to 2 dimensions because of negligible along-shore transport (Gilcoto et al. 2001).

Intensive hydrographic sampling was performed in the Ría de Vigo during 4 contrasting periods in 1997: 7 to 23 April (spring), 1 to 18 July (summer), 15 September to 2 October (autumn), and 1 to 11 December (winter). There were 5 sampling stations, 4 along the main axis of the embayment and 1 at the shallower entrance, north of the Isles Cies (Fig. 1). Full-depth continuous conductivity-temperature-depth profiles were recorded at each sampling site with a SBE 25 CTD device. Conductivity measurements were converted into practical salinity-scale values (UNESCO 1986). Subsequently, seawater samples for pH and A_T determination were collected from 3 to 5 depths with 5 l Niskin bottles. This procedure was repeated every 2 to 4 d during each of the 4 sampling periods. A total of 22 surveys were performed: 6 during spring, summer and autumn, and 4 during the winter period. pH was measured potentiometrically (Pérez & Fraga 1987a). A_T was determined by 1 end-point potentiometric titration (Pérez & Fraga 1987b). The electrodes were calibrated to the National Bureau of Standards (US) scale. The accuracy of pH and A_T measurements was ± 0.002 and $1.4 \mu\text{mol kg}^{-1}$, respectively, as determined using samples of Batches 33, 35 and 37 of the certified reference material (CRM) provided by Dr. A. Dickson, University of California. C_T and pCO_2 were calculated from pH and A_T using the carbonic acid constants of Mehrbach et al. (1973) and the solubility constant of

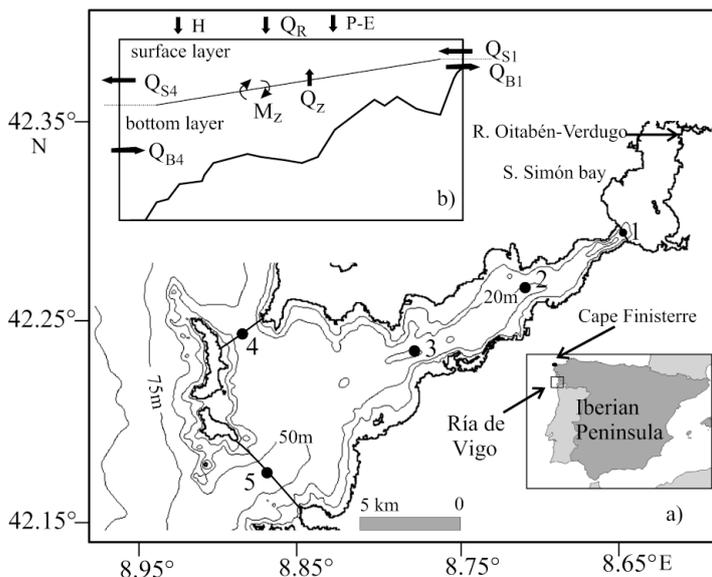


Fig. 1. (a) Chart of survey area (Ría de Vigo, NW Iberian upwelling system), showing 5 sampling sites (●) distributed along the embayment. Inner (Stn 1) and outer (Stns 4 and 5) boundaries delimit the study area; meteorological observatory at Cape Finisterre is indicated. Isobaths of -20 , -50 and -75 m are shown. (b) Box geometry of the system. $Q_R + P - E$: hydrological balance (Q_R = river runoff, P = precipitation and E = evaporation); Q_B and Q_S : surface and bottom horizontal advective fluxes; Q_Z and M_Z : vertical advective and mixing fluxes, respectively; H : heat exchange across the sea surface. Subscripts 1 and 4 refer to the inner and outer boundary, respectively

Weiss (1974). The accuracy of pH and A_T measurements produces an estimated error of $\pm 3 \mu\text{mol kg}^{-1}$ and $3 \mu\text{atm}$ for calculated C_T and pCO₂, respectively. The CO₂ fluxes across the air-seawater interface were taken from Gago et al. (2003). Finally, offshore Ekman transport was calculated for Cape Finisterre (Fig. 1) according to Wooster et al. (1976).

Partitioning of physical and biogeochemical components using an inverse-box method. The study system is delimited by 2 boundaries (Fig. 1). The inner boundary separates the ría from San Simón Bay, the estuary of the river Oitabén-Verdugo; the outer boundary separates the ría from the continental shelf. The geometry of the Ría de Vigo (surface and cross-sectional areas and volume) was obtained from accurate charts published by the Spanish 'Instituto Hidrográfico de la Marina'. The study system is divided into 2 layers (surface and bottom), flowing in opposite directions; the thin stratum of water between the surface and bottom layer with no horizontal motion constitutes the gravity center. Average salinity and temperature of the surface and bottom layers at each boundary were obtained by simple numeric integration of the CTD profiles. Average concentrations of C_T and A_T in the surface and bottom layer at each boundary and in the box (volume of water considered) were calculated from C_T and A_T data from 3 to 5 discrete samples. Continental runoff to the Ría de Vigo (Q_R) was estimated according to Ríos et al. (1992) from precipitation in the drainage basin.

To quantify the net effect of physical and biogeochemical processes on the pCO₂ of the surface layer of the ría, a first-order removal mechanism for salinity, temperature, C_T and A_T was assumed. This approach has long been used to study the fate of chemicals dissolved in marine systems (see Martin et al. 1986 for a complete review on this topic), and we apply it here to the study of short-term variability of inorganic carbon species. With regard to net input to and output from the surface layer, the temporal changes in thermohaline and chemical variables between 2 consecutive surveys for a situation of upwelling can be expressed as:

$$\frac{\Delta(C \times V)}{\Delta t} = \bar{F} + Q_{S1} \times C_{S1} + Q_Z \times C_Z + M_Z \times C_L + Q_R \times C_R - Q_{S4} \times \frac{C_{S4}}{C} \times C - M_Z \times C + \overline{\text{NEB}} \quad (1)$$

where C is average salinity, temperature, C_T or A_T in the box between 2 consecutive surveys. In this way, outflux is proportional to the value of C in the upper layer. The term \bar{F} accounts for the air-sea exchange of CO₂ ($\bar{F}\text{CO}_2$) in the case of C_T and heat (\bar{H}) in the case of temperature; \bar{H} was estimated by Álvarez-Salgado et al. (2000) for the 1997 surveys. Subscripts

1 and 4 refer to the inner and outer boundaries of the ría, respectively (Fig. 1); subscripts L, Z and R represent bottom layer, level of no motion and river runoff, respectively (see Table 1). The term $\langle C_{S4} \rangle / \langle C \rangle$, the ratio of average C concentrations in the outer boundary and the box between 2 consecutive surveys, is introduced to correct the lack of homogeneity of the surface layer of the ría ($\sim 1.2 \text{ km}^3$).

