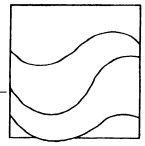

Temporal variability of atmospheric CO_2 of the Spanish Atlantic Coast

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Abstract − The variability of the molar fraction of atmospheric CO_2 (xCO_2^a) and wind speed and direction were investigated in a coastal embayment located in the west European coast, *ría de Vigo*, NW Spain, along daily and seasonal time scales. Observations in the *ría* showed that xCO_2^a on a short time scale presented a much wider variability than seawater molar fraction (xCO_2^w), in addition, a significant covariation between xCO_2^a and wind was found. A sluggish atmospheric renewal due to weak winds was associated with high values of xCO_2^a, whereas higher oceanic winds renovate the air column with more stable and constrained xCO_2^w values (from 350 to 370 ppm). The impact of anomalously high xCO_2^a on CO_2 air–sea fluxes is practically not significant, due to the kinetic control exerted by wind speed by means of the gas exchange coefficient. A seasonal cycle for the atmospheric molar fraction of CO_2 in the Southwest European Coast was obtained. Using this approach for xCO_2^a in calculating the air–sea CO_2 fluxes avoids under/overestimations of the fluxes on particular short periods of time, whilst using a mean xCO_2^a seasonal value for longer time scales has no significant effect on the final net magnitude of the air–sea flux.

Résumé − Variabilité temporelle du CO_2 atmosphérique au large de la côte ouest d'Espagne. La variabilité de la fraction molaire du CO_2 atmosphérique (xCO_2^a), la vitesse et direction du vent ont été étudiés sur une baie côtière de la côte ouest de l'Europe, la *ría de Vigo*, au nord-ouest de l'Espagne, de l'échelle journalière à celle de la saison. Des observations dans la *ría* ont montré que la xCO_2^a, à courte échelle de temps, présentait une variabilité plus grande que la fraction molaire de l'eau de mer (xCO_2^w). Une corrélation significative a été trouvée entre la xCO_2^a et le vent. Une lente rénovation atmosphérique, due aux faibles vents, est associée aux hautes valeurs de la xCO_2^a, tandis que les vents océaniques les plus forts renouvellent la colonne d'air avec une xCO_2^w plus stable et dans une gamme plus étroite (de 350 à 370 ppm). L'impact d'une xCO_2^w anormalement élevée sur les flux air–mer n'est pas significatif, en raison du contrôle cinétique exercé par la vitesse du vent, par le lien du coefficient d'échange air–mer. Un cycle saisonnier pour la fraction molaire atmopshérique de CO_2 est mis en évidence. En utilisant cette approximation pour la xCO_2^a, on pourra calculer les flux air–mer en évitant les sous-estimations et les sur-estimations des flux pour les courtes périodes de temps. En utilisant une valeur moyenne saisonnière de la xCO_2^a pour des échelles de temps longues, on ne rencontrera pas d'effet significatif sur la grandeur nette finale du flux air–mer.

temporal variability / atmospheric CO_2 / air–sea exchange / Spanish Atlantic Coast

variabilité temporelle / CO_2 atmosphérique / échange air–mer / côte atlantique espagnole

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1. INTRODUCTION

The net flux of CO_2 through the air–sea interface is described as:

$$F = Kw \times S \times (pCO_2^w - pCO_2^a) \quad (1)$$

where *Kw* is the gas transfer velocity, *S* is the CO_2 solubility, and pCO_2^w and pCO_2^a stand for the partial pressure of CO_2 in seawater and air, respectively. Several parameterisations of *Kw* have been proposed based on laboratory and field studies, taking into account a wide variety of factors affecting air–sea exchange: wind, bubbles, turbulence, temperature, atmospheric boundary layer stability, and drag coefficients (Smethie et al., 1985; Liss and Merlivat, 1986; Woolf, 1997; Tans et al., 1990; Wanninkhof, 1992; Wanninkhof and McGillis, 1999). Examples of the most widely used parameterisations of *Kw* with wind speed are shown in *figure 1*. Despite the differences, it is clear that wind speed exerts a kinetic control on the fluxes through its non-linear relationship with *Kw*.

