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 result 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...
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 CO₂ to the atmosphere? (e.g. Watson 1995). We try to clarify this question by separating the physical and biogeochemical components of seawater pCO₂ 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 (CT) and total alkalinity (AT).

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 pCO₂ 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 km³) 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 AT determination were collected from 3 to 5 depths with 5l 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). AT 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 AT measurements was ±0.002 and 1.4 µmol 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. CT and pCO₂ were calculated from pH and AT using the carbonic acid constants of Mehrbach et al. (1973) and the solubility constant of...
Weiss (1974). The accuracy of pH and AT measurements produces an estimated error of ±3 μmol kg⁻¹ and 3 µatm for calculated CT 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 Oitábén-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 CT and AT in the surface and bottom layer at each boundary and in the box (volume of water considered) were calculated from CT and AT 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, CT and AT was assumed. This approach has long been used to study the fate of chemicals discharged 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:

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

(1)

where C is average salinity, temperature, CT or AT 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 (\(\bar{F}_{\text{CO₂}}\)) in the case of CT 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 \(<C_{S2}>/C>_\text{box}\), 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 (~1.2 km²).

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, CT and AT convective and diffusive fluxes. NEB represents the net ecosystem budget of C (salinity, temperature, CT or AT). For salinity and temperature, NEB = 0; for CT, NEB = \(-\Delta C_{\text{org}} - \Delta CaCO_3\), where \(\Delta C_{\text{org}}\) and \(\Delta CaCO_3\) are the net ecosystem production of organic carbon and calcium carbonate, respectively. According to Broecker & Peng (1982), the NEB of AT equals – NEB of nitrate (= [^{15}N] × \(\Delta C_{\text{org}}\)) in the case of phytoplankton organic carbon, and equals – 2 × \(\Delta CaCO_3\) in the case of calcium carbonate. Therefore, the NEB of AT is equal to \((106/16) \times \Delta C_{\text{org}} - 2 \times \Delta CaCO_3\). Integration of Eq. (1) between 2 consecutive surveys yields:

\[
C_2 = C_1 \times e^{–B_s \Delta t} + \left(\frac{A}{B}\right) \times (1 - e^{–B_s \Delta t})
\]

\[
+ \left(\frac{\text{NEB}}{B}\right) \times (1 - e^{–B_s \Delta t})
\]

(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 (\(B \sim \frac{1}{\text{t}_\text{m}}, \text{d}^-1\)) of the surface layer of the ría, and the term \(1/B \times (1 - e^{–B_s \Delta t})\) is the time factor that indicates the temporal extension of the contributions of physical transport (A) and biogeochemistry (NEB) to the net change of C between 2 consecutive surveys.