Water flow (Q_S , Q_Z , Q_R and M_Z , see Fig. 1 and Table 1 for definitions) for the 1997 surveys had already been obtained by Álvarez-Salgado et al. (2000) using a multiparameter inverse method. Data on water flow and the average concentrations of the different inorganic carbon species in the upper and lower layers, allows calculation of salinity, temperature, C_T and A_T convective and diffusive fluxes. $\overline{\text{NEB}}$ represents the net ecosystem budget of C (salinity, temperature, C_T or A_T). For salinity and temperature, $\overline{\text{NEB}} = 0$; for C_T , $\overline{\text{NEB}} = -\Delta C_{\text{org}} - \Delta \text{CaCO}_3$, where ΔC_{org} and ΔCaCO_3 are the net ecosystem production of organic carbon and calcium carbonate, respectively. According to Broecker & Peng (1982), the $\overline{\text{NEB}}$ of A_T equals $-\overline{\text{NEB}}$ of nitrate ($= [^{16}_{106}] \times \Delta C_{\text{org}}$) in the case of phytoplankton organic carbon, and equals $-2 \times \Delta \text{CaCO}_3$ in the case of calcium carbonate. Therefore, the $\overline{\text{NEB}}$ of A_T is equal to $(^{106}_{16}) \times \Delta C_{\text{org}} - 2 \times \Delta \text{CaCO}_3$. Integration of Eq. (1) between 2 consecutive surveys yields:

$$C_2 = C_1 \times e^{-B \times \Delta t} + \left(\frac{A}{B} \right) \times (1 - e^{-B \times \Delta t}) + \left(\frac{\overline{\text{NEB}}}{B} \right) \times (1 - e^{-B \times \Delta t}) \quad (2)$$

where $\Delta t = t_2 - t_1$. Table 2 shows the equations that describe A and B for upwelling and downwelling conditions. During upwelling, surface water flows are directed toward the shelf because northerly winds enhance the positive estuarine circulation pattern. During downwelling conditions, circulation results from the balance between the intensity of southerly winds (which tend to introduce shelf waters into the ría) and river runoff (which tends to release continental waters onto the shelf). In general, there is an oceanic surface water inflow to the ría that returns to the shelf through the bottom layer and a surface flow from San Simón Bay to the ría from river runoff.

A/B is the expected value of C in the surface layer of the ría arising from the physical transport of C to the system; B is equivalent to the inverse of the flushing rate ($B \sim 1/t_{tr}$, d^{-1}) of the surface layer of the ría, and the term $1/B \times (1 - e^{-B \times \Delta t})$ is the time factor that indicates the temporal extension of the contributions of physical transport (A) and biogeochemistry ($\overline{\text{NEB}}$) to the net change of C between 2 consecutive surveys.

Eq. (2) in the case of C_T and A_T should be written as follows:

Table 1. Symbols used throughout the study and their definitions, presented in alphabetical order. Average values determined from data of 2 consecutive surveys

Symbol	Definition
A_T	Total alkalinity ($\mu\text{mol kg}^{-1}$)
C_T	Total inorganic carbon concentration ($\mu\text{mol kg}^{-1}$)
C_L	Average value of variable C in the bottom layer
C_R	Average value of variable C in the river flow
C_U	Average value of variable C in the upper layer
C_S	Average value of variable C in the upper layer of the outer boundary
C_Z	Average value of variable C in the boundary between the upper and lower layers
ΔCaCO_3	Average net ecosystem production ($\text{g C m}^{-2} \text{d}^{-1}$) of calcium carbonate
$\Delta\text{C}_{\text{org}}$	Average net ecosystem production ($\text{g C m}^{-2} \text{d}^{-1}$) of organic carbon
$\bar{F}\text{CO}_2$	Average air-sea exchange of CO_2 (mmol s^{-1})
\bar{H}	Average air-sea exchange of heat ($^\circ\text{C m}^3 \text{s}^{-1}$)
$\overline{M_Z}$	Average vertical turbulent diffusion flux ($\text{m}^3 \text{s}^{-1}$)
$\overline{\text{NEB}}$	Average net ecosystem budget of variable C
$p\text{CO}_2$	Partial pressure of carbon dioxide (μatm)
$p\text{CO}_2\text{f}$	$p\text{CO}_2$ (μatm) resulting from advection and diffusion
$\Delta p\text{CO}_2\text{w}$	$p\text{CO}_2$ (μatm) change due to <i>in situ</i> warming
$\Delta p\text{CO}_2\text{org}$	$p\text{CO}_2$ (μatm) change due to net organic carbon production
$\Delta p\text{CO}_2\text{Ca}$	$p\text{CO}_2$ (μatm) change due to net calcium carbonate production
$-Q_x$	Offshore Ekman transport ($\text{m}^3 \text{s}^{-1} \text{km}^{-1}$ coast)
Q_b, Q_s	Average bottom and surface horizontal convective water fluxes ($\text{m}^3 \text{s}^{-1}$) at the open boundaries of the study area
Q_z	Average vertical convective water flux ($\text{m}^3 \text{s}^{-1}$)
Q_R	Average river water flux ($\text{m}^3 \text{s}^{-1}$)
t_f	Average flushing time (d)
V_U	Average volume (m^3) of the upper layer

$$C_{T_2} = C_{T_1} \times e^{-B(C_T) \times \Delta t} + \left[\frac{A(C_T)}{B(C_T)} \right] \times [1 - e^{-B(C_T) \times \Delta t}] - \left[\frac{\Delta\text{C}_{\text{org}} + \Delta\text{CaCO}_3}{B(C_T)} \right] \times [1 - e^{-B(C_T) \times \Delta t}] \quad (3)$$

and

$$A_{T_2} = A_{T_1} \times e^{-B(A_T) \times \Delta t} + \left[\frac{A(A_T)}{B(A_T)} \right] \times [1 - e^{-B(A_T) \times \Delta t}] + \left[\frac{\frac{16}{106} \times \Delta\text{C}_{\text{org}} - 2 \times \Delta\text{CaCO}_3}{B(A_T)} \right] \times [1 - e^{-B(A_T) \times \Delta t}] \quad (4)$$

The use of 2 equations (Eqs. 3 & 4) with 2 unknowns ($\Delta\text{C}_{\text{org}}$ and ΔCaCO_3) allows estimation of the net ecosystem production of organic carbon ($\Delta\text{C}_{\text{org}}$) and calcium carbonate (ΔCaCO_3) in the surface layer of the

ría between 2 consecutive surveys. The different values necessary to solve Eqs. (3) & (4) are presented in Table 3. Table 4 shows average values of salinity, temperature, C_T , A_T and $p\text{CO}_2$ for the upper layer of the ría.