The spatio-temporal variability of the atmospheric molar fraction of CO_2 (xCO_2^a) is much smaller than that of seawater (xCO_2^w), mainly because of the high lateral atmospheric mixing rates, which tend to rapidly homogenise xCO_2^a. Several factors contribute to control xCO_2^w: thermohaline variability, biological activity and air–sea exchange. The atmospheric molar fraction of CO_2 is mainly affected by exchanges with terrestrial biosphere and the ocean, anthropogenic emissions, such as burning of fossil fuels, and punctual sources, such as volcanic eruptions. The magnitude of the seasonal variation of xCO_2^a is highest at northern latitudes and decreases southwards (Komhyr et al., 1985; Conway et al., 1988; Conway et al., 1994), going from 1–2 ppm in the Southern Hemisphere, to 16 ppm in the North Pole, and temperate regions in the Northern Hemisphere having a mean seasonal cycle of 6 ± 2 ppm (Komhyr et al., 1985). This contrasting behaviour of xCO_2^a in both hemispheres stems mainly from the different land-to-ocean area ratios, the terrestrial area in the Southern Hemisphere being much lower, and the effect of the terrestrial ecosystems being rapidly homogenised by the atmospheric circulation. In contrast, in the Northern Hemisphere the agricultural, industrial or even the forest areas are much wider.

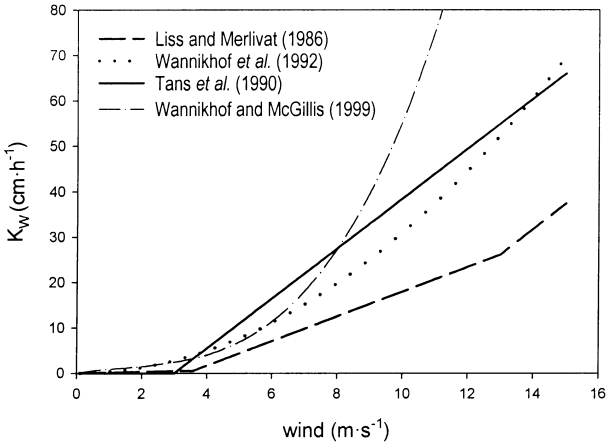

Figure 1. Gas exchange (*Kw*, in cm h^{-1}) relationships with wind (m s^{-1}) reported in the literature, solid line from Tans et al. (1990), dotted curve from Wanninkhof (1992), dashed line from Liss and Mervilat (1986) and dotted dashed line from Wanninkhof and McGillis (1999).

As an example of the seasonal and inter-annual variation of xCO_2^a in the temperate Northern Hemisphere, *figure 2* shows the temporal variability of xCO_2^a at the Izaña station (Canary Islands), comprised within the global air-sampling network of the 'Climate Monitoring and Diagnostic Laboratory'. From 1991 to 1998 xCO_2^a showed an annual increasing tendency coupled with a seasonal cycle, which have been fitted in a least-squares sense to the equation:

$$xCO_2^a = 355.3 + 1.57\,(t - 33560)/365.25 + 3.35 \sin(2\pi/365.25\,t) - 1.12 \sin[4\pi/365.25\,(t - 24)] \quad (2)$$

where *t* is the julian day. The equation adjusts a 92.5% of the observed data variability, with a mean error of 1 ppm. On the basis of this equation, xCO_2^a increased by 1.57 ± 0.03 ppm year^{-1} for the past seven years, and the seasonal cycle had two harmonics, an annual and a seasonal one, with a peak-to-peak amplitude of 7.4 ± 0.2 ppm. The reliability of this equation to predict xCO_2^a is also shown in *figure 2*, where mean values of measured xCO_2^a data from the region north of the Canary Islands (January 1997) and the area south of the Azores Islands (August 1998) are also represented.