Eq. (2) in the case of CT and AT 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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_T)</td>
<td>Total alkalinity (µmol kg(^{-1}))</td>
</tr>
<tr>
<td>(C_T)</td>
<td>Total inorganic carbon concentration (µmol kg(^{-1}))</td>
</tr>
<tr>
<td>(C_L)</td>
<td>Average value of variable (C) in the bottom layer</td>
</tr>
<tr>
<td>(C_R)</td>
<td>Average value of variable (C) in the river flow</td>
</tr>
<tr>
<td>(C_U)</td>
<td>Average value of variable (C) in the upper layer</td>
</tr>
<tr>
<td>(C_S)</td>
<td>Average value of variable (C) in the upper layer of the outer boundary</td>
</tr>
<tr>
<td>(\Delta C)</td>
<td>Average value of variable (C) in the boundary between the upper and lower layers</td>
</tr>
<tr>
<td>(\Delta C_{\text{CaCO}_3})</td>
<td>Average net ecosystem production (g C m(^{-2}) d(^{-1})) of calcium carbonate</td>
</tr>
<tr>
<td>(\Delta C_{\text{org}})</td>
<td>Average net ecosystem production (g C m(^{-2}) d(^{-1})) of organic carbon</td>
</tr>
<tr>
<td>(\Delta pC)</td>
<td>Partial pressure of carbon dioxide (µatm)</td>
</tr>
<tr>
<td>(\Delta pC_{\text{org}})</td>
<td>Partial pressure of carbon dioxide (µatm) resulting from advection and diffusion</td>
</tr>
<tr>
<td>(\Delta pC_{\text{CaCO}_3})</td>
<td>Partial pressure of carbon dioxide (µatm) change due to net calcium carbonate production</td>
</tr>
<tr>
<td>(\Delta pC_{\text{org}})</td>
<td>Partial pressure of carbon dioxide (µatm) change due to net organic carbon production</td>
</tr>
<tr>
<td>(\Delta pC_{\text{CaCO}_3})</td>
<td>Partial pressure of carbon dioxide (µatm) change due to net calcium carbonate production</td>
</tr>
<tr>
<td>(Q_{\text{off}})</td>
<td>Offshore Ekman transport (m(^3) s(^{-1}) km(^{-1}) coast)</td>
</tr>
<tr>
<td>(Q_{\text{in}}, Q_{\text{out}})</td>
<td>Average bottom and surface horizontal convective water fluxes (m(^3) s(^{-1})) at the open boundaries of the study area</td>
</tr>
<tr>
<td>(Q_{\text{z}})</td>
<td>Average vertical convective water flux (m(^3) s(^{-1}))</td>
</tr>
<tr>
<td>(Q_{\text{r}})</td>
<td>Average river water flux (m(^3) s(^{-1}))</td>
</tr>
<tr>
<td>(t_{\text{f}})</td>
<td>Average flushing time (d)</td>
</tr>
<tr>
<td>(V_U)</td>
<td>Average volume (m(^3)) of the upper layer</td>
</tr>
</tbody>
</table>

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

and

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

The use of 2 equations (Eqs. 3 & 4) with 2 unknowns \((\Delta C_{\text{org}}\) and \(\Delta C_{\text{CaCO}_3}\) allows estimation of the net ecosystem production of organic carbon \((\Delta C_{\text{org}})\) and calcium carbonate \((\Delta C_{\text{CaCO}_3})\) 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 \(pC\) for the upper layer of the ría.

Quantification of effects of different factors on seawater \(pC\). The observed \(pC\) of the surface layer of the ría is the result of physical transport of salt, heat, \(C_T\) and \(A_T\) (\(pC_{\text{off}}\) and \(pC_{\text{in}}\)), in situ warming (\(pC_{\text{CaCO}_3}\)), in situ net organic carbon production (\(\Delta pC_{\text{org}}\)) and in situ net calcification (\(\Delta pC_{\text{CaCO}_3}\)). Over short timescales, the air-sea exchange of \(CO_2\) does not have an important effect on variability of seawater \(pC\) (e.g. Frankignoule 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 \(pC\) can be expressed as:

\[
pC = pC_{\text{off}} + \Delta pC_{\text{org}} + \Delta pC_{\text{CaCO}_3} \tag{5}
\]

The effect of transport (advection and turbulent diffusion) and in situ warming on \(pC\) (\(pC_{\text{off}} + \Delta pC_{\text{CaCO}_3}\)) can be evaluated by calculating \(C_T\) and \(A_T\) with Eqs. (3) & (4) for \(\Delta C_{\text{org}} = 0\) and \(\Delta C_{\text{CaCO}_3} = 0\) and then estimating the \(pC\) with the carbonic acid system constants.

\(\Delta pC_{\text{CaCO}_3}\) was determined by comparing \(pC_{\text{off}} + \Delta pC_{\text{CaCO}_3}\) for the observed temperature of the surface layer with \(pC_{\text{off}} + \Delta pC_{\text{CaCO}_3}\) for the temperature expected if the heat exchange across the sea surface \((\tilde{H})\) is set to zero when solving Eq. (2) for temperature.