Quantification of effects of different factors on seawater $p\text{CO}_2$. The observed $p\text{CO}_2$ of the surface layer of the ría is the result of physical transport of salt, heat, C_T and A_T ($p\text{CO}_2\text{f}$), *in situ* warming ($\Delta p\text{CO}_2\text{w}$), *in situ* net organic carbon production ($\Delta p\text{CO}_2\text{org}$) and *in situ* net calcification ($\Delta p\text{CO}_2\text{Ca}$). Over short timescales, the air-sea exchange of CO_2 does not have an important effect on variability of seawater $p\text{CO}_2$ (e.g. Frankignoulle et al. 1996, this study). Air-sea CO_2 exchange within the ría contributes very little to the CO_2 equilibration with the atmosphere due to enhanced flushing rates; the equilibration with the atmosphere takes place in the adjacent shelf, once the water mass has left the ría. The observed $p\text{CO}_2$ can be expressed as:

$$p\text{CO}_2 = p\text{CO}_2\text{f} + \Delta p\text{CO}_2\text{w} + \Delta p\text{CO}_2\text{org} + \Delta p\text{CO}_2\text{Ca} \quad (5)$$

The effect of transport (advection and turbulent diffusion) and *in situ* warming on $p\text{CO}_2$ ($p\text{CO}_2\text{f} + \Delta p\text{CO}_2\text{w}$) can be evaluated by calculating C_{T_2} and A_{T_2} with Eqs. (3) & (4) for $\Delta\text{C}_{\text{org}} = 0$ and $\Delta\text{CaCO}_3 = 0$ and then estimating the $p\text{CO}_2$ with the carbonic acid system constants.

$\Delta p\text{CO}_2\text{w}$ was determined by comparing $p\text{CO}_2\text{f} + \Delta p\text{CO}_2\text{w}$ for the observed temperature of the surface layer with $p\text{CO}_2\text{f} + \Delta p\text{CO}_2\text{w}$ for the temperature expected if the heat exchange across the sea surface (\bar{H}) is set to zero when solving Eq. (2) for temperature.

The effect of *in situ* net calcium carbonate production ($\Delta p\text{CO}_2\text{Ca}$) was evaluated by comparing $p\text{CO}_2\text{f} + \Delta p\text{CO}_2\text{w}$ with the $p\text{CO}_2$ resultant from C_{T_2} and A_{T_2} calculated with Eqs. (3) & (4) for $\Delta\text{C}_{\text{org}} = 0$. (Note that Eqs. 3 & 4 were initially to determine $\Delta\text{C}_{\text{org}}$ and ΔCaCO_3 .) In this estimation we used the calculated ΔCaCO_3 and assumed $\Delta\text{C}_{\text{org}} = 0$ to evaluate C_{T_2} and A_{T_2} . Finally, the effect of *in situ* net organic carbon production ($\Delta p\text{CO}_2\text{org}$) was evaluated following the same procedure but with $\Delta\text{CaCO}_3 = 0$ and the $\Delta\text{C}_{\text{org}}$ initially calculated.

Robustness of estimation of effects of different factors on seawater $p\text{CO}_2$. Inverse methods usually involve the calculation of fluxes and budgets of many different properties with many possible sources of error. In our case, salinity, temperature, C_T and A_T are the properties under consideration and possible errors could arise from (1) convective and diffusive water flows; (2) water, heat and CO_2 air-sea exchange fluxes; (3) representativeness of the salinity, temperature, C_T and A_T determinations at certain sampling stations for

Table 2. Expressions for A and B in Eq. (2), where A/B and B are expected C value in surface layer arising from physical transport and inverse of flushing rate of surface layer, respectively. Situations 1 and 2 correspond to upwelling and downwelling conditions, respectively. See Table 1 for definitions of symbols here and in subsequent tables and in figures

Situation	A	B
1	$\frac{Q_{S1} \times C_{S1} + Q_R \times C_R + Q_Z \times C_Z + \bar{F} + M_Z \times C_L}{V_U}$	$Q_{S4} \times \frac{\langle C_{S4} \rangle}{\langle C \rangle} + M_Z + \frac{dV}{dt}$
2	$\frac{Q_{S1} \times C_{S1} + Q_{S4} \times C_{S4} + Q_R \times C_R + \bar{F} + M_Z \times C_L}{V_U}$	$Q_Z \times \frac{\langle C_{S4} \rangle}{\langle C \rangle} + C_Z + \frac{dV}{dt}$

the average properties of the surface layer; and (4) error transmission in the calculation of pCO₂ from C_T and A_T . According to Matsukawa & Suzuki (1985), the terms and properties involved in these calculations are so numerous that the averaging effect acting on the independent errors is sufficient to decrease the final errors considerably. On this basis, Maamaatuaiahutapu et al. (1992) developed a method based on the random perturbation of the measured variables within the limits of their respective independent error of estimation to assess the robustness of calculations derived from the multiparameter analysis of oceanic water-masses. More recently, Gilcoto et al. (2001) adopted the method for inverse-box methods. In our case, a system of 50 equations for salinity and temper-

ature (Eq. 2), C_T (Eq. 3), and A_T (Eq. 4) were solved for each sampling interval between 2 consecutive surveys. The 50 equations were obtained by random modification of calculated flows and measured variables within the limits of their independent error of estimation. Table 5 shows the error for the estimation of the convective (Q_S , Q_Z) and diffusive (M_Z) water flows provided by Álvarez-Salgado et al. (2000). Despite the fact that the error percentages are larger in spring and autumn than in summer and winter (Table 5), the absolute errors of estimation for the convective fluxes are

very similar for the 4 study periods (Álvarez-Salgado et al. 2000). The error of the freshwater flow (Q_R) and the heat-exchange flux (\bar{H}) were fixed at 10% according to Álvarez-Salgado et al. (2000). Following Gilcoto et al. (2001), the possible error associated with the sampling strategy was taken into consideration assuming that this represents 20% of the vertical gradient of salinity, temperature, C_T and A_T . The standard deviation of the 50 solutions is the error of the estimation, providing an index of the robustness of the complex calculations performed to separate the different physical and biogeochemical contributions to the observed pCO₂.