Until the development and extensive use of underway CO_2 equilibration systems, xCO_2^a variability in open ocean waters was disregarded and assumed as constant

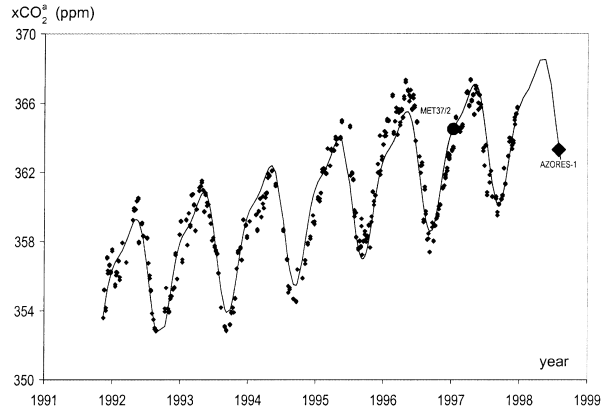

Figure 2. Temporal series of atmospheric CO_2 molar fraction measured at Izaña (Canary Islands) and its fitted curve. Mean $xCO_2{}^a$ measured in the area north of the Canary Islands in January 1997 on board *Meteor* (solid circles). Mean $xCO_2{}^a$ measured in the Azores area in August 1998 on board the *BIO Hespérides* (diamonds).

in the air–sea CO_2 exchange calculations (Kempe and Pegler, 1991; Metzl et al., 1991; DeGrandpre et al., 1998), or even in coastal or estuary areas (Frankignoulle et al., 1996; Boehme et al., 1998). However, nowadays $xCO_2{}^a$ and $xCO_2{}^w$ are widely monitored, showing that $xCO_2{}^a$ can suffer significant variations in open oceans (Andrié et al., 1986; Lundberg, 1994; Wong et al., 1995; Goyet et al., 1998), estuaries (Raymond et al., 1997), lakes (Cole and Caraco, 1998) and coastal areas (Bakker et al., 1996).

Previous studies in the coastal margin of the Iberian Peninsula have assumed no significant impact of the seasonal and daily $xCO_2{}^a$ variations on the air–sea exchanges (Ríos et al., 1995; Pérez et al., 1999; Rosón et al., 1999; Álvarez et al., 1999). In this work we will evaluate the reliability and degree of confidence of this hypothesis, using meteorological and $xCO2^a$ data recorded in a coastal embayment in the NW Iberian Peninsula, *ría de Vigo*, during daily and seasonal time scales.

2. MATERIALS AND METHODS

In order to assess the daily variability of $xCO_2{}^a$, an hour-long transect in the *ría de Vigo* (*figure 3*) was sampled during 25 h (11–12 July 1997). Meteorological variables, wind speed and direction, along with $xCO_2{}^a$ and $xCO_2{}^w$ were measured. Both $xCO_2{}^a$ and $xCO_2{}^w$ were

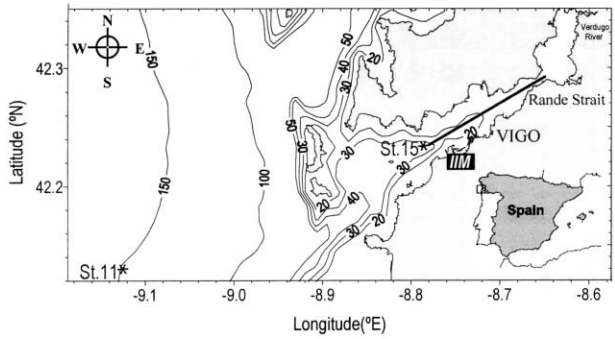

Figure 3. Location of the *ría de Vigo*, with the position of the *Instituto de Investigaciones Marinas* (IIM), the 1-h transect and the stations sampled by Álvarez et al. (1999) in the inner *ría* (St. 15) and the adjacent platform (St. 11).

determined using an underway equilibration system coupled with a non-dispersive infrared detector for CO_2 and H_2O, as described in Körzinger et al. (1996). The equipment was calibrated with two standards, CO_2-free air and high CO_2 standard gas, with a certified concentration of 407 ppm (*Instituto Meteorologico Nacional*, Izaña, Canary Islands). The time constant of the system is about 65 s, and the accuracy is less than 0.5 ppm.