The effect of in situ net calcium carbonate production (\(\Delta pC_{\text{CaCO}_3}\)) was evaluated by comparing \(pC_{\text{off}} + \Delta pC_{\text{CaCO}_3}\) with the \(pC\) resultant from \(C_T\) and \(A_T\) calculated with Eqs. (3) & (4) for \(\Delta C_{\text{org}} = 0\). (Note that Eqs. 3 & 4 were initially to determine \(\Delta C_{\text{org}}\) and \(\Delta C_{\text{CaCO}_3}\)). In this estimation we used the calculated \(\Delta C_{\text{CaCO}_3}\) and assumed \(\Delta C_{\text{org}} = 0\) to evaluate \(C_T\) and \(A_T\). Finally, the effect of in situ net organic carbon production (\(\Delta pC_{\text{org}}\)) was evaluated following the same procedure but with \(\Delta C_{\text{CaCO}_3} = 0\) and the \(\Delta C_{\text{org}}\) initially calculated.

Robustness of estimation of effects of different factors on seawater \(pC\). 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
the average properties of the surface layer, and (4) error transmission in the calculation of $pCO_2$ 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 temperature (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 ($Q_{S1}$, $Q_{S4}$) 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 ($Q_B$) 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 $pCO_2$.

Table 6 summarises the error that each flux ($Q_{S1}$, $Q_{S4}$, $Q_Z$, $M_Z$ and $Q_B$ m$^3$ s$^{-1}$), air-sea heat transfer ($\bar{H}$ °C m$^3$ s$^{-1}$) and $C_T$ and $A_T$ concentrations ($C_{S1}$, $C_{S4}$, $C_L$, $C_U$ and $C_Z$ μmol kg$^{-1}$) for 18 sampling intervals between 2 consecutive surveys performed in the Ría de Vigo during 1997.
when the effects of advection + diffusion, warming, net organic carbon production and net calcification are considered separately. Note that the errors produced by Q and H are quite low (0.2 µatm). Vertical and horizontal advection and mixing as well as the error associated with the representativeness of the property determinations introduce errors of ~3 µatm. $\Delta C_{\text{org}}$ and $\Delta \text{CaCO}_3$ 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 $\Delta C_{\text{org}}$ and $\Delta \text{CaCO}_3$ are ~4 and ~1 µatm, respectively. Finally, note that the random perturbation procedure leads to an average total error of 7.2 µatm, which is much lower than the sum of the independent contribution of each flux and property (13.4 µatm).

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)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_Z$</td>
<td>44</td>
<td>7</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>$Q_S$, $Q_H$</td>
<td>15</td>
<td>5</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>$M_Z$</td>
<td>48</td>
<td>13</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

### 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 $t_r \times (1 - e^{-B t_r})$, which modulates the effects of net input and the NEB of C, is not significantly different from $t_r \times (1 - e^{-B t_r})$, the latter being independent of species (salinity, temperature, $C_T$ or $A_T$). Fig. 2 shows the short-term evolution of $t_r$ and $t_r \times (1 - e^{-B t_r})$ 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 m³ s⁻¹ 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 $t_r \times (1 - e^{-B t_r})$ 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 m³ s⁻¹ km⁻¹. In contrast, continental runoff was extremely low at <7 m³ s⁻¹. A decrease of $t_r$ from the beginning to the end of the