Table 6 summarises the error that each flux (Q_S , Q_B , Q_Z , M_Z , Q_R and \bar{H}) and property (salinity, temperature, C_T and A_T) produces in the pCO₂ estimation (in μatm)

Table 3. Summary of average water fluxes (Q_{S1} , Q_{S4} , Q_Z , M_Z and Q_R ; $\text{m}^3 \text{s}^{-1}$), air-sea heat transfer (\bar{H} ; $^\circ\text{C} \text{m}^3 \text{s}^{-1}$) and C_T and A_T concentrations (C_{S1} , C_{S4} , C_L , C_U and C_Z ; $\mu\text{mol kg}^{-1}$) for 18 sampling intervals between 2 consecutive surveys performed in the Ría de Vigo during 1997

Date	Q_{S1}	Q_{S4}	Q_Z	M_Z	Q_R	\bar{H}	C_T					A_T				
							C_{S1}	C_{S4}	C_L	C_U	C_Z	C_{S1}	C_{S4}	C_L	C_U	C_Z
7–10 Apr	298	-6004	-5885	2259	4.3	1864	2071	2053	2115	2064	2089	2279	2341	2339	2338	2342
10–14 Apr	515	2135	691	2717	6.0	1735	2048	2059	2107	2062	2082	2269	2337	2340	2333	2338
14–17 Apr	257	-73	64	2025	6.7	1638	2015	2055	2112	2058	2083	2271	2335	2345	2329	2337
17–21 Apr	579	-2338	-2608	1561	10.4	346	2045	2039	2107	2049	2078	2264	2328	2337	2322	2335
21–23 Apr	1817	1024	338	2051	16.8	447	2079	2029	2108	2049	2076	2269	2321	2333	2318	2331
1–4 Jul	186	401	861	1184	7.3	1919	1929	2026	2103	2013	2054	2167	2335	2340	2317	2330
4–8 Jul	281	4637	4065	1895	5.4	4234	1938	2034	2102	2020	2056	2190	2339	2341	2326	2336
8–11 Jul	129	-1175	-948	1216	3.2	4710	1915	2041	2094	2029	2052	2198	2341	2345	2331	2337
11–15 Jul	212	5562	4411	2228	2.7	4285	1949	2048	2101	2041	2065	2213	2337	2346	2328	2336
15–18 Jul	212	5933	5874	4690	3.6	6228	2011	2069	2114	2072	2091	2248	2340	2349	2332	2341
15–18 Sep	442	-2295	-1930	2207	2.7	3279	2086	2068	2118	2067	2087	2277	2337	2335	2333	2337
18–22 Sep	404	602	330	1509	2.3	2996	2100	2057	2109	2054	2069	2279	2339	2327	2331	2336
22–25 Sep	269	792	-209	514	2.6	2130	2092	2053	2112	2052	2076	2281	2334	2323	2320	2328
25–29 Sep	216	105	118	1227	4.8	1755	2061	2055	2117	2049	2080	2273	2331	2338	2317	2327
29 Sep–2 Oct	336	-2421	-2242	2433	5.2	1919	2046	2060	2118	2059	2086	2265	2334	2339	2327	2335
1–5 Dec	352	7772	6402	2074	52.2	-3600	1363	2005	2073	1945	2014	1448	2241	2331	2158	2244
5–8 Dec	298	-4478	-1904	3789	42.6	-4027	1694	2027	2066	2009	2035	1835	2278	2325	2258	2281
8–11 Dec	20	-15857	-15276	6769	26.5	-934	1582	1991	2025	1978	1999	1702	2239	2276	2223	2243

Table 4. Summary of the average salinity, temperature ($^{\circ}\text{C}$), C_T and A_T ($\mu\text{mol kg}^{-1}$) and pCO_2 (μatm) in the upper layer of the Ría de Vigo during the 22 surveys performed in 1997

Survey	Salinity	Temperature	C_T	A_T	pCO_2
7 Apr	35.7	14.9	2067	2341	325
10 Apr	35.6	15.5	2060	2336	329
14 Apr	35.6	15.9	2063	2330	349
17 Apr	35.6	16.3	2053	2327	342
21 Apr	35.3	16.4	2045	2318	339
23 Apr	35.3	16.2	2052	2319	347
1 Jul	35.5	17.1	2014	2313	308
4 Jul	35.6	16.7	2012	2321	291
8 Jul	35.7	15.8	2028	2333	290
11 Jul	35.6	16.4	2029	2329	303
15 Jul	35.6	15.7	2058	2327	341
18 Jul	35.7	15.3	2085	2336	370
15 Sep	35.7	15.3	2089	2328	392
18 Sep	35.7	15.5	2048	2338	309
22 Sep	35.6	16.0	2059	2324	352
25 Sep	35.6	16.7	2045	2316	350
29 Sep	35.6	16.8	2054	2319	363
2 Oct	35.6	16.9	2065	2334	361
1 Dec	31.3	16.0	1892	2096	359
5 Dec	33.9	16.2	2022	2249	387
8 Dec	34.6	15.7	2003	2262	329
11 Dec	33.7	15.6	1956	2188	348

when the effects of advection + diffusion, warming, net organic carbon production and net calcification are considered separately. Note that the errors produced by Q_R and \bar{H} are quite low ($0.2 \mu\text{atm}$). Vertical and horizontal advection and mixing as well as the error associated with the representativeness of the property determinations introduce errors of $\sim 3 \mu\text{atm}$. ΔC_{org} and ΔCaCO_3 rates for the 4 sampling periods were estimated using Eqs. (3) & (4) with average errors of 17 and 35%, respectively. The errors produced by the introduction of ΔC_{org} and ΔCaCO_3 are ~ 4 and $\sim 1 \mu\text{atm}$, respectively. Finally, note that the random perturbation procedure leads to an average total error of $7.2 \mu\text{atm}$, which is much lower than the sum of the independent contribution of each flux and property ($13.4 \mu\text{atm}$). As pointed out previously, the averaging effect acting on the errors of physical and biogeochemical terms decreases the actual errors considerably.

Table 5. CV (%) in horizontal and vertical convective fluxes during 4 sampling periods (spring, summer, autumn and winter)

Variable	Spring	Summer	Autumn	Winter
Q_Z	44	7	60	8
Q_S, Q_B	15	5	15	7
M_Z	48	13	18	18

RESULTS

Net organic and inorganic carbon production and flushing rates

The hydrographic and meteorological conditions of the Ría de Vigo during 1997 have already been reported in several works (e.g. see Álvarez-Salgado et al. 2000 and Gago et al. 2003 for a detailed description of the space and time evolution of the variables necessary to run the inverse method). The variable that probably best expresses the effect of hydrodynamics on biogeochemistry is flushing time (t_r , d), i.e. the ratio between the volume of the study system and the incoming or outgoing water fluxes. The term $1/2 \times (1 - e^{-B \times \Delta t})$, which modulates the effects of net input and the NEB of C , is not significantly different from $t_r \times (1 - e^{-\Delta t/t_r})$, the latter being independent of species (salinity, temperature, C_T or A_T). Fig. 2 shows the short-term evolution of t_r and $t_r \times (1 - e^{-\Delta t/t_r})$ for the 4 survey periods.