In this case CO_2 fluxes were calculated using equation 1, thus, both $xCO_2{}^a$ and $xCO_2{}^w$ were converted to $pCO_2{}^a$ and $pCO_2{}^w$ as described in Wanninkhof and Thoning (1993) and DOE (1994). We have employed the parameterisation of *Kw* suggested by Liss and Merlivat (1986), which is based on laboratory and lacustrine experiments, and supported by the results from ocean experiments at high wind speed (Watson et al., 1991). Solubility, *S*, was calculated from Weiss (1974).

The seasonal variability of $xCO_2{}^a$ was assessed measuring meteorological variables, and $xCO_2{}^a$ (as previously described) at the meteorological station located in the *Instituto de Investigacións Mariñas* (*figure 3*), 15 m above the sea level and 300 m inshore, from February 1998 to April 1999.

3. RESULTS AND DISCUSSION

3.1. Daily variability

Figure 4a shows the 25 h variability of $xCO_2{}^a$, $pCO_2{}^w$, and the wind component parallel to the *ría* axis (v_P), and

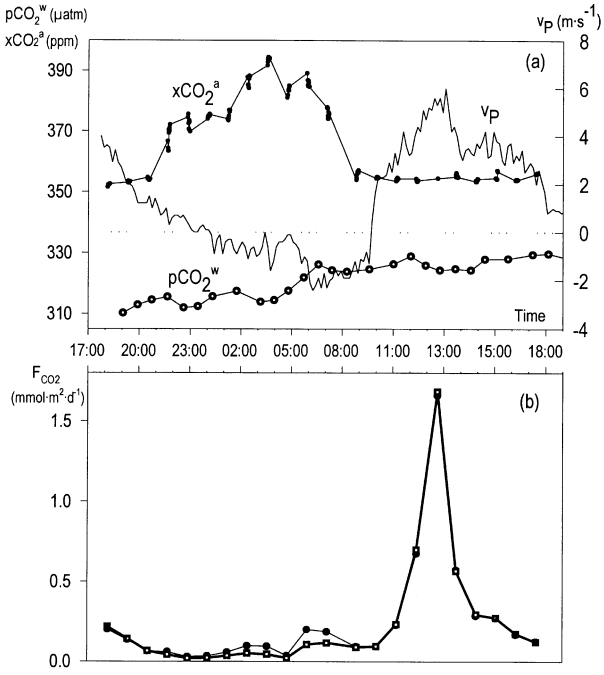

Figure 4. a. Molar fraction of air (xCO_2^a, in ppm), partial pressure of seawater CO_2 (pCO_2^w, in µatm), and parallel to the *ría* axis wind component (v_P, in m s^{-1}) measured during 25 h (11–12 July 1997) along the 1-h transect in the *ría*. **b.** Air–sea CO_2 fluxes (in mmol m^{-2} d^{-1}) calculated with a constant value for pCO_2^w of 321 µatm and measured pCO_2^a (solid circles), or a constant pCO_2^a value equal to 355 µatm (open squares).

figure 4b the CO_2 fluxes along a transect in the *ría de Vigo* (*figure 3*). The wind regime is dominated by sea breezes, light winds blowing from land (negative v_P) during the night, and stronger winds blowing from the sea during the day. Seawater pCO_2 presented a mean value of 321 ± 8 µatm, increasing from 305 to 330 µatm at a rate about 0.8 µatm h^{-1} due to the strong upwelling event in the *ría* in this period, which elevates enriched-CO_2 water into the *ría* (Álvarez et al., 1999; Gago, 2000).

The xCO_2^a range of variation is much wider, reaching the highest values (> 380 ppm) during the night when the wind is lower than 2 m s^{-1} and mainly blowing from land. Whereas during the day, xCO_2^a was quite stable with a mean value of 355 ± 1 ppm and winds stronger than 3 m s^{-1} blowing from the sea. Therefore, the xCO_2^a variability seemed to be modulated by the wind regime in the *ría*: when the atmosphere is stagnating because of prevalent weak winds xCO_2^a increases because of local anthropogenic and terrestrial effects, whereas when the winds blow stronger the atmosphere column is rapidly renovated, and xCO_2^a tends to reach a stable seasonal mean value.