Table 6. Average error in estimation of calculated pCO₂ (µatm), standard deviation of 50 solutions, due to errors in river flow and heat-exchange flux ($Q_S$, $H$, respectively), vertical advection ($Q_Z$), horizontal advection ($Q_S$, $Q_H$), vertical mixing ($M_Z$) and representativeness of property concentrations (salinity, temperature, $A_T$ and $C_T$)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Advection</th>
<th>Heat</th>
<th>$\Delta C_{\text{org}}$</th>
<th>$\Delta \text{CaCO}_3$</th>
<th>Net error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_S$, $H$</td>
<td>0.3</td>
<td>0.2</td>
<td>-0</td>
<td>-0</td>
<td>0.2</td>
</tr>
<tr>
<td>$Q_Z$</td>
<td>2.8</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2.8</td>
</tr>
<tr>
<td>$Q_S$, $Q_H$</td>
<td>1.6</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
<td>1.7</td>
</tr>
<tr>
<td>$M_Z$</td>
<td>2.9</td>
<td>0.1</td>
<td>0.1</td>
<td>-0</td>
<td>3.0</td>
</tr>
<tr>
<td>$S$, $T$, $A_T$, $C_T$</td>
<td>2.8</td>
<td>-0</td>
<td>4.4</td>
<td>1.3</td>
<td>5.7</td>
</tr>
<tr>
<td>Total</td>
<td>4.8</td>
<td>0.2</td>
<td>4.3</td>
<td>1.4</td>
<td>7.2</td>
</tr>
</tbody>
</table>
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 offshore Ekman transport ranged from –30 to 160 m$^3$ s$^{-1}$ km$^{-1}$, with an average value of 109 m$^3$ s$^{-1}$ km$^{-1}$, and the continental runoff was again quite limited: <5 m$^3$ 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 m$^3$ s$^{-1}$ km$^{-1}$ on 1 to 5 December to downwelling-favorable southerly winds producing an offshore Ekman transport of –1500 m$^3$ s$^{-1}$ km$^{-1}$ on 8 to 12 December. Continental runoff was very high during the winter period (average 40 m$^3$ 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 ($\Delta \text{C}_{\text{org}}$) and of calcium carbonate ($\Delta \text{CaCO}_3$) in the upper layer of the Ría during the 4 survey periods is also presented in Fig. 2. $\Delta \text{CaCO}_3$ was very low during the 4 periods, being slightly intensified in the autumn surveys (18 to 25 September average, 0.2 g C m$^{-2}$ d$^{-1}$). An increase in $\Delta \text{C}_{\text{org}}$ 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 $\Delta \text{C}_{\text{org}}$ values were observed ($\Delta \text{C}_{\text{org}} = -0.86$ g C m$^{-2}$ d$^{-1}$), denoting the dominance of respiration processes. At the beginning of the summer (Fig. 2f), the highest $\Delta \text{C}_{\text{org}}$ for this period was observed (4 to 8 July = 2 g C m$^{-2}$ d$^{-1}$). In contrast, strong upwelling occurred at the end of this period (the lowest $t_r$ was observed) and $\Delta \text{C}_{\text{org}}$ was reduced. The highest $\Delta \text{C}_{\text{org}}$ was found on 15 to 18 September (2.5 g C m$^{-2}$ 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). $\Delta \text{C}_{\text{org}}$ rates during the other surveys in September fluctuated between 0.0 and 0.8 g C m$^{-2}$ 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 $\Delta \text{C}_{\text{org}}$ (Fig. 2h): from a production of 1.4 g C m$^{-2}$ d$^{-1}$ during 5 to 8 December to a respiration of –1.3 g C m$^{-2}$ d$^{-1}$ during 8 to 11 December. The pronounced $\Delta \text{C}_{\text{org}}$ minimum at the end of the winter period coincided with remarkably negative values of $-Q_X$. 

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 ($\Delta \text{C}_{\text{org}}$) and calcium carbonate ($\Delta \text{CaCO}_3$) during (a,e) spring, (b,f) summer, (c,g) autumn and (d,h) winter survey periods of 1997. Dates given as d/mo.
Physical and biogeochemical components of surface pCO₂ variability