Shelf winds were moderate in intensity and variable in direction during the spring survey. The average offshore Ekman transport for this period was $190 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$ (Álvarez-Salgado et al. 2000). There was a notable increase in t_r (Fig. 2a), from 2 to more than 6 d, for 7 to 10 April and 14 to 17 April, respectively. The term $t_r \times (1 - e^{-\Delta t/t_r})$ ranged from 1.5 to 2.5 d. The summer period coincided with northerly winds that produced intense offshore Ekman transport values: the average transport was $365 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$. In contrast, continental runoff was extremely low at $< 7 \text{ m}^3 \text{ s}^{-1}$. A decrease of t_r from the beginning to the end of the

Table 6. Average error in estimation of calculated pCO_2 (μatm), standard deviation of 50 solutions, due to errors in river flow and heat-exchange flux (Q_R, \bar{H} , respectively), vertical advection (Q_Z), horizontal advection (Q_S, Q_B), vertical mixing (M_Z) and representativeness of property concentrations (salinity, temperature, A_T and C_T)

Variable	Advection	Heat	ΔC_{org}	ΔCaCO_3	Net error
Q_R, \bar{H}	0.3	0.2	~ 0	~ 0	0.2
Q_Z	2.8	0.1	0.1	~ 0	2.8
Q_S, Q_B	1.6	0.1	0.4	0.1	1.7
M_Z	2.9	0.1	0.1	~ 0	3.0
S, T, A_T, C_T	2.8	~ 0	4.4	1.3	5.7
Total	4.8	0.2	4.3	1.4	7.2

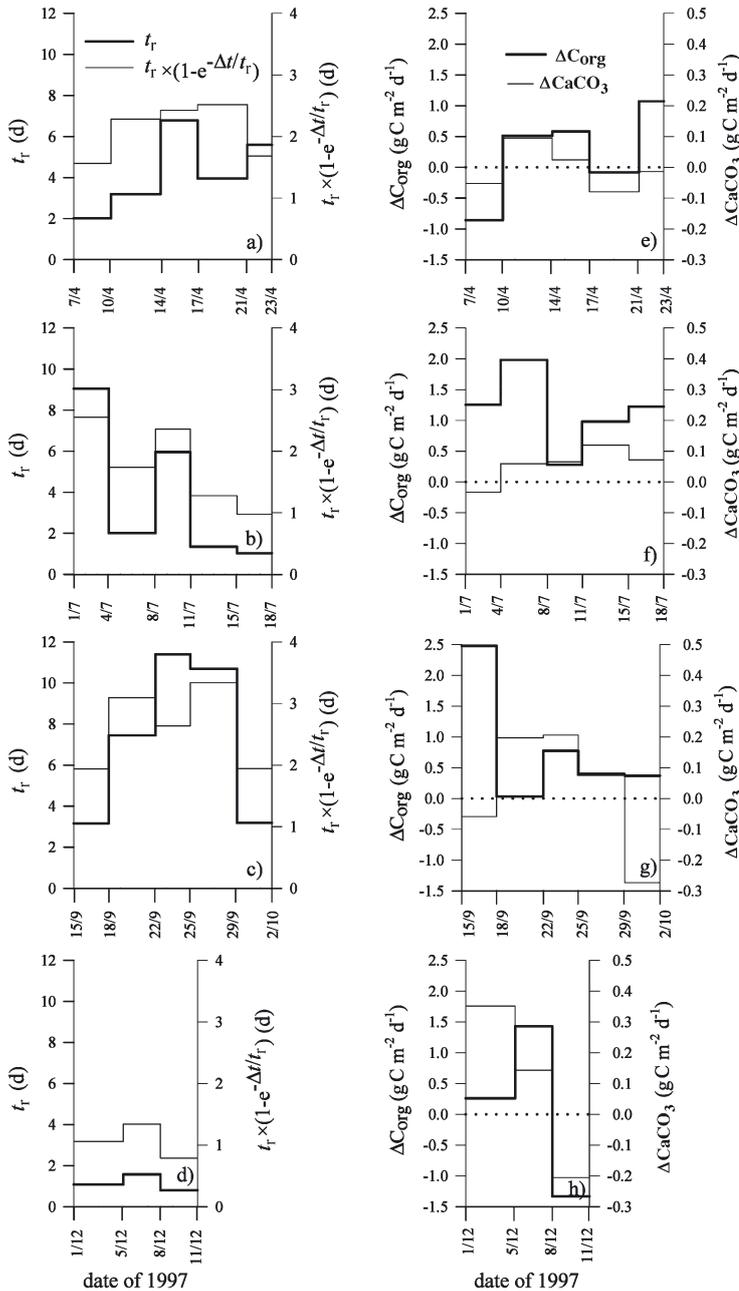


Fig. 2. Temporal evolution of (left panels) t_r and $t_r \times (1 - e^{-\Delta t/t_r})$ and of (right panels) net ecosystem production of organic carbon (ΔC_{org}) and calcium carbonate (ΔCaCO_3) during (a,e) spring, (b,f) summer, (c,g) autumn and (d,h) winter survey periods of 1997. Dates given as d/mo

summer survey was observed (Fig. 2b) due to upwelling intensification during this period. At the end of the summer period, strong upwelling reduced flushing time to 1 d. A prolonged (>10 d) wind calm—characteristic of the transition from the upwelling to the downwelling season (Álvarez-Salgado et al. 2000)—was monitored during the autumn period. The off-

shore Ekman transport ranged from -30 to $160 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$, with an average value of $109 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$, and the continental runoff was again quite limited: $< 5 \text{ m}^3 \text{ s}^{-1}$, with t_r and $t_r \times (1 - e^{-\Delta t/t_r})$ reaching maximum values (always more than 4 and 3 d, respectively) (Fig. 2c). Dramatic changes in the wind regime occurred during the winter (1 to 11 December), evolving from upwelling-favorable northerly winds producing an offshore Ekman transport of $200 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$ on 1 to 5 December to downwelling-favorable southerly winds producing an offshore Ekman transport of $-1500 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-1}$ on 8 to 12 December. Continental runoff was very high during the winter period (average $40 \text{ m}^3 \text{ s}^{-1}$). t_r and $t_r \times (1 - e^{-\Delta t/t_r})$ remained approximately constant at 1 d as a result of the intensified circulation (Fig. 2d).