Which is the effect of these short-time wide variations of xCO_2^a on CO_2 air–sea exchange? In order to elucidate the effect of wide variations of xCO_2^a on CO_2 air–sea exchange we calculated the CO_2 air–sea fluxes with a mean value for pCO_2^w of 321 µatm. If this pCO_2^w is combined with the measured values for pCO_2^a, the mean daily flux is 0.24 ± 0.36 mmol m^{-2} day^{-1}. Whilst if we use a mean and constant value for pCO_2^a of 355 µatm (corresponding seasonal value from fitted curve in *figure 2*, equation 2), the mean flux is 0.23 ± 0.37 mmol m^{-2} day^{-1}. The difference between both approaches is very low (*figure 4b*), with maximum values in the transition from low to high wind speeds. Thus, although xCO_2^a varied significantly, its influence on the CO_2 air–sea exchange was hampered due to the non-linear relationship between wind speed and *Kw*, which acted as a threshold for the influence of high values of xCO_2^a on CO_2 fluxes. Hence, with the aim of investigating the relationship between the wind regime and xCO_2^a we proceeded to record their variation for a longer period of time.

3.2. Seasonal variability

As previously commented, during a 14-month period wind speed and direction along with xCO_2^a were measured every 10 min at the meteorological station. The data set was reduced calculating 20 min averages.

Figure 5 shows the wind components perpendicular (v_T) and parallel (v_P) to the *ría* axis. The component v_P was mainly positive, indicating prevalent southwesterly winds, blowing from the ocean. Periods with negative v_P indicate northeasterly winds, usually associated with the sea breeze regime.

Wind speed and xCO_2^a presented a similar coupling as explained in the previous paragraph. As an example, v_P and xCO_2^a from an 8-day period in October 1998 are showed in *figure 6*. The breeze regime is clearly noticed, strong westerly winds are associated with low xCO_2^a, between 360–370 ppm. Whereas, low winds preferentially blowing from land were related with high and more variable xCO_2^a, generally higher than 400 ppm.

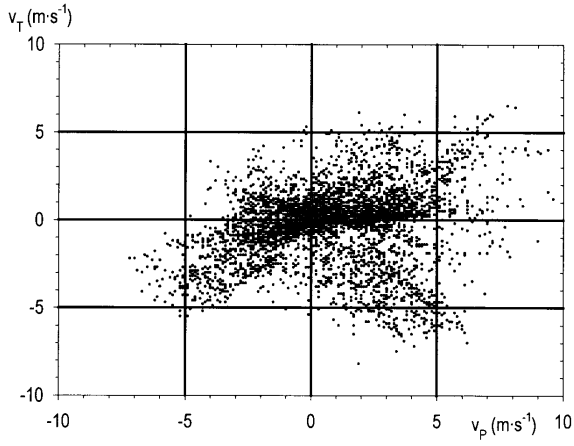

Figure 5. Wind components, parallel (v_P, in m s^{-1}) and perpendicular (v_T, in m s^{-1}) to the *ría* axis measured during the period from February 1998 to April 1999.

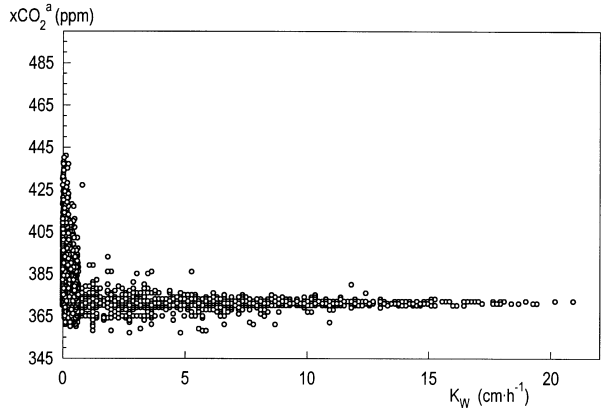

Figure 7. Atmospheric molar fraction of CO_2 (xCO_2^a in ppm) versus gas exchange coefficient (Kw, in cm h^{-1}) calculated as Liss and Merlivat (1986) for the series of data recorded from February 1998 to April 1999 in the *ría*.