Fig. 3 shows the short-term evolution of observed pCO₂ (see Table 4), the pCO₂ expected if only advection and turbulent diffusion of carbon species occur (pCO₂f) and the pCO₂ expected if in situ warming due to heat exchange with the atmosphere is also considered (pCO₂f + ΔpCO₂w). During spring, the observed pCO₂ increased from 325 to 345 µatm (Fig. 3a). As a consequence of the net respiration during 7 to 10 April, pCO₂f was slightly lower than observed pCO₂. The most intense effect of in situ warming on pCO₂ was observed during 10 to 17 April, being almost nil on the other dates in April. During the summer period, pCO₂ (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 pCO₂ increase resulted from upwelling intensification. pCO₂f was always higher than the observed pCO₂. Biological activity had an important effect on pCO₂ during 1 to 7 July. Thereafter, the modulating effect of ΔCorg on pCO₂ 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 pCO₂f + ΔpCO₂w value of the 4 periods studied was reached on 18 July. This resulted from the combined effect of upwelling and warming on pCO₂.

During the autumn surveys (Fig. 3c), the large ΔCorg observed between 15 and 18 September had a dramatic effect on pCO₂, which was reduced by almost 70 µatm compared with pCO₂f. On the other dates, pCO₂ values ranged from 350 to 360 µatm, very close to the mean atmospheric value for 1997 (365 µatm) according to Gago et al. (2003). pCO₂f exhibited the lowest variability of the 4 periods and the effect of warming on pCO₂ was nearly constant at approximately +5 µatm. During the winter, pCO₂ 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, pCO₂f 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 pCO₂f + ΔpCO₂w compared with pCO₂f. 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 pCO₂ compared with pCO₂f.

Fig. 3 also shows the net effect of in situ warming, in situ ΔCorg and in situ ΔCaCO₃ on the observed pCO₂, taking pCO₂f as a reference value. Net in situ calcification had no important effect on pCO₂, 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 pCO₂ 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
this provoked an average decrease of 4 µatm in the observed pCO₂ (Fig. 3h) compared with pCO₂f. In all cases, ΔCorg was the most important process affecting ΔpCO₂. The highest average effects of ΔCorg 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 ΔCorg 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, pCO₂f, pCO₂f + ΔpCO₂w and the 1:1 line for the 18 periods between 2 consecutive surveys sampled during 1997. As can be seen, the pCO₂f + ΔpCO₂w term was almost identical to the observed pCO₂ values.

### 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 (ΔCorg and ΔCaCO₃) and the time period (t). 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 pCO2 undersaturation.

Our $\Delta C_{\text{org}}$ (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 g C m$^{-2}$ 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 g C m$^{-2}$ 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 g C m$^{-2}$ 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 $\Delta C_{\text{org}}$ values themselves explain ~50% of the short-term (2 to 4 d) variability in surface pCO2 and are responsible for the pCO2 undersaturation normally observed in the Ría de Vigo despite reduced flushing times and elevation of pCO2-rich ENACW during upwelling events.

Our $\Delta C_{\text{CaCO3}}$ (net ecosystem production of calcium carbonate) estimates for the Ría de Vigo, with average values ranging from 0.07 to 0.22 g C m$^{-2}$ 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 pCO2 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 pCO2 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 ~5 × 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 CaCO3 (Rosón et al. 1999), the mussels of the Ría de Vigo would have produced an average of ~0.06 g C m$^{-2}$ d$^{-1}$ of CaCO3 during 1997. This is reflected in our low $\Delta C_{\text{CaCO3}}$ estimates. The effect of calcification on surface pCO2 variabiliy 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, pCO2 ranges from –6 to +11 µatm at in situ warming values from –0.4 to +0.8°C respectively. This is again negligible compared with the effects of circulation and $\Delta C_{\text{org}}$. 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°S) coastlines and in Southern California (<35°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 pCO2 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 pCO2 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 pCO2 variability in the Southern Ocean on a monthly scale. Sabine & Key (1998) applied a process analysis to CO2 data for the Southern Ocean and determined that pCO2 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 pCO2 variability on a monthly scale. Our quantitative approach has shown for the first time that contributions of physical and biogeochemical factors to surface pCO2 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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