The net ecosystem production of organic carbon (ΔC_{org}) and of calcium carbonate (ΔCaCO_3) in the upper layer of the Ría during the 4 survey periods is also presented in Fig. 2. ΔCaCO_3 was very low during the 4 periods, being slightly intensified in the autumn surveys (18 to 25 September average, $0.2 \text{ g C m}^{-2} \text{ d}^{-1}$). An increase in ΔC_{org} from the beginning to the end of the period was observed during spring (Fig. 2e), parallel to the temporal evolution of t_r . In the period 7 to 10 April, negative ΔC_{org} values were observed ($\Delta C_{\text{org}} = -0.86 \text{ g C m}^{-2} \text{ d}^{-1}$), denoting the dominance of respiration processes. At the beginning of the summer (Fig. 2f), the highest ΔC_{org} for this period was observed (4 to 8 July = $2 \text{ g C m}^{-2} \text{ d}^{-1}$). In contrast, strong upwelling occurred at the end of this period (the lowest t_r was observed) and ΔC_{org} was reduced. The highest ΔC_{org} was found on 15 to 18 September ($2.5 \text{ g C m}^{-2} \text{ d}^{-1}$; Fig. 2g), as a result of favorable physical and biological conditions. It is known that upwelling systems achieve maximum productivity during moderate wind conditions when longer flushing times allow phytoplankton to adapt to the new light and nutrient conditions (Wroblewski & Hoffmann 1989). ΔC_{org} rates during the other surveys in September fluctuated between 0.0 and $0.8 \text{ g C m}^{-2} \text{ d}^{-1}$. The high values of t_r and $t_r \times (1 - e^{-\Delta t/t_r})$ resulted in an intense effect of the NEB and A (ratio of the C input to the system divided by the volume of the reservoir) on the final concentration of C. Finally, the winter period was characterized by strong changes in ΔC_{org} (Fig. 2h): from a production of $1.4 \text{ g C m}^{-2} \text{ d}^{-1}$ during 5 to 8 December to a respiration of $-1.3 \text{ g C m}^{-2} \text{ d}^{-1}$ during 8 to 11 December. The pronounced ΔC_{org} minimum at the end of the winter period coincided with remarkably negative values of $-Q_x$.

Physical and biogeochemical components of surface $p\text{CO}_2$ variability

Fig. 3 shows the short-term evolution of observed $p\text{CO}_2$ (see Table 4), the $p\text{CO}_2$ expected if only advective

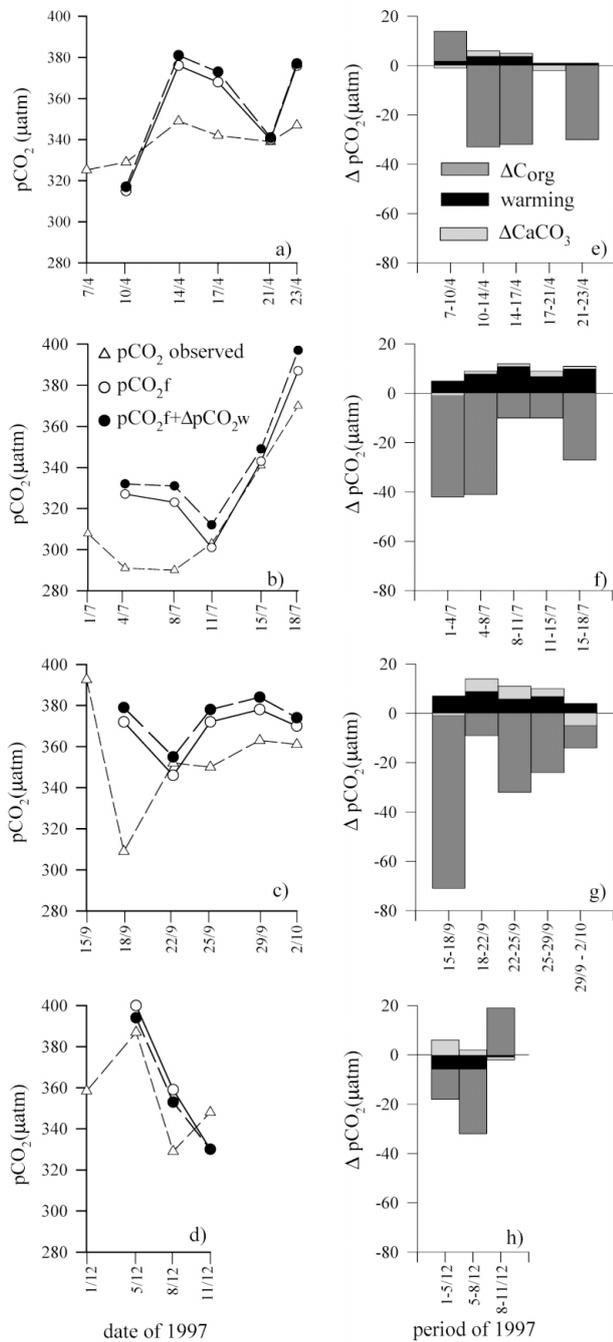


Fig. 3. Temporal evolution of (left panels) $p\text{CO}_2$, $p\text{CO}_2f$ and $p\text{CO}_2f + \Delta p\text{CO}_2w$ and of (right panels) the net effect on $p\text{CO}_2$ of warming and net ecosystem production of organic carbon (ΔC_{org}) and calcium carbonate ($\Delta CaCO_3$) during (a,e) spring, (b,f) summer, (c,g) autumn and (d,h) winter survey periods of 1997. Dates given as d/mo

tion and turbulent diffusion of carbon species occur ($p\text{CO}_2f$) and the $p\text{CO}_2$ expected if *in situ* warming due to heat exchange with the atmosphere is also considered ($p\text{CO}_2f + \Delta p\text{CO}_2w$). During spring, the observed $p\text{CO}_2$ increased from 325 to 345 μatm (Fig. 3a). As a consequence of the net respiration during 7 to 10 April, $p\text{CO}_2f$ was slightly lower than observed $p\text{CO}_2$. The most intense effect of *in situ* warming on $p\text{CO}_2$ was observed during 10 to 17 April, being almost nil on the other dates in April. During the summer period, $p\text{CO}_2$ (Fig. 3b) showed a time evolution inverse to t_r (Fig. 2b), with a steep increase from 290 μatm on 4 July to 370 μatm on 18 July. This $p\text{CO}_2$ increase resulted from upwelling intensification. $p\text{CO}_2f$ was always higher than the observed $p\text{CO}_2$. Biological activity had an important effect on $p\text{CO}_2$ during 1 to 7 July. Thereafter, the modulating effect of ΔC_{org} on $p\text{CO}_2$ was weakened as a result of reduced flushing times. Warming was more important in this period than during April, due to enhanced irradiance. The highest $p\text{CO}_2f + \Delta p\text{CO}_2w$ value of the 4 periods studied was reached on 18 July. This resulted from the combined effect of upwelling and warming on $p\text{CO}_2$.