As Kw kinetically controls the CO_2 fluxes, we represented xCO_2^a and Kw for the whole data set. *Figure 7* clearly shows that it is possible to measure any xCO_2^a between 350 and 480 ppm when values of Kw are low. At high Kw, and therefore high wind speeds, xCO_2^a tends to reach the seasonal expected values in a narrow band from 350 to 370 ppm.

Taking into account that the turnover time of the *ría* varies from a half to three weeks (Rosón et al., 1999; Pérez et al., 2000), the time scale of phytoplankton blooms is about one to two weeks (Gómez et al., 1996),

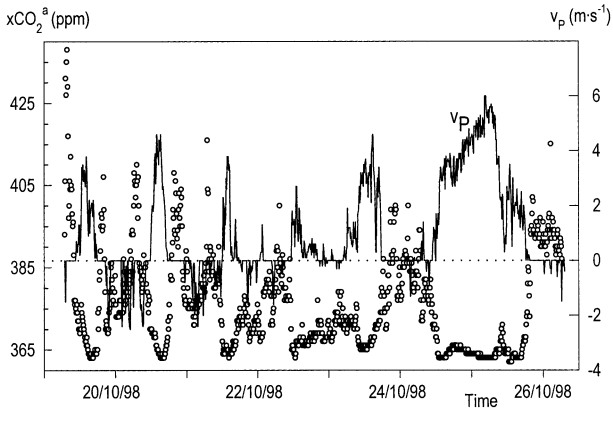

Figure 6. Eight days (mid October 98) example of the seasonal series of measurements of atmospheric molar fraction of CO_2 (xCO_2^a, in ppm, open circles) and wind component parallel to the *ría* axis (v_P, in m s^{-1}, solid line) recorded from February 1998 to April 1999 in the *ría*.

the close relationship between xCO_2^a and Kw, xCO_2^a weighted by Kw was averaged in 0.5 week intervals, and despite the wide variability in the averaged xCO_2^a data, a seasonal pattern is distinguished in *figure 8*. A non-linear least squares fit for averaged xCO_2^a weighted by Kw was performed:

$$xCO_2^a = 366.8 + 1.57\,(t - 36800)/365.25 + 7.4\sin[6.28\,(t + 42)/365.25] - 3.2\sin[12.6\,(t + 17)/365.25] \quad (3)$$

where t is the julian day. This equation explains a 6% of the total variance of the data, with an error of ± 1 ppm, containing a yearly increasing term taken from the Izaña data (equation 2), and two seasonal harmonics, an annual and a six month one. The peak-to-peak amplitude is 17.4 ppm, which is about twice that observed in Izaña (*figure 8a*), of these 17.4 ppm, 14.8 ppm stem from the annual cycle. Both harmonics couple to yield minimum values in August and a quite stable maximum in winter. The seasonal minimum observed in the *ría* was slightly lower and ahead than that of Izaña, whereas the winter maximum was higher and extended during a longer period, until mid spring. It must be taken into account the stronger influence of photosynthesis and respiration in terrestrial ecosystems, contributing to broaden the seasonal variability of xCO_2^a in our station. Local anthropogenic emissions in the *ría* are clearly discerned in the strong deviations from the fitted curve. Likewise, biospheric fluxes also contribute to this short-term variability. In order to avoid this local anthropogenic 'contami-

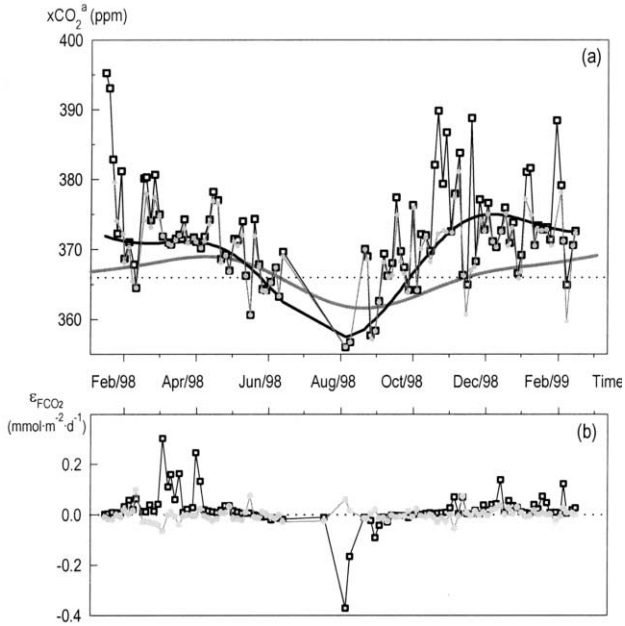

Figure 8. a. Half week averages of the atmospheric molar fraction of CO_2 (xCO_2^a, in ppm) recorded from February 1998 to April 1999 in the *ría*: unfiltered xCO_2^a (open squares), xCO_2^a for v_P higher than 2 m s^{-1} (pale circles), fitted least-squared seasonal curve for the first previous data (equation 3 in the text, black solid line), fitted curve for the Izaña data (*figure 2*, equation 2 in the text, pale solid line), annual mean for the Izaña data (366.3 ppm, *figure 2*, dotted line). **b.** Estimated errors of the CO_2 air–sea exchange (ε_F, in mmol m^{-2} d^{-1}) calculated with regard to the seasonal cycle obtained in the *ría de Vigo* (*figure 8a*, equation 3 in the text) when the three days averaged xCO_2^a data base (pale solid circles) and the annual mean for the Izaña data (open squares) are used.

nation', we suggest filtering the xCO_2^a data for wind speeds lower than 2 m s^{-1}, in agreement with the sampling protocol for collecting air samples proposed by Komhyr et al. (1985). If we had used xCO_2^a filtered data for calculating equation 3 we would have obtained a very similar fitting, but the explained variance would have been significantly increased to 33%. In fact, weighting by *Kw* acts as a filter, attributing a higher weight to those values of xCO_2^a recorded at high *Kw* (high wind speeds), therefore the curve tends to fit the 'uncontaminated' xCO_2^a values, revealing the seasonal cycle in the area. Likewise, if we had used the parameterisation of *Kw* proposed by Wanninkhof and McGillis (1999) instead of that from Liss and Merlivat (1986) we would have obtained a fit slightly more biased (–0.3 ± 0.4 ppm) towards the local 'uncontaminated' xCO_2^a data.

Despite the differences between the fitted seasonal curves for Izaña and Vigo (*figure 8a*), the seasonal xCO_2^a means are 366.3 and 366.8 ppm for Izaña and Vigo, respectively, indicating that the global anthropogenic effect due to the increasing atmospheric CO_2 in both locations is very similar. However, are the local anthropogenic xCO_2^a deviations in Vigo relevant enough to significantly affect the CO_2 air–sea fluxes?

Disregarding the effect of water vapour and atmospheric pressures, the error in CO_2 fluxes (ε_F) due to using xCO_2^a values ($x_{new}CO_2^a$) different from the real ones ($x_{real}CO_2^a$), can be expressed as:

$$\varepsilon_F = 0.24\, S\, Kw\, (x_{new}\, CO_2^a - x_{real}\, CO_2^a) \qquad (4)$$

where all the terms have been defined previously, 0.24 being just a unit conversion factor to obtain the error in mmol m^{-2} day^{-1}. Using as $x_{new}CO_2^a$ the 0.5-week averaged values of xCO_2^a and as real values the seasonal cycle of xCO_2^a in the *ría*, equation 3, the mean error in the CO_2 fluxes would be 0.001 ± 0.024 mmol m^{-2} day^{-1} (*figure 8b*). If using the annual mean of Izaña (366.3 ppm) as new values, the errors would be higher, 0.02 ± 0.07 mmol m^{-2} day^{-1} (*figure 8b*). Thus, in the first case the error in using the seasonal cycle of xCO_2^a instead of the real data is practically zero because of the threshold effect of *Kw* on anomalous xCO_2^a data, sieving their effect. In the second case, neglecting the seasonal cycle of xCO_2^a has a stronger, but low, influence in the flux magnitude (a global averaged around 1.3 mmol m^{-2} d^{-1}; Takahashi et al., 1999): in summer xCO_2^a would be underestimated, and in winter overestimated with regard to the seasonal cycle (*figure 8a* and *b*), so that the final error committed in the flux magnitude would be compensated.