During the autumn surveys (Fig. 3c), the large ΔC_{org} observed between 15 and 18 September had a dramatic effect on $p\text{CO}_2$, which was reduced by almost 70 μatm compared with $p\text{CO}_2f$. On the other dates, $p\text{CO}_2$ values ranged from 350 to 360 μatm , very close to the mean atmospheric value for 1997 (365 μatm) according to Gago et al. (2003). $p\text{CO}_2f$ exhibited the lowest variability of the 4 periods and the effect of warming on $p\text{CO}_2$ was nearly constant at approximately +5 μatm . During the winter, $p\text{CO}_2$ values ranged from 387 μatm on 5 December to 329 μatm on 8 December (Fig. 3d). As a result of the strong upwelling event at the beginning of this period, $p\text{CO}_2f$ during 1 to 5 December was the highest of all survey periods (400 μatm). In this case, a net transfer of heat from the sea to the atmosphere provoked a net decrease of 6 μatm in $p\text{CO}_2f + \Delta p\text{CO}_2w$ compared with $p\text{CO}_2f$. The effect of cooling was negligible during 8 to 11 December. Net respiration during 8 to 11 December provoked an important increase of the observed $p\text{CO}_2$ compared with $p\text{CO}_2f$.

Fig. 3 also shows the net effect of *in situ* warming, *in situ* ΔC_{org} and *in situ* $\Delta CaCO_3$ on the observed $p\text{CO}_2$, taking $p\text{CO}_2f$ as a reference value. Net *in situ* calcification had no important effect on $p\text{CO}_2$, with average values ranging from 0 to 2 μatm in April and December, respectively. Air-sea heat exchange was positive during the periods of April, July and September. Therefore there was a thermodynamic increase of $p\text{CO}_2$ due to surface heating. The average value during July was the highest, 8 μatm (Fig. 3f). In December there was a cooling of the surface layer of the ría, and

Table 7. Summary of significant regression between pCO₂, pCO_{2f}, ΔpCO_{2w}, ΔpCO_{2org} and ΔpCO_{2Ca} (n = 18 in all cases; the origin intercept is not significant in all cases, p > 0.1)

Case	Statistical results
pCO ₂ vs pCO _{2f}	r ² = 0.53; p < 0.001
pCO ₂ vs pCO _{2f} + ΔpCO _{2w}	r ² = 0.48; p < 0.001
pCO ₂ vs pCO _{2f} + ΔpCO _{2Ca}	r ² = 0.54; p < 0.001
pCO ₂ vs pCO _{2f} + ΔpCO _{2org}	r ² = 0.96; p < 0.001

this provoked an average decrease of 4 μatm in the observed pCO₂ (Fig. 3h) compared with pCO_{2f}. In all cases, ΔC_{org} was the most important process affecting ΔpCO₂. The highest average effects of ΔC_{org} occurred during July and September: −26 and −29 μatm, respectively. As indicated above, the highest decrease, 70 μatm, was observed between 15 and 18 September.

The linear correlations between observed pCO₂ and the different contributions (physical transport, *in situ* warming, *in situ* net organic carbon production and *in situ* calcification) are summarized in Table 7. It should be stressed that the advection + turbulence diffusion term explained nearly 50% of the observed variance and the ΔC_{org} term contributed the remaining 50%. The other terms, warming and calcification, had almost no effect on the correlations. When included, the term *in situ* calcification marginally improved the correlation. Fig. 4 shows observed pCO₂, pCO_{2f}, pCO_{2f} + ΔpCO_{2org} and the 1:1 line for the 18 periods between 2 consecutive surveys sampled during 1997. As can be seen, the pCO_{2f} + ΔpCO_{2org} term was almost identical to the observed pCO₂ values.

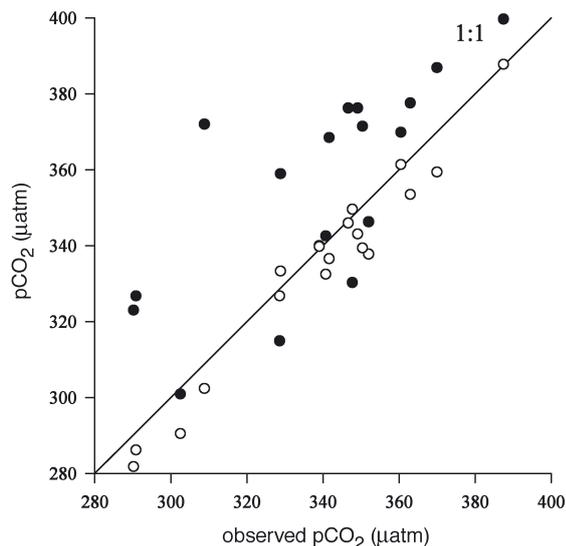


Fig. 4. Observed pCO₂ versus pCO_{2f} (●) and pCO_{2f} + ΔpCO_{2org} (○). The 1:1 line is shown

DISCUSSION AND CONCLUSIONS

According to previous studies, pCO₂ transient undersaturation generally exists in surface waters of the Spanish Rías Baixas under conditions of moderate upwelling as a result of intense inorganic carbon uptake by phytoplankton. In contrast, pCO₂ transient oversaturation occurred during strong upwelling events (Álvarez et al. 1999, Rosón et al. 1999, Gago et al. 2003) due to strong upwelling of aged pCO₂-rich Eastern North Atlantic Central Water (ENACW). During downwelling events, pCO₂-undersaturated oceanic surface waters penetrate into the rías (Pérez et al. 1999, Borges & Frankignoulle 2002).

Despite the fact that box models have been extensively used for studies of pollutant dispersal, carbon and nutrient biogeochemistry, or phytoplankton dynamics in estuaries and coastal embayments (e.g. Downing 1971, Chang & Carpenter 1985, Pérez et al. 2000), they have never been used to study the short-term variability of surface pCO₂. In this work, we present a reliable method for objectively quantifying the net effect of physical (advection and diffusion of inorganic carbon species, *in situ* warming) and biogeochemical (production and consumption of inorganic carbon species) processes on the observed surface pCO₂ that is suitable for estuaries and coastal inlets with only 1 open boundary (although it could easily be adapted to more complex coastal systems). In general, the net effect of carbon biogeochemistry upon surface pCO₂ depends on the intensity of the processes involved (ΔC_{org} and ΔCaCO₃) and the time period (t_i). Therefore, the effect of carbon biogeochemistry on surface pCO₂ is (1) determined (transport of aged pCO₂ and nutrient-rich subsurface ocean waters) and (2) modulated (flushing time) by the physical conditions of coastal upwelling systems. These general (and expected) conclusions are discussed below.