3.3. Case study

As commented in the introduction, the aim of this work was to evaluate the reliability of assuming a constant atmospheric xCO_2 value in the calculation of CO_2 air–sea fluxes in the coastal margin of the Iberian Peninsula. This hypothesis was evaluated applying the obtained seasonal cycle for $xCO2^a$ in the *ría de Vigo* (equation 3) to a series of meteorological and seawater pCO_2 data measured at two stations located in the inner and adjacent continental platform of the *ría*, obtained from May 1994 to September 1995 and published by Álvarez et al. (1999). These authors used a constant value of 357 µatm for atmospheric CO_2 in calculating

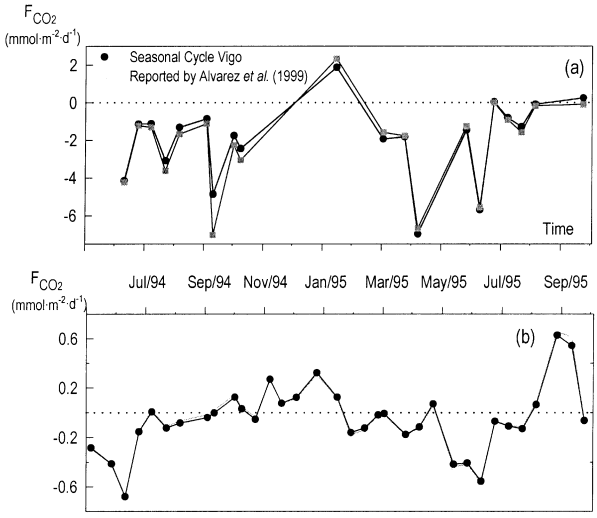

Figure 9. Air–sea CO_2 fluxes (mmol m^{-2} d^{-1}) reported by Álvarez et al. (1999) (pale solid squares) and those calculated using the seasonal cycle for xCO_2^a obtained here (equation 3 in the text) (solid black circles), for station 11 located in the platform (**a**) and station 15 located in the inner *ría* (see *figure 3*) (**b**).

their CO_2 fluxes (*figure 9*). Considering the annual cycle given by equation 3, the CO_2 fluxes are very similar to those reported by the authors, the differences being preferentially less than 10%. Major deviations appear in the platform station (station 11) were higher winds, and therefore *Kw* values, were reported. At this station, the mean values for the whole sampling period practically do not change, being initially 1.96 mmol m^{-2} day^{-1} and 1.93 mmol m^{-2} day^{-1} when using the seasonal cycle equation (3); at station 15 the mean values are even equal. As previously commented, this case study corroborates our previous suggestions, that on a long seasonal time scale the error committed in using a constant value for xCO_2^a is compensated along the cycle, so that the final net flux magnitude is just slightly affected. However, on shorter time scales the effect of using a mean seasonal value would under/overestimate significantly the flux magnitude in that specific period.

4. CONCLUSIONS

Continuous measurements of atmospheric CO_2 molar fraction in a coastal embayment of the NW Iberian Peninsula, *ría de Vigo*, along daily and seasonal time scales showed a significant variability due to the combined effect of local anthropogenic emissions and the seasonal cycle of terrestrial photosynthetic activity. Anomalous high atmospheric CO_2 values are associated with local anthropogenic emissions reported during periods of low winds, mainly blowing from land, and therefore, when the renewal with clean or uncontaminated oceanic air is highly reduced. On the other hand, the impact of these anomalous high atmospheric CO_2 values on the CO_2 air–sea fluxes is greatly attenuated due to the kinetic control exerted by the gas exchange coefficient on the air–sea CO_2 fluxes. Therefore, air–sea CO_2 gradients recorded at low wind speeds have almost no effect on the net flux magnitude along a seasonal cycle or even shorter time scales. For long seasonal periods, using a constant mean seasonal value for the atmospheric CO_2 molar fraction does not significantly affect the final net magnitude of the flux, whereas for shorter time scales the seasonal variability of the atmospheric CO_2 molar fraction must be taken into account in the calculations. We conclude that the air–sea CO_2 fluxes in the West European margin can be calculated using our parameterised seasonal variation of atmospheric CO_2.

Acknowledgements

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