Compared with other coastal upwelling systems, 2 conspicuous characteristics of the NW Iberian shelf should be considered: (1) The coast of NW Spain lies within the North Atlantic ventilated thermocline (Castro et al. 2000), and therefore nutrient and pCO₂ levels of the upwelled ENACW are much lower than in the central waters of the South Atlantic (which upwell along the Namibia-Benguela coastline), South Pacific waters (which upwell along the Perú-Chile coastline) and those of the North Pacific (which upwell along the California-Oregon coastline). As an example, phosphate and pCO₂ levels of upwelled ENACW in NW Spain rarely exceed 1.0 μM and 450 μatm, respectively (Castro et al. 2000), whereas subsurface waters off Perú can exceed 2 μM and 1000 μatm, respectively (Copin-Montegut & Raimbault 1994). (2) Coastal winds off NW Spain are very variable, following successive

stress-relaxation cycles with a periodicity of between 5 and 15 d (Álvarez-Salgado et al. 1993); this allows efficient utilization of upwelled nutrients during the relaxation events because of enlarged flushing times that lead to $p\text{CO}_2$ undersaturation.

Our $\Delta\text{C}_{\text{org}}$ (net ecosystem production of organic carbon) estimates for the Ría de Vigo exceed the average annual net primary production of the global coastal zone (0.14 to 0.33 $\text{g C m}^{-2} \text{d}^{-1}$; Wollast 1993) and are similar to the annual mean of gross primary production proposed by Boynton et al. (1982) for coastal upwelling areas (0.82 $\text{g C m}^{-2} \text{d}^{-1}$). In support of our results, Moncoiffé et al. (2000), using the oxygen incubation method, reported an average net primary production rate in the central Ría de Vigo of 0.7 to 0.9 $\text{g C m}^{-2} \text{d}^{-1}$ during the upwelling season of 1991. The extreme short-term variability of net organic carbon production rates in our study is in accordance with the results of Tilstone et al. (1999), Moncoiffé et al. (2000) and Pérez et al. (2000). These relatively high and very variable $\Delta\text{C}_{\text{org}}$ values themselves explain ~50% of the short-term (2 to 4 d) variability in surface $p\text{CO}_2$ and are responsible for the $p\text{CO}_2$ undersaturation normally observed in the Ría de Vigo despite reduced flushing times and elevation of $p\text{CO}_2$ -rich ENACW during upwelling events.

Our ΔCaCO_3 (net ecosystem production of calcium carbonate) estimates for the Ría de Vigo, with average values ranging from 0.07 to 0.22 $\text{g C m}^{-2} \text{d}^{-1}$, are in agreement with those obtained by Rosón et al. (1999) for the adjacent Ría de Arousa. Coccolithophore blooms and coral reefs are commonly considered as being primarily responsible for calcification in the marine environment. Robertson et al. (1994) determined a mean increase in $p\text{CO}_2$ of 15 μatm due to the effect of calcification during a Northeast Atlantic coccolithophore bloom in the spring of 1991, while Frankignoulle et al. (1996) estimated that the effect of coral reefs on surface $p\text{CO}_2$ in French Polynesia is negligible on a daily scale. The latitude and the hydrographic regime of the NW Iberian upwelling system do not allow development of either coccolithophore blooms (e.g. Figueiras & Ríos 1993) or corals. However, another conspicuous characteristic of the Spanish Rías Baixas should not be forgotten: they support the most intensive mussel cultures in the world (Tenore et al. 1982), representing 40% of the European and 20% of the world production in 1997 (Labarta 2000). The culture of mussels on hanging ropes in the Ría de Vigo produced $\sim 5 \times 10^7$ kg wet weight in 1997. Since mussel shelves represent ~50% of the wet weight of commercial mussels and ~90% of the shelves are comprised of CaCO_3 (Rosón et al. 1999), the mussels of the Ría de Vigo would have produced an average of $\sim 0.06 \text{ g C m}^{-2} \text{d}^{-1}$ of CaCO_3 during 1997. This is reflected in our low

ΔCaCO_3 estimates. The effect of calcification on surface $p\text{CO}_2$ variability in the Ría de Vigo is less than 5 μatm .

With regard to the effect of *in situ* warming of the surface layer of the Ría de Vigo through heat exchange across the sea surface, $p\text{CO}_2$ ranges from -6 to $+11$ μatm at *in situ* warming values from -0.4 to $+0.8^\circ\text{C}$ respectively. This is again negligible compared with the effects of circulation and $\Delta\text{C}_{\text{org}}$. The effect of *in situ* warming is probably more pronounced in coastal upwelling systems at lower latitudes than NW Spain (40 to 43°N), e.g. along Namibia-Benguela and Perú ($<35^\circ\text{S}$) coastlines and in Southern California ($<35^\circ\text{N}$), because of enhanced solar irradiation. *In situ* warming would also be important in upwelling systems in which the upwelled central waters are colder than off NW Spain (12 to 14°C), e.g. Oregon (8 to 10°C), because of enhanced heat exchange across the sea surface.

In this study, we have separated the effects of advection + diffusion, air-sea heat exchange, net organic carbon production and calcification on surface $p\text{CO}_2$ variability of a coastal upwelling system. The coupling of physical and biological processes—upwelling of cool aged subsurface ocean waters to the photic layer of the coastal ecosystem, where they undergo heating and promote intensified primary production rates—has been extensively described in the literature, but no studies have determined quantitatively the net effect of these processes on surface $p\text{CO}_2$ dynamics on a short time-scale. Using a simple box model, Louanchi et al. (1999) found that biological activity can contribute up to 45% of sea-surface $p\text{CO}_2$ variability in the Southern Ocean on a monthly scale. Sabine & Key (1998) applied a process analysis to CO_2 data for the Southern Ocean and determined that $p\text{CO}_2$ variability is strongly dependent on biological as well as physical processes. This methodology was applied to the Ría de Vigo by Álvarez et al. (1999), who showed that organic matter production explains almost 60% of the $p\text{CO}_2$ variability on a monthly scale. Our quantitative approach has shown for the first time that contributions of physical and biogeochemical factors to surface $p\text{CO}_2$ variability on a half-weekly scale are of the same order in highly dynamic coastal upwelling systems such as the Ría de Vigo.

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